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Working Group On Arsenic,
Cadmium And Nickel Compounds

European Commission
DG Environment

Table of contents

EXECUTIVE SUMMARY

The position paper on arsenic, cadmium and nickel compounds in ambient air

- compiles the available knowledge, relevant to standard setting in the EC,
- proposes limit values on the basis of current risk assessments, and
- outlines the assessment and monitoring methods appropriate for compliance checking.

On a global and even more on an European scale, anthropogenic releases considerably outweigh natural emissions.

Recent emission inventories are available on a national scale (11 Member States) as well as for Europe (inventories by TNO and EMEP).

According to a TNO report published in 1990, stationary combustion causes 87 % of European anthropogenic arsenic, 59 % of nickel and 29 % of cadmium emissions. The other important source category are industrial processes such as the iron and steel industry and the non-ferrous metal industry. The remaining arsenic emissions, 38 % of cadmium emissions and 4 % of nickel emissions are due to this sector.

For the sectors road transport (18 % of cadmium emissions) and other mobile sources and machinery (30 % of nickel emissions), however, the TNO data are at variance with recent national inventories. According to the latter ones, the TNO data represent a considerable overestimattion. This is confirmed by monitoring data. The national inventories assign about 90 % of nickel emissions and between 30 % and 70 % of cadmium emissions to stationary combustion.

Several Member States have demonstrated emission trends, which show large reductions in the eighties and early nineties and lower or no reduction afterwards. This is also reflected by the monitoring data.

Ambient air quality data almost exclusively refer to total arsenic, cadmium and nickel contents in the airborne aerosol or in settled dust. Although the available data are far from giving a comprehensive picture for all Member States, they nevertheless allow for deriving typical levels in different environments. For cadmium and arsenic, they range from 0.2 - 1.5 ng/m³ (As) and 0.1 - 0.4 ng/m³ (Cd) in rural areas, 0.5 - 3 ng/m³ (As) and 0.2 - 2.5 ng/m³ (Cd) at urban background and traffic-related sites, and up to 50 ng/m³ (As) and up to 20 ng/m³ (Cd), at industrial sites. Typical nickel levels are somewhat higher (0.4 - 2 ng/m³ in rural areas, 1.4 - 13 ng/m³ at urban background and traffic-related sites and up to 50 ng/m³ near industry). The same general pattern emerges from deposition data. The concentration gap of one order of magnitude between urban areas and the surroundings of certain industrial facilities clearly points to the difficulty of setting standards applicable to both kinds of micro-environments.

Whereas in the majority of Member States the emissions of heavy metal and metalloid compounds are regulated, only three Member States have adopted legally binding air quality standards.

Heavy metal and metalloid emissions are also regulated either directly or indirectly (via dust limit values) by EC legislation such as the IPPC directive and the directives on waste incineration. In addition, international agreements like the UNECE protocol on cadmium or an upcoming OSPAR decision or recommendation will help to further reduce the input into ecosystems by long-range transport. Under the framework of UNECE, EMEP has set up a comprehensive monitoring network in rural and remote areas to measure this input. Consequently, a close cooperation between the EC and these international bodies is highly recommended by the Working Group.

In comparison to gaseous substances, the risk assessment of arsenic, cadmium and nickel compounds as constituents of the aerosol is rendered more difficult due to the following:

- Metallic and metalloid compounds are present as different chemical species with different toxic and carcinogenic properties.

- A number of physico-chemical factors such as water solubility, particle size distribution and surface enrichment or encapsulation within the aerosol can affect bioavailability.

Unfortunately, the species occurring in ambient air and their physico-chemical properties have been poorly characterized so far by measurements. Consequently, the assessment of effects is impaired by considerable uncertainties, and more research on speciation is urgently needed.

Arsenic compounds predominantly exist as variable mixtures of arsenites and arsenates, the measured share of arsenite ranging from about 0.3 to more than 0.5 of total arsenic.

There are no ambient air data on speciation for cadmium compounds available.

The kind of nickel species emitted depends strongly on the source type. Combustion plants predominantly emit nickel sulfate and oxidic nickel. Industrial sources may emit also metallic nickel and, in the case of two nickel refineries in Europe, nickel subsulfide. The limited number of ambient air speciation measurements suggest oxidic nickel to be the main fraction (about 50 %), followed by soluble nickel compounds (20 - 40 %) and smaller portions of metallic and sulfidic nickel (5 - 8 %).

Cadmium and arsenic compounds are enriched in the fine particle mode about or below 1 µm and, consequently, can penetrate deeply into the respiratory system and have long residence times in the atmosphere. In contrast, up to 30 % of the total nickel compounds may be found in the coarse mode.

As toxicity and carcinogenic potency of the various metal and metalloid compounds differ considerably, they are discussed substance by substance in this report. The general approach chosen is to look at non-cancer and cancer effects separately. First, a limit value proposal is derived for each element based on non-cancer effects. In a second step, the carcinogenic risk resulting from this concentration is estimated. If the proposal based on non-cancer effects also provides sufficient protection with respect to cancer, taking a risk of one-in-a-million as starting point, the proposed limit value remains unchanged. If this is not the case, the proposed limit value is adapted.

With regard to the proposed limit values, agreement could not always be reached within the Working Group. Reservations of some Working Group members are included in chapter 2.6.

The oral uptake of arsenic generally is the most important route of exposure, whereas inhalation normally contributes less than 1 % to the total dose. Non-cancer effects observed after inhalation of air with high arsenic levels at workplaces are increased mortality from cardiovascular diseases, neuropathy and gangrene of the extremities. Based on non-cancer effects, a limit value of 100 ng As/m³ is derived.

There is sufficient evidence that inorganic arsenic compounds are skin and lung carcinogens in humans. At present the possibility cannot be ruled out that any form of inorganic arsenic may be carcinogenic. Consequently, lung cancer can be considered the critical effect following inhalation exposure.

There is evidence (though limited) that indirect mechanisms are at least in part underlying the carcinogenic properties of arsenic. However, the possibility of the element being a genotoxic carcinogen cannot reasonably be excluded.

WHO proposes a unit risk of 1.5×10^{-3} $(\mu g/m^3)^{-1}$, which would yield a concentration of 0.66 ng/m³ associated with a one-in-a-million risk by linear extrapolation. The Working Group is of the opinion that this unit risk-based approach is likely to overestimate the true risk. Instead of extrapolating linearly, the Working Group therefore bases its proposal on the "pseudo threshold" approach proposed by the UK, resulting in a range of 4 - 13 ng/m³ as annual mean for total arsenic concentrations in air. Taking into account the current urban background concentrations of arsenic in Europe, a limit value near the lower bound of this range seems to be appropriate for the majority of the Working Group.

Under average circumstances, in non-smokers the oral uptake of cadmium via food and drinking water contributes most to the total dose, the percentage for cadmium uptake via ambient air being less than 3 %. The kidney is the critical organ with respect to long-term exposure to cadmium. Cadmium-induced nephropathy is characterized by an increased excretion of proteins, amino acids and other substances in urine, which can be used as "markers" for the renal cadmium burden and possible adverse renal effects. Based on occupational studies, WHO has derived a cumulative dose of 100 µg/m³ • years as a threshold for an increased excretion of markers of renal function changes. From this cumulative dose, an air quality limit value of 5 ng/m³ can be derived, which is likely to prevent renal damage due to inhalation exposure. This proposed limit value is in agreement with the AQG proposed by WHO.

From studies on workers in the non-ferrous metal industry, an excess in lung cancer mortality was reported. IARC has classified cadmium to be a human carcinogen. According to the EC classification, cadmium and several cadmium compounds should be regarded as carcinogenic to man. However, the importance of cadmium as a carcinogen at environmental concentrations is not generally accepted, one of the reasons being that concomitant arsenic exposure may have been involved in the induction of lung cancer.

The results of genotoxicity tests suggest direct as well as indirect mechanisms contributing to the carcinogenic activity.

Whereas WHO classifies available epidemiologic data as being not appropriate for qualitative risk estimates, a unit risk for lung cancer of 1.8×10^{-3} $(\mu g/m^3)^{-1}$ has been derived by U.S. EPA, which was recently proposed to be increased to 4.15×10^{-3} $(\mu g/m^3)^{-1}$.

Keeping in mind the uncertainties mentioned above, the Working Group thinks that the value of 5 ng/m^3 as annual mean of total airborne cadmium derived by WHO from non-cancer effects provides also an appropriate level of protection from cancer risks.

As cadmium compounds act as systemic pollutants and as their transfer into the food chain is of particular relevance, the Working Group proposes to supplement the concentration limit value by a deposition limit value. Based on a tolerable daily dose of 0.75 - 0.95 µg (kg body weight)$^{-1}$d^{-1} for total cadmium intake and taking into consideration the cadmium uptake of vegetables from the soil, the direct dust deposition on the above-ground parts of plants as well as the protection of groundwater and the uptake of soil by playing children, the majority of the Working Group recommends a number between 2.5 - 5 $\mu g \cdot m^{-2} \cdot d^{-1}$ as a deposition limit value for the local scale in urban and industrialized areas. Reservations by EEB in respect to this proposal are presented in chapter 2.5.

The toxicology-based proposal for the local scale does not protect from a slow accumulation of cadmium in soils. In order to avoid such slow accumulation and applying the precautionary principle, it can be inferred from cadmium balances calculated for Swedish and Dutch soils that the cadmium input by deposition should not exceed 10 - 100 µg Cd m^{-2}year^{-1} (0.03 – 0.27 $\mu g \cdot m^{-2} \cdot d^{-1}$). Such low inputs can only be reached by a joint EC policy for cadmium in all media and a close co-operation with UNECE.

The method used to derive a deposition limit value for cadmium can also be applied for other persistent pollutants. It has to be emphasized that one of the benefits of setting a deposition limit value is that this draws the attention to the fact that air pollution control - in a cross-media approach - needs to widen its scope to prevent damage to the other environmental media, water and soil.

Also in the case of nickel, which may be an essential trace element, the oral uptake via food contributes the largest amount to the total dose. Non-cancer effects on health are allergic skin reactions (generally not caused by inhalation), effects on the respiratory tract, the immune and defense system and on endocrine regulation. As well-documented human data are scarce, animal data have to be used for the assessment of non-cancer effects. In experimental animals, effects on the respiratory system of inhalation exposure to nickel have been observed and quantified in dose-response relationships. With respect to the interpretation of the most comprehensive NTP nickel sulfate hexahydrate study in rats, two options have been discussed as starting points by the Working Group, that is either to use 30 $\mu g/m^3$ as a NOAEL or 60 $\mu g/m^3$ as a LOAEL in combination with an uncertainty factor of 10 for the extrapolation to a NOAEL. Based on these options, limit values for non-cancer effects of 10 - 50 ng/m^3 can be derived.

In the EC classification, several nickel compounds are classified to be known human carcinogens, whereas other nickel compounds are classified to be possible carcinogens. With the exception of metallic nickel, IARC has classified nickel compounds to be known human carcinogens.

The available information is not sufficient to permit a clear classification of nickel compounds as non-genotoxic carcinogens. Therefore, under precautionary aspects, the existence of a threshold should not be assumed.

WHO gives a unit risk of 3.8 x $10^{-4}(\mu g/m^3)^{-1}$, whereas U.S. EPA has estimated the lifetime cancer risk from exposure to nickel refinery dust to be 2.4 x $10^{-4}(\mu g/m^3)^{-1}$. These estimates lead to a concentration range of 2.6 - 4 ng/m³, when extrapolated to the one-in-a-million excess lifetime risk.

Bearing in mind the likely overestimation of the risk due to the fact that the limit value will be based on total nickel, that is without speciation, and other uncertainties, a limit value in the range 10 - 50 ng/m³ as derived from non-cancer effects can be judged as yielding sufficient protection from cancer effects as well. The majority of the Working Group proposes a limit value at the lower end of this range.

Metal and metalloid compounds can be incorporated by plants and ecosystems either directly via deposition or via uptake from soils. The knowledge of possible effects of arsenic, cadmium and nickel compounds on terrestrial ecosystems is still rather limited and furthermore restricted to single compartments, i.e. plants or parts of the edaphon. Hence, the available data do not allow to derive specific ecological limit values. However, limit values protective with respect to adverse health effects (including deposition) will generally also cover the protection of terrestrial ecosystems with respect to phytotoxicity, accumulation in soils and harmful effects on the edaphon. Instead of focussing on ecological limit values, the Working Group recommends an abatement of emissions as the strategy of first choice, which will also reduce the input of arsenic, cadmium and nickel compounds into eco-systems via long-range transport. Again, a close cooperation with UN-ECE and EMEP is called for.

In summary, the majority of the Working Group proposes the following ranges or numbers for setting limit values:

- 10 - 50 ng/m³ (annual mean) for total nickel content in airborne dust, with a majority vote for the lower end of the range
- 4 - 13 ng/m³ (annual mean) for the total arsenic content in airborne dust, with a majority vote for the lower end of the range
- 5 ng/m³ (annual mean) for the total cadmium content in airborne dust
- 2.5 - 5 $\mu g/m^{-2}\ d^{-1}$ (annual mean) for the deposition of cadmium in urban and industrialized areas.

In spite of the regulations of emissions by EC legislation and international agreements mentioned above, the majority of the Working Group is of the opinion that the emission-oriented approach should be supplemented by an effect-based approach using the proposed limit values due to the following reasons:

- the regulation of emissions alone cannot exclude that the simultaneous presence of emissions from various sources may cause adverse effects even though each of the single sources may meet set emission standards;
- emission limits can hardly be applied to fugitive sources;

- local and regional authorities have considerable leeway in applying BAT. Therefore, effect-based limit values are needed as goals for action plans, to prevent harmful effects in polluted regions.

With regard to the assessment strategy it can be concluded from the risk assessment and the emission inventories that (i) the protection from long-term effects (by setting limit values as annual means) is sufficient, (ii) deposition of cadmium should be measured, (iii) the urban background and residential and agricultural areas near industrial hot spots are the environments of concern.

Although no ecological limits have been proposed, some background monitoring (1 station per 100.000 km²) and a close co-operation with the EMEP network is recommended.

Network design in urban background areas closely follows the requirements laid down in the first daughter directive (principle of collocation, where possible). However, the number of fixed monitoring stations can be reduced, as traffic exposed sites have not to be monitored explicitly.

Criteria are given in the position paper for the identification of relevant industrial hot spots. The relevant sources being identified, monitors should be placed at sites where long-term exposure coincides with the highest pollution levels.

The time coverage of measurements necessary for compliance checking and indicative measurements has been calculated from quasi-continuous time-series from some Member States. Minimum time coverage is 75 % (cadmium, industrial sites), 50 % (arsenic, nickel (all sites) and cadmium, urban background) for compliance checking and 14 % for indicative measurements. These figures should be checked, when time-series from more Member States will become available. The maximum permissible uncertainty for mandatory measurements is proposed to be 25 % for cadmium, 40 % for arsenic and nickel, and 50 % for indicative measurements and modelling. Guidance for the quality assurance of the measurements is given.

Upper and lower assessment thresholds were derived analyzing the interannual variability from time-series. For the upper assessment threshold, values of 60 % (arsenic and cadmium) and 70 % (nickel) were found, the corresponding percentages for the lower assessment threshold being 40 % and 50 %, respectively. For cadmium deposition, percentages of 40 % (upper assessment threshold) and 20 % (lower assessment threshold) have been derived.

The measurement methods (sampling, digestion and analysis) currently used by the Member States are outlined in the position paper, with a short characterization of their advantages and disadvantages. All routinely used measurement methods refer to the total contents of metals and metalloids in suspended particulate matter. As methods for species-specific analysis are still in the stage of research and development, none of these methods can yet be recommended for routine monitoring.

Until the upcoming CEN standard will be available, the Working Group recommends to use a provisional reference method. This method would include sampling for PM10 as described in EN 12341, complete digestion, and atomic absorption spectrometry for analysis. Any other method which can be demonstrated to be equivalent can be used by the Member States. For deposition monitoring, it is proposed to use the Bergerhoff or the NILU sampler, complete digestion and analysis by atomic absorption spectrometry as an intermediate reference method.

For the various scales to be considered (microscale, mesoscale and long-range transport), the dispersion models currently applied in Europe are shortly characterized.

As accumulation of metals in plants caused by pollution can be easily determined by active or passive biomonitoring with subsequent chemical analysis, the use of bioindicators is described and recommended as an additional tool.

0. BACKGROUND AND SCOPE

The European Union is currently reshaping their clean air policy inter alia by launching a new generation of ambient air quality directives which will substitute the existing ones for sulphur dioxide, total suspended particulates, nitrogen dioxide, lead and ozone and will cover additional pollutants. The process reached its first stage in September 1996, when the Council directive on ambient air quality assessment and management [1], in the following called „framework directive“, was adopted. Annex I of this directive [1] contains a list of 13 priority pollutants which have to be taken into consideration when assessing and managing ambient air quality. Regulations for these pollutants are laid down in daughter legislation to the framework directive and the time table in article 4 of the framework directive for the daughter directives states that the Commission shall submit to the council proposals for the last set of pollutants (polycyclic aromatic hydrocarbons, arsenic, cadmium, nickel and mercury) on 31. December 1999 at the latest.

In establishing the daughter legislation, the Commission has launched a process of broad participation of principal stakeholders as the Member States, industry, NGOs and scientific and technical European organisations as CEN or WHO Europe. The process is accompanied by the so called steering group of national experts on ambient air quality which consists of the principal stakeholders. A second element of participation are Working Groups set up by the Commission and the steering group, which have the mission to collect the available data in the Member States on particular pollutants within so called „position papers“, and to propose therein elements of the upcoming daughter legislation. The Commission will then draw on the expertise laid down in the position papers by establishing its proposals for the daughter directive.

The Working Groups are either led by the Commission itself (e.g. sulphur dioxide, carbon monoxide, ozone), or by Member States (lead countries), and also involve the principal stakeholders mentioned above. Though the Commission thus takes part in the Working Groups, the position papers do not necessarily reflect its position, but reflect the positions of the majority of the Working Group. Consequently, the position papers are independent documents and will be published after adoption by the steering group. The Working Groups are cofunded by the Commission and the lead countries.

At the steering group meeting on 18 and 19 October 1998, it has been decided to establish a Working Group on arsenic, cadmium and nickel compounds under the lead of Germany and with the participation of Belgium, France, Spain, the EEB, UNICE, the WHO, EEA, JRC, a representative from EMEP and the Commission. Annex A contains a full list of the Working Group members. This position paper is the result of the data collected and discussed by the Working Group.

As the framework directive aims at the management of ambient air, the working places, indoor air, smoking or other important routes of exposure for heavy metal and metalloid compounds are not covered by the scope of the Working Group (compare art. 2 of the framework direcitve). However, unlike gaseous pollutants covered so far such as nitrogen dioxide or ozone, heavy metal and metalloid compounds are persistent in the environment and may accumulate in soils or on other surfaces. The medium air is thus directly linked to the soil and to the vegetation for these pollutants via their deposition. Consequently, the relations between the media air and soil have to be included in the scope of this paper, following the requirement of an integrated approach to the protection of air, water and soil in art. 7.2 of the framework directive.

As stated above, it is the purpose of the position paper to collect the available expertise in the Member States and to make proposals for some important elements of the daughter legislation as limit values, assessment techniques, or information of the public from the viewpoint of the Working Group. The position paper thus starts in presenting the necessary background data on air emissions, ambient air levels, occurrence in ambient air and national legislation in chapter 1. Chapter 2 deals with risk assessment and ends with proposals for limit values. Chapter 3 is dedicated to the monitoring strategy, measurement methods and other assessment methods such as modelling.

The main results of all chapters are contained in an executive summary at the beginning of the position paper.

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1. INTRODUCTION AND CHARACTERIZATION OF THE POLLUTANTS

1.1 Metal And Metalloid Compounds Occurring In Ambient Air

In contrast to gaseous specific compounds such as, e.g., benzene or carbon monoxide, the assessment of metal and metalloid compounds in ambient air is complicated by the fact that different species with considerably differing toxicity and/or carcinogenic potency (see chapter 2) may be encountered. Therefore, to fully evaluate the health effects, it is important to know which species do occur in the environment or at least which compounds form the main constituents.

In ambient air, metals, metalloids and their compounds are mainly encountered as part of particulate matter. They may be present in the non soluble, non stoichiometric mixture phase (for example as spinels) or as soluble ionic compounds (salts). To a lesser extent and under certain environmental conditions, gaseous forms (e.g. organometallic compounds) occur which may or may not be adsorbed on particles.

In respect to their effects on the environment and on human health, these compounds can be characterized by other parameters, such as water solubility (extended to solubility in biological fluids), particle size distribution (compare chapter 1.2), morphology and specific surface area, and chemical heterogeneity of the particles (for example, a metal compound encapsulated in another aerosol or surface enrichment of volatile species), or the concentration of metals and metalloids in the particles ultimately contacting target tissues in the human body.

All parameters mentioned will influence the bioavailability and possible effects. In addition, metal and metalloid containing substances can undergo various chemical and physical transformations in the atmosphere on their way from the source to a possible receptor. For example, As (III) compounds may be oxidized to As (V).

Unfortunately, analytical methods normally only identify the elements which are present in atmospheric particles, species specific analysis being extremely difficult in the concentration range occurring in ambient air (typically several ng/m^3, see chapter 1.4). In addition, the state of oxidation may change during sampling. Consequently, information on the concentration of different species in ambient air is very limited at present. The analytical procedures enabling such differentiation are described in chapter 3.3.1.3. Another possibility to gain some insight into species is to analyze which compounds are emitted by the most important natural (e.g. by weathering processes) and anthropogenic sources. In the following, the limited knowledge available on the occurrence of species is outlined. It must be borne in mind that few measured data which really refer to ambient air exist, and that those few measurements are far from being representative. Most accounts in the literature are still based on assumptions or data from other media.

1.1.1 Arsenic

Species originating from natural sources and chemical transformations

Arsenic is a metalloid with a rich chemistry which forms a variety of inorganic and also organic compounds [3]. Arsenic can exist in the oxidation states -3,0, +3 and +5, whereas in the environment, oxides of the oxidation state +3 (arsenites) and +5 (arsenates) are the most common compounds, the stablest form being As_2O_3 (arsenic trioxide).

The mountainous regions in Europe are rich in sulfidic ore deposits, the predominant ore being arsenical pyrite [2]. Arsenic rarely occurs as free element, but is contained in the sulfidic ores as arsenide [3]. Weathering processes set free arsenic from these ores as arsenite (oxidation state +3, compare table 1.1). The arsenic concentrations in the ores may range from traces to several percent [3]. Another important natural source is vulcanic activity, from which arsenic is emitted into the atmosphere predominantly as particulate sulfidic compound or as oxide [4, 5].

Depending on the conditions in the environmental departments, tri- and pentavalent forms can be interconverted. Methylation of inorganic arsenic is known to occur in water and soil. Consequently, methylated species such as monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) may be present in air as well [6], especially near swamps or litoral areas. For example, at Tampa Bay area (USA), approximately 20 % of the As were found as alkyl-arsenic [6]. Data on arsenic emissions from natural sources are presented in chapter 1.3.1.

Species originating from anthropogenic sources

Most of man-made emissions of arsenic stem from metal smelters and the combustion of fuels, where arsenic is mostly emitted in the form of arsenites (As_2O_3 or as salts of the corresponding acid) or arsenates (AS_2O_5 or the salts of the arsenic acid) [3]. In the past, the application of pesticides used to be an important source as well, but emissions have declined since its restriction in several countries [4]. By and large, it may be stated that variable mixtures of arsenites and arsenates are the most common arsenic species in the atmosphere, as anthropogenic sources are dominating (compare chapter 1.3.1).

The ratio of arsenites to arsenates was determined in three studies in Darmstadt (Germany, 1986), Los Angeles (USA, 1989) and recently in Isfahan (Iran). The ratio As(III) to As(V) was found to range from 27 % (rural area near Darmstadt), and 43 % (Darmstadt, urban area) [7] over ratios close to 1 (Los Angeles) [8] to a percentage of As(III) above 50 % at Isfahan [9] (for the analytical methods used see chapter 3.3.1.3). From measured size distributions of arsenic containing particles in Germany (compare section 1.2) and vapour pressure data, a share of about 80 % for As(III) in aerosols has recently been estimated [10].

The arsenic compounds anticipated in ambient air are summarized in table 1.1 together with some of their physical properties. They are arranged in decreasing importance.

Table 1.1: The most commonly found (or anticipated) arsenic compounds in air

Name (Synonyms)	Chemical formular	State of Oxidation	Physical condition	CAS Number	Melting point	Solubility in water
Arsenic trioxide (trivalent As oxide (arsenious acid arseneous oxide, „arsenite„) [(a)]	As_2O_3, $(AsO_3)^{3-}$	+3	solid (gaseous)	1327-53-3	312.3 °C	37 g/l (20 °C)
Arsenic pentoxide (pentavalent As oxide, arsenic acid anhydride, „arsenate„) [(b)]	As_2O_5, $(AsO_3)^{-}$/ $(AsO_4)^{3-}$/$(As_2O_7)^{4-}$	+5	solid	1303-28-2	Decomposes at 315 °C	1500 g/l (16 °C)
Arsenic Acid (orthoarsenic acid)	H_3ASO_4	+5	solid	7778-39-4	35.5 °C	3020 g/l (12.5 °C)
Monomethylarsonic acid (MMA)	$(CH_3)AsO(OH)_2$	+5	solid	124-59-3	161 °C	soluble
Dimethylarsinic acid (DMA)	$(CH_3)_2AsO(OH)$	+5	solid	75-60-5	195-196 °C	660 g/l (25 °C)
Other trivalent As compounds	$AsCl_3$ [(c)]	+3	liquid	7784-34-1	131 °C	soluble
	As_2S_3	+3	solid	12255-89-9	320 °C	insoluble
Realgar	As_4S_4	0/+3	solid	12279-90-20	307 °C	insoluble
Other pentavalent As compounds	As_2S_5	+5	solid	1303-34-0	Decomposes at ~ 500 °C	insoluble
Arsin (arsenic trihydride, hydrogen arsenide, arsenic hydride)	AsH_3	-3	gaseous	7784-42-1	-117 °C	20 % (20 °C)
Metallic As (arsenic black, colloidal arsenic)	As	0	solid	7440-38-2	817 °C (28 atm)	insoluble

(a) Due to its high vapour pressure it can be present in the vapour phase.
(b) The arsenate species are defined by the pH on the medium (liquid or liquid film on a particle).
© This arsenic halide is liquid at room temperature, but can be air-dispersed either in liquid or in vapour state.

1.1.2 Cadmium

Cadmium is a relatively rare element (0,2 mg/kg in the earth crust). It occurs mainly in association with the sulfide ores of zinc, lead and copper and is produced mainly as by-product of the zinc industry.

As no species specific measurements of cadmium compounds in ambient air have been performed, there are no data on the speciation of cadmium in suspended particulate matter at present. The limited knowledge is based on assumptions and few investigations at working places and of flue gases.

Cadmium compounds originating from natural sources

Cadmium in the atmosphere stems from a wide variety of natural and anthropogenic sources. About 25 % of natural cadmium emissions is estimated to come from vegetation (as exudates, slough, etc.), whereas about 12 %, 62 %, and 2 % are attributable to airborne soil particles, volcanogenic aerosols and forest fires, respectively [11]. Although the degassing of crustal rocks has been suggested as an important source of metals in the atmosphere [12], the release of cadmium from such source remains to be quantified.

Cadmium compounds originating from anthropogenic sources

Cadmium compounds are released into the atmosphere from production processes of zinc, copper and lead [11], from combustion processes (coal and oil), from refuse incineration [13] (from stabilizers and pigments in plastics), and from iron and steel production (compare chapter 1.3). More than 55 % of the total cadmium production is consumed by the manufacturing of cadmium-nickel batteries. Limited evidence on the species occurring in ambient air can therefore be obtained by the analysis of dusts and effluents from the sources mentioned above.

Cadmium emitted from combustion processes has been shown to occur as metallic cadmium and as cadmium oxide, often as mixed oxide with other metals whereas emissions from refuse incineration consist predominantly of $CdCl_2$ [13]. In an analysis of dust emitted by a lead smelter in France [14], CdS and $CdSO_4$ could recently be identified (sampling at the furnace and the grill after filters). In effluents from a lead smelter in Montana [15] and in ambient dust collected near the smelter, elemental cadmium and cadmium sulfide were detected.

In coarse dust (about 100 µm) collected from three parts of an iron smelter in Hungary (multicyclone, deposits from flue gases and fly ash), cadmium was generally present as silicates and cadmium sulfide [16].

As cadmium and many of its compounds are quite volatile, condensation on aerosols is common after the emission from high temperature processes. This leaves cadmium compounds condensed on the surface of particles which may increase the bioavailability [17].

Recently, the occurrence of cadmium species in ambient aerosols was estimated from measured size distributions (compare section 1.2) and vapour pressure data [10]. According to this study, cadmium chloride, cadmium sulfate and cadmium oxide are supposed to be the predominant species in ambient air.

As to cadmium compounds found either in atmospheric dust or in effluents of principal sources, it can be stated that cadmium sulfate and cadmium chloride are quite soluble in water, whereas elemental cadmium, cadmium oxide and cadmium sulfide are almost insoluble [18].

1.1.3 Nickel

Nickel is very abundant in meteorites and in the core of the terrestrial globe (fifth element by order of abundance), but less abundant in the terrestrial crust. Nickel ores exist under two forms: sulphidic and oxidic [19].

Sulphidic nickel ores are principally associated with nickeliferous pyrrhotite (Fe_7S_8), pentlandite $(Ni.Fe)_9S_8$ and chalcopyrite ($CuFeS_2$). Other minerals which occur in small but significant amounts include magnetite (Fe_30_4), ilmenite ($FeTiO_3$), pyrite (FeS_2), cubanite ($CuFe_2S_3$), and violarite (Ni_2FeS_4) [19].

Pentlandite, the most common of the sulphidic minerals, probably accounts for 60 % of the world nickel production. Nickeliferous pyrrhotite is normally the most abundant phase in a nickel ore. It contains nickel in solid solution (0.2 - 0.5 % Ni) in addition to very finely divided pentlandite inclusions.

Major sulphidic orebodies occur in Canada, the former Soviet Union, the Republic of South Africa, Australia, Zimbabwe and Finland.

The lateritic nickel ores, unlike the sulphidic ones, were formed over long periods of time as a result of weathering of exposed nickel-containing rocks. Nickel was dissolved from the host rocks and precipitated elsewhere in the form of hydrated oxides or silicates. One type of laterite is nickeliferous limonite [(Fe, Ni) O(OH) (xH_20]. This is primarily a hydrated ferric oxide, goethite, in which the nickel is dispersed in solid solution. The other commercially important type of laterite is nickel silicate in which nickel forms a solid solution in hydrated magnesium-iron minerals such as garnierite $(NiFeMg)_6Si_4O_{10}(OH)_8$].

Divalent nickel (+2) is the most abundant oxidation state and the only important one in aqueous solutions. Other higher oxidation states (+3, +4) exist only as impure sesquioxide (Ni_2O_3) and dioxide (NiO_2), which are very unstable and of variable stoichiometry. As a transition metal, nickel easily forms complexes with coordination numbers of four (square, planar, or, rarely, tetrahedral) or six (octahedral).

Physical and chemical properties of important nickel compounds are summarized in Table 1.2 [20].

Table 1.2: Physical and chemical properties of important nickel compounds

Name	Chemical Formula (IUPAC)	Molecular Mass	Density g/cm³	Melting Point °C	Solubility (g/100 ml)		Dissolution Half-Times in Body Fluids (T_{50})
					Water	Other Reagents	
Metallic Nickel							
Nickel massive	Ni	58.71	8.9	1455 1555	i.	s.dil.HNO_3, i. NH_3	
Nickel powder	Ni	58.71	8.5-8.9		i.	sl.s.HCl, H_2SO_4	>11 years rat serum, 8.4 years renal cytosol
Oxidic Nickel							
Nickel monoxide (low temp.)	Ni(1-2% Ni^{3+})	74.69	4.83	d. 600	i.	s. hot HCl sl.s.HCl, i.a.	
Nickel monoxide (high-temp.)	NiO	74.69	6.67 (7.45)	1984	i.	s.a., NH_4OH	>11 years rat serum, >11 years renal cytosol
Nickel carbonate (basic)	$CH_4Ni_3O_7 \cdot 4H_2O$	376.17	2.6	d.	i.	s.a., NH_4OH	
	$C_2H_6NiO_{12} \cdot 4H_2O$	352.84	2.6	d.	i.	s.a., NH_4OH	
Nickel hydroxide	H_2NiO_2	92.70	4.15 (3.65)	d. 230	0.013		
Sulphidic Nickel							
Nickel sulphide	NiS	90.75	5.3-5.6	797	0.0003618	s. HNO_3, A.R., KHS	2.6 years rat serum, 1.4 years renal cytosol
Nickel subsulphide	Ni_3S_2	240.19	5.82	790	i.	s. HNO_3, A.R.	34 days rat serum, 21 days renal cytosol
Nickel arsenide	AsNi	133.61	7.57	968	i.	s. A.R.	46 days rat serum, 14 days renal cytosol
Nickel Salts (soluble)							
Nickel acetate	$C_4H_6NiO_4$	176.80	1.798	d.	16.64		
Nickel acetat, hydrate	$C_4H_6NiO_4 \cdot 4H_2O$	248.84	1.744	d.	s.	s. dil. alc. 10.0 EtOH	
Nickel chloride	Cl_2Ni	129.60	3.55	1001	64.2, 87.6	sl.s. MeOH s. alc.	

Table 1.2: Physical and chemical properties of important nickel compounds

Name	Chemical Formula (IUPAC)	Molecular Mass	Density g/cm³	Melting Point °C	Solubility (g/100 ml)		Dissolution Half-Times in Body Fluids (T_{50})
					Water	Other Reagents	
Nickel Salts (soluble)							
Nickel chloride, hydrate	$Cl_2Ni\cdot 6H_2O$	237.69	1.92^8	1001	254, 599	s. alc.	
Nickel fluoroborate	$B_2F_8Ni\cdot 6H_2O$	340.42	2.14^8		s.	s. alc.	
Nickel hydrate, formate	$C_2H_2NiO_4\cdot 2H_2O$	184.76	2.154		s.	i. alc., i. formic a.	
				d.		s. alc.,	
Nickel nitrate	$N_2NiO_6\cdot 6H_2O$	290.79	2.05	d.	238.5 56.7 s.	NH_4OH	
Nickel sulphamate, hydrate	$H_4N_2NiO_6S_2\cdot 4H_2O$	322.95		13.7		i. alc.	
				d. 200			
Nickel Salts (soluble)							
Nickel sulphate	NiO_4S	154.75	3.68	d. 848	29.3, 87.3 100 9	i. alc., eth.	
Nickel sulphate, hydrate	$NiO_4S\cdot 6H_2O$	262.84	2.07	-5 H_2O 103, -1 H_2O 280^5	65.5 131 280	12.5 MeOH, s. EtOH, s. NH_4OH	
	$NiO_4S\cdot 7H_2O$	280.85	1.95		75.6	s. alc. s. NH_4OH	
Nickel ammonium sulphate	$H_8N_2NiO_8S_2\cdot 6H_2O$	395.00	1.923		2.5, 39.2		
Nickel Carbonyl	C_4NiO	170.73	1.32^{17}	-25 -19.3^{10}	0.018 9...8	s.A.R., alc. eth. i. dil. alc., dil. alk	

a. =	acid	EtOh =	ethyl alcohol
A.R. =	aqua regia	flam. =	flammable
alc. =	alcohol	i. =	insoluble
alk. =	Alkali (i.e. aq. NaOH, KOH)	liq. =	liquid
aq. =	aqueous or water solution	KHS =	potassium hydrogen sulphide
col. =	colourless	MeOH =	methyl alcohol
cr. =	crystals or crystalline	NH_4OH =	ammonium hydroxide solution
d. =	decomposes	s. =	soluble
d. 200 =	decomposes at 200 °C	sl. =	slightly soluble in all proportions
delq. =	deliquescent	$-5H_2O$ 103 =	loses 5 moles of water per formula mass at 103 °C
dil. =	dilute		
et. =	ethyl ether		

Species originating from natural sources

Natural sources of nickel, which are responsible for about 35 % of total global emissions, include windblown soil, vulcanoes, vegetation, forest fires, sea salt and meteoric dust [21]. More recent estimates [22] give somewhat lower percentages (15 %) for the natural share of global nickel emissions. Pollution with nickel and its ores is particularly relevant in countries with ore deposits and a primary nickel industry. In European countries without relevant nickel deposits, nickel is mainly emitted from anthropogenic sources.

Nickel compounds of natural origin are likely to be silicate-oxidic in nature (complex oxides), and then insoluble in water.

Species originating from anthropogenic sources

As presented in chapter 1.3, nickel compounds are mainly emitted by combustion (heavy residual oil and coal burning units). Other sources are:

- high temperature metallurgical operations (stainless steel and nickel alloys manufacturing),
- nickel primary production operations (mining, grinding, smelting and refining).

The species emitted heavily depend on the type of industrial process.

Combustion:
Different analyses of nickel in stack fly ash from oil-fired combustion units have shown that the predominant species are soluble nickel compounds such as nickel sulphate with lesser amounts of oxidic nickel, and complex metal oxides containing nickel (spinels, possibly trevorite ($NiFe_2O_4$)) [23, 24, 127]. According to a thermodynamical analysis [25], nickel subsulphide and metallic nickel may not be present in dust emitted by combustion plants but nickel sulphate and complex nickel oxides could predominate, in accordance with measurements [127]. However, the following caveat seems necessary: Results from fly ash analyses are unlikely to completely match the actual emissions from high temperature processes. It has been demonstrated that metal compounds with higher vapour pressures are enriched in the emissions relative to fly ashes (for the results from first ambient air measurements see below).

The incineration of municipal garbage and sewage sludge accounts for only a small fraction of nickel released to the atmosphere, primarily in "soluble" (39 to 58 %), "sulphidic" (< 10 %), and "oxidic" (40 to 61 %) forms (Steinsberger et al. [128]). This finding is consistent with earlier findings that 35 to 52 % of the nickel in fly ash from incinerated sludge was in the form of soluble nickel chloride and sulphate, and the remainder was in the form of less soluble oxides and silicates [129].

Other minor sources of atmospheric emissions of nickel from high temperature processes include cement manufacturing and coke ovens. During cement manufacturing, nickel is emitted either as a component of the clays, limestones, and shales (raw materials) or as an oxide formed in high-temperature process kilns. The emissions from coke ovens are likely in the form of sulphides (Ni_3S_2 and NiS) and metallic nickel, owing to the highly reducing atmosphere of the coke ovens (IPCS, [130]).

Metallurgical operations (stainless steel and nickel alloys production):
Based on processes involved, it can be anticipated that species emitted are soluble salts (around 20 % - see below), and metallic nickel, nickel alloys and insoluble oxidic nickel, inter alia spinel forms.

Nickel primary production (mining, grinding, smelting and refining):

- During mining and grinding operations, dusts consisting of ore are emitted (one site in Europe).
- During smelting, it can be assumed that metallic nickel, soluble nickel compounds and complex nickel oxides should be emitted.
- During refining, only during the operation of matte grinding, nickel subsulphide is emitted (two sites in Europe have this process). During the other operations, soluble nickel sulphate and chloride, nickel hydroxide and complex nickel oxides are emitted.

Data giving percentages of 50 % of nickel subsulphide in refinery dust quoted in chapter 2.6.3.3 refer to old processes which have not been in operation since the 1950s.

From measured size distributions and vapour pressure data, it has been assumed that predominant nickel species present in ambient air (urban background and rural) are soluble salts such as nickel sulfate, nickel chloride, nickel nitrate and insoluble oxidic nickel [10].

First results from species specific measurements in ambient air

Species-specific measurements of nickel compounds in ambient air have just started. By applying multistage extraction schemes with various solvents to the particulate matter collected on filters, the nickel compounds can be separated in fractions of different solubility (compare chapter 3.3.1.3 for details of the method).

A two stage extraction scheme has recently been applied in first investigations to samples of total suspended particulate matter collected near two industrial sites and one urban background site in Dortmund (Germany). One site was near a plant producing structural steel (nickel content 0 - 1 %, depending on charge), the other measurement site was near a plant producing stainless steel (nickel content up to 10 %). Prior to analysis the collected dust samples were digested with 0.1 M aqueous EDTA solutions. The nickel fractions soluble in EDTA can thus be separated from those insoluble and be analysed by GF-AAS and ICP-MS, respectively, after total digestion of the fraction insoluble in EDTA.

The results of the two measurement campaigns at the industrial sites that lasted four months each are shown in Figures 1.1 and 1.2 [26].

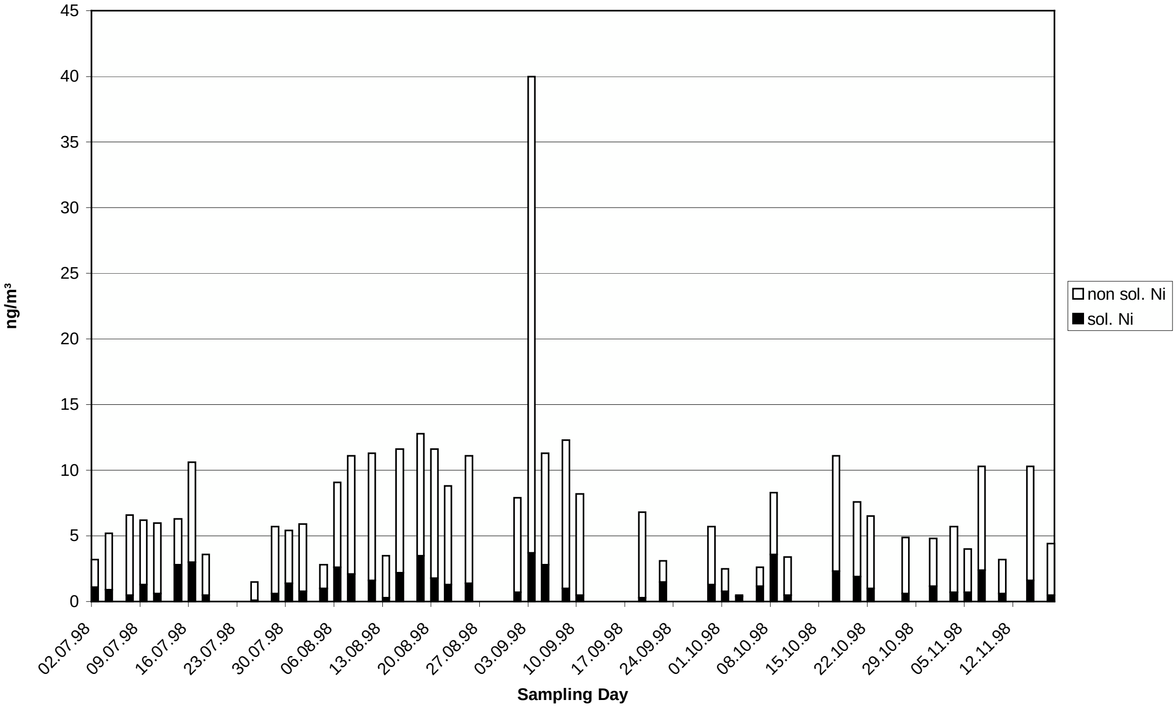


Figure 1.1: Nickel speciation (soluble/insoluble fractionating) of ambient air samples near a plant producing structural steel

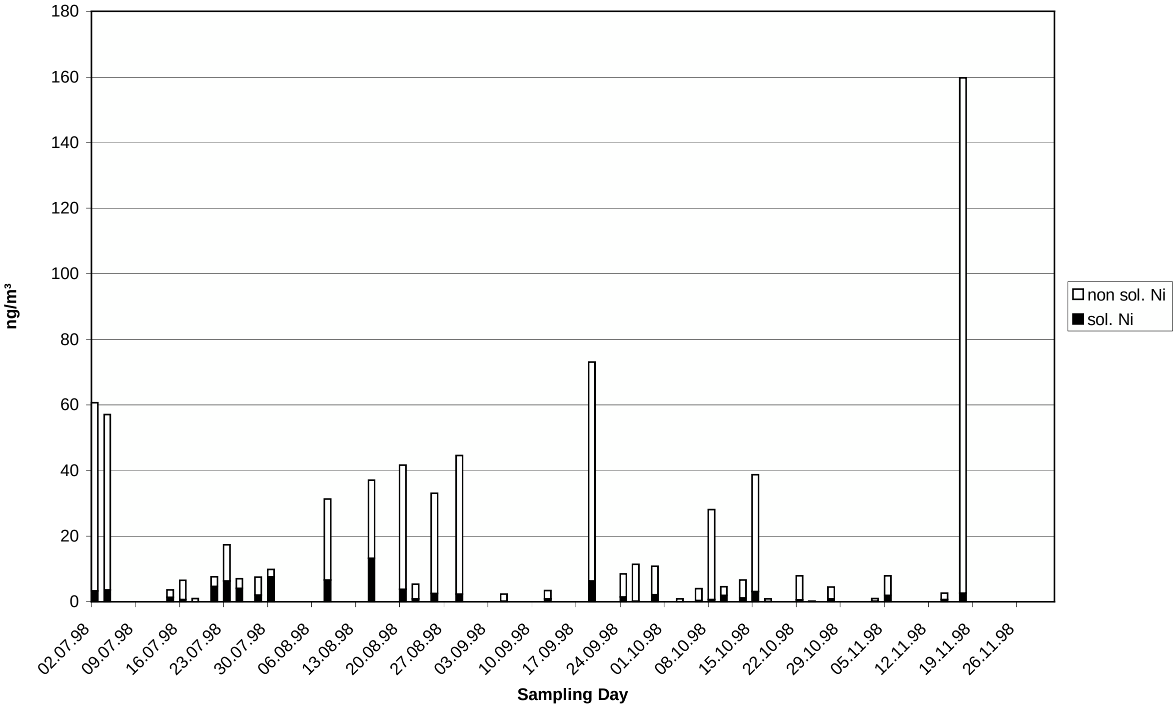


Figure 1.2: Nickel speciation (soluble/insoluble fractionating) of ambient air samples near a plant producing stainless steel

Plotted are the total nickel concentrations in ng/m³ (X-axis) as well as the EDTA soluble insoluble fraction (black and white parts of columns). The total nickel concentrations (daily means) ranged from 0.2 ng/m³ up to 40.0 ng/m³ (plant producing structural steel) and 160 ng/m³ (plant producing stainless steel), respectively. These large concentration ranges are typical for measurements near sources (compare chapter 1.4).

The percentages of soluble nickel also varied strongly from day to day. Maximum percentages were found to be 48.4 % and 77.1 % of the total nickel content, respectively. Although such high percentages were found on several days, the arithmetic means for nickel soluble in H_2O/EDTA were nearly the same for both sites and were less than 20 % (18.6 % and 17.3 %, respectively), the medians being 16.6 % and 10.1 %.

The high variability of the percentage of the soluble fraction of nickel compounds in ambient air seems to depend on the production processes and meteorological conditions, but up to now no clear correlation has emerged. The high percentages of insoluble nickel compounds in figures 1.1 and 1.2 may be site-specific and may differ from typical urban background levels. A third monitoring campaign including a typical urban background site has just started. The first ten samples (daily means) measured at an urban background site south of downtown Dortmund had an average percentage of soluble nickel compounds of 32 %, about 10 % higher than at the industrial sites.

Within this campaign, the multistage extraction process has been extended by means of a flow injection system to include nickel compounds from four different fractions (soluble, sulfidic, metallic and oxidic, for the method see chapter 3.3.1.3). 4 samples (daily means) from an urban background site at Dortmund, Germany [131] and 8 samples from an industrial site near a steel mill have been analyzed so far [131]. The results are shown in table 1.3. As expected from the results of nickel compounds in fly ashes, oxidic nickel takes the lion's share (about 50 %), with soluble compounds next. Surprisingly, however, 5 - 8 % of the nickel compounds belong to the sulfidic fraction. Unfortunately, no further separation of the sulfidic fraction was possible (for example nickel subsulfide from nickel sulfide), so that the portion of nickel subsulfide is still open to question. It can be concluded from the data that a share of several percent of nickel subsulfide as upper limit in ambient air cannot be ruled out.

Further studies are underway to enlarge the data base.

Table 1.3: First results from species specific measurements of nickel compounds in ambient air (daily means) at two sites in Dortmund, Germany [131]. Given are the percentages of the different fractions and the sum of total nickel in ng/m³, corrected for blanks

urban background (Do, FRG)	soluble (%)	sulfidic (%)	metallic (%)	oxidic (%)	sum (ng/m³)
4 samples, mean	22.4	8.3	18.6	50.7	7.4

industrial, near steel mill (Do, FRG)	soluble (%)	sulfidic (%)	metallic (%)	oxidic (%)	sum (ng/m³)
8 samples, mean	42.1	4.5	7.4	46.0	11.9

1.2 Size Distribution Of Particles Containing As, Cd And Ni Compounds

As pointed out already in chapter 1.1, the size distribution is one of the crucial parameters to characterize the airborne aerosol. The size of the particles will determine how deeply they can penetrate into the respiratory system, and which organ may be the target for possible noxious effects. This has direct consequences for the choice of the appropriate sampling method (compare chapter 3). If, for example, the systemic action of metal compounds is linked with the very coarse mode of the particles, sampling can not be restricted to the fraction less than 10 µm (PM10) or even less than 2.5 µm (PM2.5).

In addition, the deposition velocity of particles, their residence time in the atmosphere and their potential for long range transport are closely tied to their size distributions [27]. Very coarse particles with mass diameters > 10 µm will quickly settle in the vicinity of sources, whereas for particles with diameters between 0.1 and 1 µm, the deposition velocity has a minimum [28]. Consequently, this particle fraction is particularly suited for long range transport.

Size distributions of particles containing arsenic, cadmium and nickel compounds have been measured in several Member States. Figure 1.3 shows size distributions measured at two sites in the Helsinki area [29]. Arsenic and cadmium compounds are predominantly concentrated in the fine particle mode (below 2.5 µm), whereas nickel compounds have a significant share in the coarse mode around or even above 10 µm. It is also interesting to note that the size distribution for nickel shows four modes, which points at different source categories. Apparently, the shapes of the size distributions from urban and rural sites do not differ much.

The Finnish results are confirmed by recent data obtained in France, Italy and Germany.

Airborne particulate matter has been sampled and analyzed by the Ecole des Mines de Douai (France) in a background urban area located 3 km away from a lead and zinc smelter. 38 samples have been measured with respect to the size distribution of cadmium and nickel compounds [30]. Again, most diameters of cadmium containing particles were centered within the range of about 0.3 to 2.7 µm, whereas particles containing nickel showed significant shares of their mass fraction around 10 µm.

Cadmium content in the PM2.5 fraction accounted for 80 % of cadmium in the PM10 fraction at a traffic exposed site in Rome, Italy (1999) [125].

At two industrial sites in Germany (Duisburg-Meiderich and Stolberg), the ratio of total suspended particles (TSP) to PM10 was measured together with the ratios of arsenic, cadmium and nickel compounds within these particle fractions [31]. Ratios for the metal and metalloid compounds which exceed the PM10/TSP ratio show enrichment in the PM10 fraction, whereas smaller ratios point at significant shares of very coarse particles with diameters above 10 µm. At Meiderich, a low PM10/TSP ratio of 0.64 was found, with corresponding ratios of 0.81 for arsenic and 0.79 for cadmium (enrichment in the PM10 mode). The ratios for Stolberg in the vicinity of a lead smelter were measured to be 0.77 for PM10/TSP, 0.82 for arsenic and 0.79 for cadmium, showing slight enrichments in the PM10 fraction even near sources. On the contrary, only 69 % of nickel particles were in the PM10 fraction, which compares nicely with the greater share of very coarse nickel particles also in Helsinki and northern France.

In agreement with the Finnish, French and German data, measurements at urban background sites in Switzerland [32] also showed enrichments in the PM10 fraction for cadmium and lead. Cadmium levels in TSP and the PM10 fraction were indentical.

Size distributions measured at urban sites in Germany with an eight-stage Andersen impactor with subsequent analysis of the elements by AAS, ICP-MS and PIXE [10] are presented in Figure 1.4.

These distributions are in good agreement with the Finnish data (please note that scales and cut-offs are different). Again, arsenic and cadmium compounds are predominantly in the fine particle mode below 2.5 µm, whereas nickel compounds have a significant share in the coarse particle mode around 10 µm.

Size distributions of cadmium and nickel compounds measured in Spain in the years 1989-1991 fit into the overall picture, but differ in some details from the data measured in Finland, Germany and France. The size distributions which were determined in rural, urban and industrial areas by means of a cascade impactor with 7 stages [33] are shown in Figure 1.5 as box and whisker plots, presenting the average, minimum and maximum concentrations of the impactor stages from 7 measurements. Again, cadmium compounds are concentrated in the fine mode below 2.1 µm (stage 4), even at the industrial site. However, one of the measurements in the rural area had a considerable contribution also in stage 2 (4.2-9.0 µm). The low average value of this stage indicates that this may have been a singular event. Somewhat in contrast to the size distributions of the other countries, nickel compounds are concentrated in the fine mode below 1.3 µm or even below 0.39 µm (rural and urban areas).

From the data available so far, the following conclusions can be drawn:

- Cadmium and arsenic compounds are enriched in the fine particle mode (below PM2.5). These particles can penetrate into the lung and are well suited for long range transport. Measurements of the PM10 fraction will generally give a good picture also of the total concentration of elements (for the definition of the particle size fractions PM2.5 and PM10 see ISO 7708 [109], equivalent to EN 481).

- Nickel compounds often show significant shares also in the coarse particle mode with diameters around 10 µm. PM10 sampling will slightly underestimate the total nickel content in TSP, especially near sources (up to 30 %). About one third of the nickel particles will settle near sources, whereas about two thirds may be subject to long range transport and can penetrate into the lungs.

- The quite uniform size distributions observed in Western, Central and Northern Europe in urban and rural areas suggest that an equilibrium of particles will be attained within the atmosphere after short transport times from the sources [27].

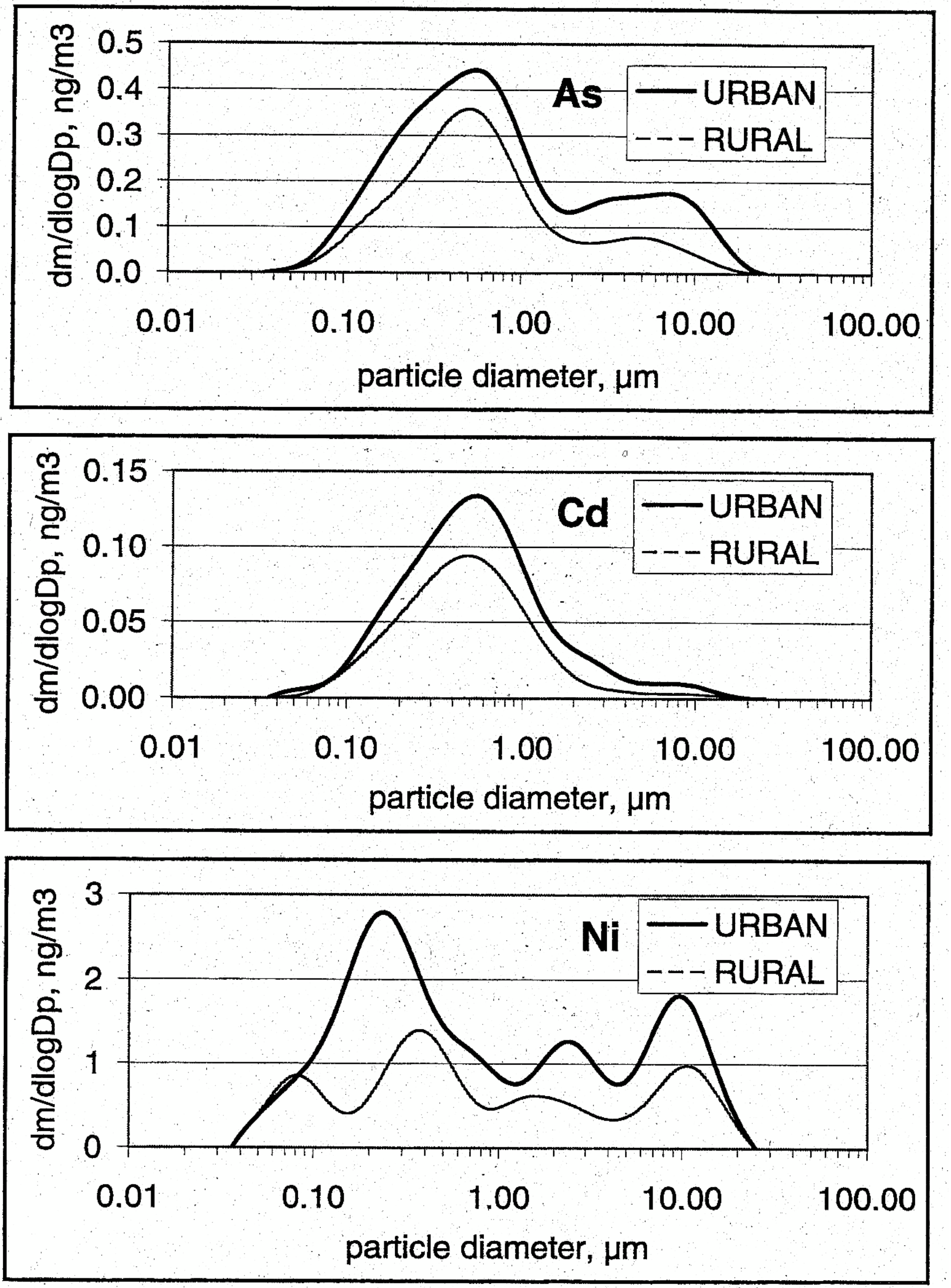


Figure 1.3: Average of 10 size distributions at two sites in the Helsinki area (Finland). The measurements were made simultaneously at the two sites during 1996 - 1997 [29]

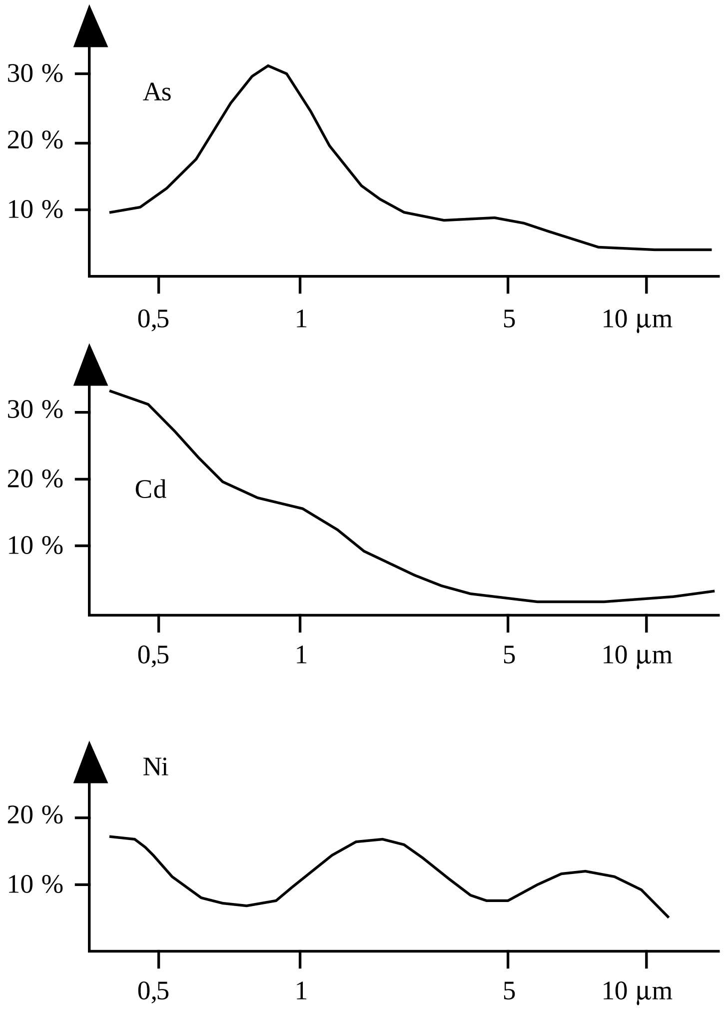
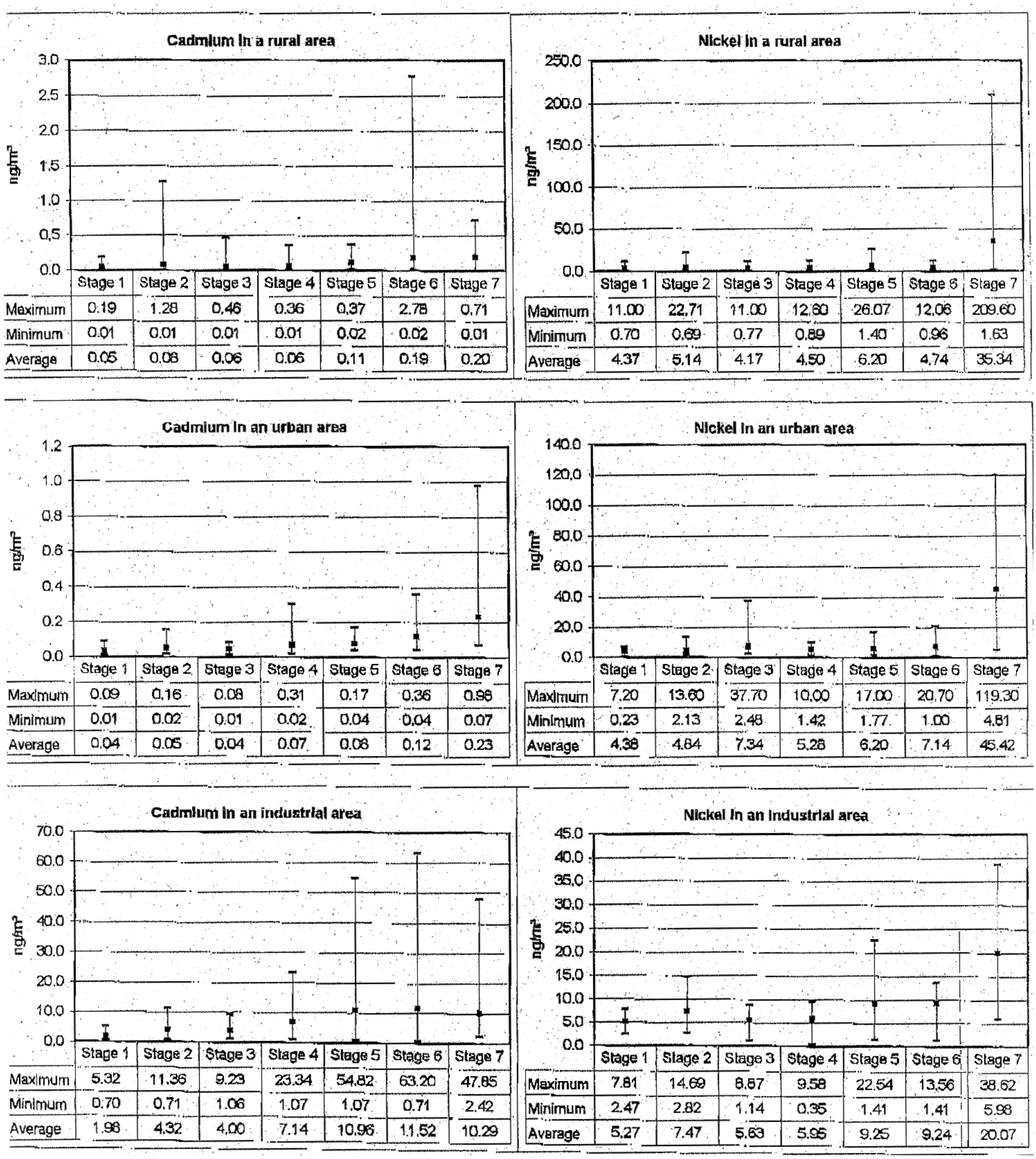


Figure 1.4: Relative size distributions of arsenic, cadmium and nickel compounds measured with an eight-stage Andersen impactor in Germany [10]



	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7
Maximum	0.19	1.28	0,46	0.36	0,37	2.78	0,71
Minimum	0.01	0.01	0,01	0.01	0,02	0.02	0.01
Average	0.05	0,08	0,06	0.06	0,11	0.19	0.20

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7
Maximum	11.00	22,71	11.00	12,60	26.07	12,06	209.60
Minimum	0.70	0,69	0.77	0,89	1.40	0.96	1.63
Average	4.37	5,14	4.17	4,50	6.20	4,74	35.34

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7
Maximum	0.09	0,16	0.08	0,31	0.17	0,36	0.98
Minimum	0.01	0.02	0.01	0.02	0.04	0,04	0.07
Average	0,04	0.05	0,04	0.07	0.08	0,12	0.23

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7
Maximum	7.20	13.60	37.70	10,00	17.00	20,70	119.30
Minimum	0,23	2.13	2,48	1.42	1.77	1.00	4.81
Average	4,38	4.84	7,34	5.28	6,20	7.14	45,42

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7
Maximum	5.32	11.36	9.23	23.34	54,82	63.20	47.85
Minimum	0.70	0.71	1.06	1.07	1,07	0.71	2.42
Average	1.98	4,32	4,00	7.14	10,96	11,52	10.29

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7
Maximum	7.81	14.69	8,87	9.58	22.54	13,56	38.62
Minimum	2.47	2.82	1,14	0.35	1.41	1.41	5.98
Average	5,27	7.47	5,63	5.95	9,25	9,24	20.07

Figure 1.5: Average, maximum and minimum of seven size distributions of cadmium and nickel compounds in rural, urban and industrial areas in Spain (1989-91). The stages of the cascade impactor in µm are as follows: stage 1 (9.0-10.0), stage 2 (4.2-9.0), stage 3 (2.1-4.2), stage 4 (1.3-2.1), stage 5 (0.69-1.3), stage 6 (0.39-0.69), stage 7 (< 0.39)

1.3 Emission Sources Of As, Cd And Ni Compounds

1.3.1 Natural Sources And Global Cycles

All three elements described in this position paper are being emitted both from natural and anthropogenic sources. Emissions of arsenic, cadmium and nickel from natural sources are generally difficult to assess because of the lack of reliable information and measurements. This is especially true when considering vegetative exudates and forest fires. More extensive studies were performed on windblown dusts and volcanic eruptions and therefore these sources are better known. In addition, the emission data from natural sources are much older than the data presented for anthropogenic sources (see chapters below) and big ranges are found in the literature. J. Pacyna has collected and interpreted the data available which are compiled in table 1.4 [34]. The values in brackets give the range of the emissions estimated by different authors and the number above is the most acceptable value according to Pacyna.

Table 1.4: Worldwide Emissions of Trace Elements from Natural Sources in 10^3 t/a [34]

Source	As [35,36,37,38]	Cd [36,37,39,40,41]	Ni [41]
Windblown dust	0.24	0.25 (0.05-0.85)	20 (0.2-44)
Volcanogenic particles	7 (0.3-39)	0.50 (0.04-7.8)	3.8 (2.4-82)
Forest wildfires	0.16	0.01 (0.01-1.5)	0.6 (0.05-3.3)
Vegetation	0.26	0.2 (0.05-2.7)	1.6 (1.6-21)
Seasalt	0.14	0.002 (0.001-0.4)	0.04 (0.01-0.05)
Total	7.8	0.96	26

For arsenic the annual global emissions from natural sources were estimated to be about 8 x10^3 t/a which makes up a quarter of the total worldwide emissions of 32000 t/a [4,5]. Most of these natural emissions result from volcanic activities whereas forest fires, mineral weathering and microbial activities (e.g. in swamps or litoral areas) can be considered as less relevant sources. More recently an atmospheric flux of arsenic was estimated to be about 73540 tons/year, 60 % resulting from natural origin [42].

The atmospheric segment of the global cadmium cycle according to Nriagu is depicted in figure 1.6 [11,18]. Only about 10 % of the emissions of 8.1 x 10^3 t/a are due to natural sources ($0.8 \cdot 10^3$ t/a) . More than a half of this input ($0.5 \cdot 10^3$ t/a) is caused by volcanic activities, e.g. in the plume of Mount Etna on Sicily concentrations of about 90 ng/m³ have been found. Other natural sources to be named are: vegetation exudates ($0.2 \cdot 10^3$ t/a and windblown dusts ($0.1 \cdot 10^3$ t/a). 2 % of the natural emissions of cadmium are supposed to be caused by forest fires. In the seventies some authors have suggested the degassing of crustal rocks as another important emission source [12], although the cadmium release has not been quantified.

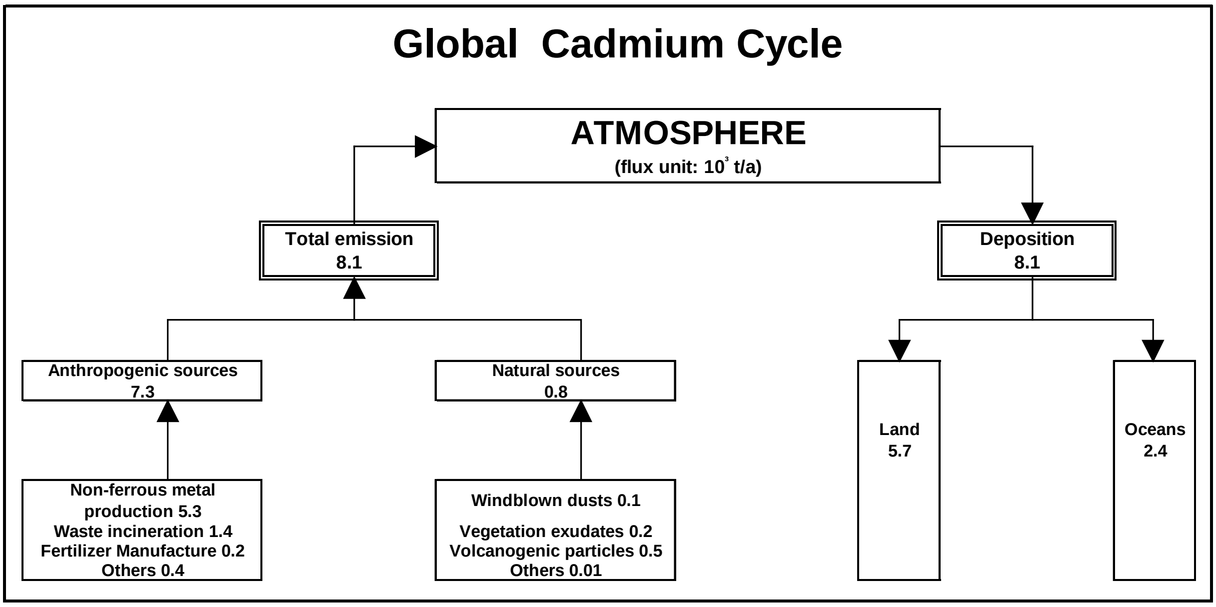


Figure 1.6: Atmospheric portion of the global cadmium cycle [18]

The total worldwide annual emissions of nickel into the atmosphere are about 10-fold as much than those calculated for arsenic and cadmium, respectively. 35 % of the emitted amount of 73 $\cdot 10^3$ t/a are attributed to natural sources [14], suggesting windblown dusts as by far the most important source (figure 1.7). However, a recent estimate of global nickel emissions yields somewhat lower global emissions and natural shares (40 – 50 $\cdot$ 10^3 t/a) anthropogenic emissions and 8,5 • 10^3 t/y natural emissions [22].

In European countries without relevant nickel deposits nickel emissions mainly result from anthropogenic sources.

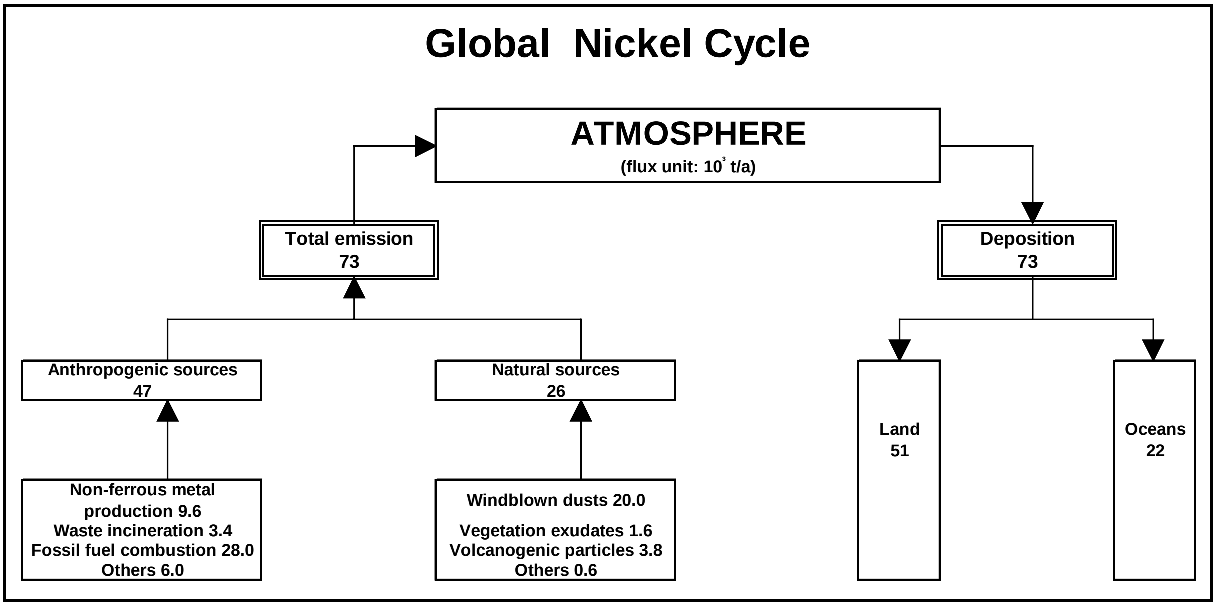


Figure 1.7: Atmospheric portion of the global nickel cycle [21]

1.3.2 Main Anthropogenic European Sources Of As, Cd And Nickel Compounds

Combustion and production processes have turned out to be the major anthropogenic emission sources for arsenic, cadmium and nickel in Europe. In the following the most relevant sources for these elements will be outlined, emission data from individual European countries as well as data published by scientific organisations like the TNO-report [43], describing the emission situation in total Europe, will be presented and an overview of emission trends will be given.

The emission sources will be categorized according to the Corinair SNAP90 structure (SNAP = Selected Nomenclature for Atmopheric Pollutants - for emission source sectors, subsectors and activities). Corinair90 was designed as a common Europe-wide data base providing a complete, consistent and transparent air pollutant emission inventory for Europe in 1990.

1.3.2.1 Combustion Sources

According to the snap code division stationary combustion sources comprise the following source categories: public power, cogeneration and district heating, commercial institutional and residential combustion (domestic burning) and industrial combustion. Waste incineration is subsumed under the category "waste treatment and disposal" and therefore is treated as a separate item. Further combustion sources to be discussed occur within the branches "road transport" and "other mobile sources and machinery".

1.3.2.1.1 Stationary Combustion

By far the most significant emission sources for arsenic (ca. 87 %) and nickel (ca. 59 %) are found within the branch "stationary combustion" in the 15 European Member States [43].

Reason for this finding is that many raw materials contain a variety of different heavy metals and heavy metal compounds as natural accompanying components which can be emitted during combustion processes. Traces of arsenic, cadmium and nickel are found in fossil fuels like lignite (brown coal), hard coal and heating oil. Emissions of heavy metals are only relevant for those fuels burning with a considerable ash residue. Therefore, the combustion of natural gas and extra light heating oil is not a significant source for emissions of As, Cd and Ni (dust content < 0.1 mg/m^3). In the flue gas the heavy metals considered normally occur as compounds (e.g. oxides, chlorides) condensed on the surface of particles. Only arsenic is supposed to be emitted to a small extent in the vapour phase. This fraction can be calculated as 0.5 % (wt) from the arsenic content in the coal [44].

Generally, the As, Cd and Ni concentrations vary not only between different fuel categories like coal and heavy fuel oil, but also within the same category. Depending on the provenance of the raw material and on its ash content heavy metal concentrations in lignite and hard coals can differ by one order of magnitude. An example for the concentration of the trace elements As, Cd and Ni in "Ruhr coals" is given in table 1.5 [45]. One can conclude that the heavy metal concentrations are increasing with higher ash content of the coals.

Table 1.5: As, Cd and Ni concentrations in "Ruhr coals" [45]

Substance	Ash content < 10 % [mg/kg]	Ash content 10 - 30 % [mg/kg]
Arsenic	2 - 20	10 - 50
Cadmium	< 1	0,5 - 5
Nickel	15 - 40	30 - 100

Another fuel type, the nearly black, high-viscosity heating oil S is a typical residual oil resulting from destillation and cracking processes. The ash fraction of about 0.1 % contains high nickel contents ranging from 0.01 to 150 mg/kg oil [46, 47]. In the clean flue gas dust of different combustion plants fired with heating oil S a weighted mean value of 48.000 ppm nickel was found (range: 7400 – 48.000 ppm) [48].

The heavy metal content emitted from combustion processes is not only due to the trace element concentration in the raw materials but also combustion conditions, combustion temperatures and secondary abatement systems play an important role. For example combustion plants equipped with a dry bottom boiler (DBB) which is mainly used for the combustion of lignite and hard coal are operating within the temperature range between 900 and 1200°C. Wet bottom boilers (WBB) applied for hard coal with low content of volatiles are working at higher temperatures of more than 1400°C which leads to higher metal and metalloid emissions into the flue gas (compare table 1.5). On the other hand lower temperatures of about 750 - 950°C are needed at large combustion plants applying the fluidized bed combustion (FBC).

Particle-bound heavy metals can be reduced by applying secondary measures for the dust separation like cyclones, wet scrubbers, electrostatic precipitators (ESP) and fabric filters. However, the dust removing potential of the systems mentioned is of different quality. 99 % of the particles can be separated using the ESP or fabric filters, whereas typical cyclones are less efficient. A comprehensive description of secondary measures comprising the latest state of the art ist given in the BREF-notes (BREF = BAT reference documents). Drafts of BREF-notes are available for the following eight sectors: iron and steel, cement and lime, paper and pulp, non-ferrous metal production, glass, chloro-alkali industry, cooling-down systems and tanneries. Drafts for another eight BREF-sectors are under preparation [49].

In table 1.6 the As, Cd and Ni emission factors for combustion plants with a thermal boiler capacity of 300 and more MW are compiled [48]. The values vary between several orders of magnitude and strongly depend on different fuel types, combustion conditions and abatement systems applied. As expected, the highest emission factors result from the combustion of heavy fuel oil.

All emissions from stationary combustion plants considered here are generally released through a stack. Therefore, there is no need of taking into account fugitive emissions, e.g. occurring from leaky seals or during the changeover and storage of raw material for the assessment of heavy metal emissions from these sources.

Table 1.6: Emission factors (g/Mg fuel) for combustion plants [48]

Type of fuel	Heavy metal element	Type of boiler			
		DBB		WBB	
		Dust control 1)	Dust control and FDG 2)	Dust control 1)	Dust control and FDG 2)
hard coal	Arsenic	0.03-0.3	0.01-0.1	0.1-0.8	0.04-0.3
	Cadmium	0.003-0.01	0.0001-0.004	0.01-0.07	0.004-0.03
	Nickel	0.03-0.4	0.01-0.5	0.2-0.5	0.1-0.2
brown coal	Arsenic	0.03-0.04	0.008-0.01	-	-
	Cadmium	0.002-0.004	0.00008-0.001	-	-
	Nickel	0.02-0.04	0.01	-	-
heavy fuel oil	Arsenic	0.5 3)	-	-	-
	Cadmium	1.0 3)	-	-	-
	Nickel	35 3)	-	-	-

1) clean gas particle concentration 50 mg/m³

2) FGD = Flue gas desulphurisation, clean gas particle concentration 20 mg/m³

3) general emission factor according to Stobbelaar 1992/ [50]

1.3.2.2 Production Processes

1.3.2.2.1 Sinter Plants

Another relevant source for the emission of heavy metals is the sintering process, an pretreatment step in the production of primary metals(both ferrous and non-ferrous) where fine particles of metal ores are agglomerated to form porous clinker, which is referred to as sinter. The sintering process consists of several steps (blending, mixing, crushing, sintering and screening), where heavy metal containing dust emissions occur, due to trace quantities contained within the ores. To remove the dust, cyclones, electrofilters, bag filters or wet scrubbers can be applied as abatement measures. The emission factors available vary, depending on the abatement measures within the following ranges: 0.009 - 0.08 gMg^{-1} product for arsenic, 0.0004 - 0.12 g Mg^{-1} product for cadmium and 0.14 -1.0 g Mg^{-1} product for nickel [51].

1.3.2.2.2 Iron & Steel Industry

Iron ores contain a huge number of heavy metal compounds which can be released as particle-bound pollutants during different production processes from the iron and steel industry. The profile of the emitted metals is dependent on the composition of the ores used. On the European level the iron and steel industry is a significant source for As, Cd and Ni (see table 1 in annex B). Nearly half of the amount of As (35.1 tons) and Cd (39.5 tons) being released from production processes is due to the iron and steel sector. According to TNO the nickel emissions in the 15 Member States (143 tons) even make three-quarters of the amount caused by all production processes [43]. In 1995 it was reported by Baart et al. that the contribution of the iron and steel industry to the total European emissions of cadmium and nickel is 22 % and 14 %, respectively [52]. Comparing this calculation to the data published by TNO, it is evident that Baart et al. attach much more importance to the impact of the iron and steel industry to the total nickel emissions than TNO does, which calculated a share of 2.9% only.

The individual production steps in the iron and steel industry contribute to a different extent to emissions in Europe. One of the main sources is iron ore sintering, which is described above. Other relevant emissions occur in connection with melting heavy metal scrap in electric arc furnaces. In contrast to this, ironmaking in the blast furnace is considered to give rise to relatively low heavy metal emissions.

1.3.2.2.3 Non-ferrous Metal Industry

Concerning production processes the non-ferrous metal industry contributes with a percentage of 14.3 % and 15.2 % to the European arsenic and cadmium emissions, respectively, whereas this branch is not an important source for nickel emissions (ca. 1.1 %). A large part of the As and Cd emissions is associated with the copper and zinc production.

There are three main processing steps occurring in the primary copper production: roasting of ores, smelting of the roaster product and converting of the copper matte to blister copper. All the steps mentioned give rise to heavy metal containing particulate matter emissions. In contrast to this, the secondary copper production which covers about 40 % of the total copper production is not regarded as a significant source for heavy metal emissions. A contribution of less than 1 % to the total atmospheric emissions is estimated for this category according to Nriagu and Pacyna (1988) [53]. In Nort Rhine Westphalia (Germany) only one secondary copper smelter is in operation having produced 215 000 t/a copper anodes and copper compounds and 10 400 t/a tin alloys in 1996. The here emitted arsenic and cadmium is about 4.7 % (70 kg/a) and 0.1 % (11,1 kg/a) of the totally emitted amount of these components in Northrine-Westfalia [54]. However, secondary copper smelters can cause increased ambient air concentrations in the neighbourhood of the plants.

About two-third of cadmium emissions coming from the branch of non ferrous-metal industry in the 15 EC countries result from the zinc industry. Zinc is produced from sulphide ores which also contain arsenic and cadmium sulphides as impurities. Heavy metal emissions can be expected from production steps like roasting and smelting of the ores as well as from storage and handling of the ores.

1.3.2.2.4 Organic Chemical Industry

Concerning the branches to be subsumed under "organic chemical industry" only the glass and cement industry contribute to a small extent of less than 1 % to the European As, Cd and Ni emissions respectively. Emissions from other types of plants in this category (halogenated hydrocarbon production, pesticide production, paper and pulp industry and road paving with asphalt, battery manufacturing) are even lower and can be neglected.

1.3.2.3 Road Transport

In the TNO-report on heavy metals it is reported that "road transport" is a considerable source for cadmium emissions, coming up to 36,6 tons or 18 % of the total emitted cadmium in Europe in 1990 [43]. These figures are based on the PARCOM-ATMOS emission factors for mobile sources which have been derived from exhaust emission studies mainly performed in the United States in the late seventies and early eighties [55, 56, 57, 58]. The origin of cadmium in the exhaust gas is supposed to be related to its presence in the gasoline and to all kind of corrosion effects of the car, eg. coatings in the exhaust pipe. The presence in the fuel might be due to a result of a series of cracking of the heavier residues of the oil, contamination from storage tanks, additives to the gasoline etc.. Thus, the PARCOM-ATMOS emission factors are results of real measurements and should not be ignored. However, it is not clear to what extent these data are still valid in the late nineties. There is strong evidence that this share could be overestimated. Neither recent national emission inventories (see annex B) nor traffic related ambient air measurements (see chapter 1.4.1) from the individual member countries confirm such an high contribution. For example, France reports a percentage of 1.7 % cadmium to be attributed to passenger cars’ emissions (1996), Flanders referred a share of 2.2 % (1997) attributed to the sector traffic, Italy (1994) and Luxemburg (1997) a value of about 1 % each to road transport. The cadmium emissions from road transport in Austria was estimated to be 4.5 % (1995).

In the Atmospheric Emission Inventory Guidebook [51] emission factors are provided for cadmium and nickel taking into account the results of comprehensive studies carried out in several Member States. For nine of the ten vehicle categories including passenger cars, light duty vehicles, heavy duty vehicles and mopeds and motorcycles emission factors of 0.01 mg/kg fuel for cadmium and 0.07 mg/kg fuel for nickel are calculated. Only passenger cars using liquid petroleum gas (LPG) as fuel are not emitting heavy metals. The authors stress that these values have to be considered as preliminary estimates only which are subjected to numerous uncertainties. Erroneous assumptions occur e.g. with regard to the vehicle park of a country and the actual vehicle usage, further errors are due to lacking measurements or non-representative driving cycles. Overall, the estimation of emissions from road traffic seems to be more difficult than from other sectors.

1.3.2.4 Other Mobile Sources And Machinery

The category „other mobile sources and machinery“ is considered by TNO as an important emission source for nickel due to the combustion of heavy fuel oil. At European level a share of more than 30 % of the total nickel emissions is assigned to this branch according to the TNO-report [43]. This high share seems to be strongly overestimated because more recent emission data submitted by the Member States present considerably lower percentages, although the informations given are incomplete and inconsistent. The figures reported for this branch vary between 0 tons (United Kingdom, 1996) and 67.8 tons or 12.5 % (Italy, 1994). Assuming that the branch category „other mobile sources and machinery“ is less important in terms of nickel emissions than described in the TNO-report, the predominant part of the nickel emissions (probably more than 90 %) can be attributed to combustion sources.

1.3.2.5 Waste Treatment And Disposal

Waste incinerators are emittors of heavy metals depending on the composition of waste, combustion conditions and gas-cleaning devices. According to the TNO-report 16.1 tons (about 8 %) of the cadmium was estimated to be due to waste incineration in the 15 Member States. Products like batteries, coating and plating, pigments and plastics and synthetic products can be the origin of cadmium emissions when they are incinerated as waste. During the 1980s and 1990s cadmium emissions from waste incinerators have decreased due to a) restrictions on the use of cadmium in some consumer products , and b) a better emission control technology of the incinerators. Recently, the relative contribution of the different emission sources was re-estimated in a perspective of human exposure.This analysis demonstrated that less than 1 % of current human exposure to cadmium originates from the production and use of cadmium containing products; emissions from incinerators, (including a significant input of cadmium from natural origin) contributed about 1.5 % of total exposure [59].

Waste sites are not considered as relevant emission sources for cadmium into the air, although the emission of methylated gaseous cadmium and arsenic compounds has been reported [60].

1.3.2.6 Other Sources

Other branches compiled in the snap code division like „extraction and distribution of fuels“, „solvent use“, „nature“ and „electrical equipment“ are not of importance for arsenic, cadmium and nickel emissions. However, it should be mentioned that cadmium emissions of about 2.5 % result from agricultural activities.

1.3.3 Emission Inventories

National emission inventories for arsenic, cadmium and nickel exist in several European countries (see 1.3.3.4). Beyond that, scientific or national organisations have published emission inventories for all Member States.

1.3.3.1 The European Atmospheric Emission Inventory Of Heavy Metals And Persistent Organic Pollutants

The Netherlands Organization for Applied Scientific Research (TNO) has established an European emission inventory for heavy metals and persistent organic compounds for the year 1990 [43]. This work has been carried out within the framework of OSPARCOM, HELCOM and the UN-ECE on behalf of the German Environmental Agency (UBA). The inventory comprises emission data from 38 European countries (including OSPARCOM and HELCOM members). Emission results are listed for individual countries and are summarized for parts of Europe. The informations are either based on official country submissions of emission data which surely are of different quality or, for lacking countries and sources, on supplementary default emission estimates carried out by TNO. It has to be emphazised that all data presented in the report are subjected to uncertainties. The authors of the TNO-report point out that the uncertainty factors for estimates of atmospheric heavy metal emissions range between 1.5 and 3.5. In general the lower value applies for the north-western part of Europe and the upper limit to Central and Eastern Europe. For southern Europe a factor in between is applicable. An uncertainty factor of 3.5 means that the lower limit of the uncertainty range for a calculated emission is 28.6 % and the upper limit is 350 % of the value given.

In table 1 of annex B the TNO data of the annual emissions of arsenic, cadmium and nickel are listed per source category for the 15 EC Member States according to a modified SNAP90 code. The data are a summation of country data and TNO data not approved by countries. An overview of the major emission sources of the three metals is given in the figures 1.8 a-c. The total arsenic emissions of 575 tons per year are practically due to only two source categories: stationary combustion of hard and brown coal and fuel oils (494 tons per year or 85.6 %) and production processes (77.3 tons per year or 13.4 %). The source category "stationary combustion" covers the three big branches "public power, cogeneration and district heating", which is responsible for the lion's share of the arsenic emissions (56.3 %), "commercial institutional and residential combustion" and "industrial combustion". According to the TNO study nearly half of the released arsenic from production processes can be assigned to the iron and steel industry (45.4 %).

The total European cadmium emissions are reported to be 203 tons per year. These emissions are also mainly caused by combustion and production processes (28.7 % and 38.6 % respectively) but other sources like road transport (18 %) and to a minor extent waste treatment and disposal are considered to contribute to the cadmium emissions as well. As already mentioned, data from recent national emission inventories and ambient air levels (see chapter 1.4.1) do not show a significant influence of road transport to cadmium emissions.

The total nickel emissions of the 15 Member States are given to be 4860 tons per year, a level about one order of magnitude higher than arsenic and cadmium values. Again the major part (58.9 %) of the emissions results from stationary combustion processes due to the application of heavy fuel oils which contain high nickel contents. As already mentioned in chapter1.3.2.4 the share of 30.5 % from the branch "other mobile sources and machinery" seems to be overestimated and out of date.

Significantly lower annual nickel emissions (1705 tons) are estimated by the authors of the CEPN-report [61]. Based on the informations collected in 1996 94 % of the nickel emissions come from combustion, 4.6 % from stainless steel production and only 1.2 % can be attributed to the primary nickel production.

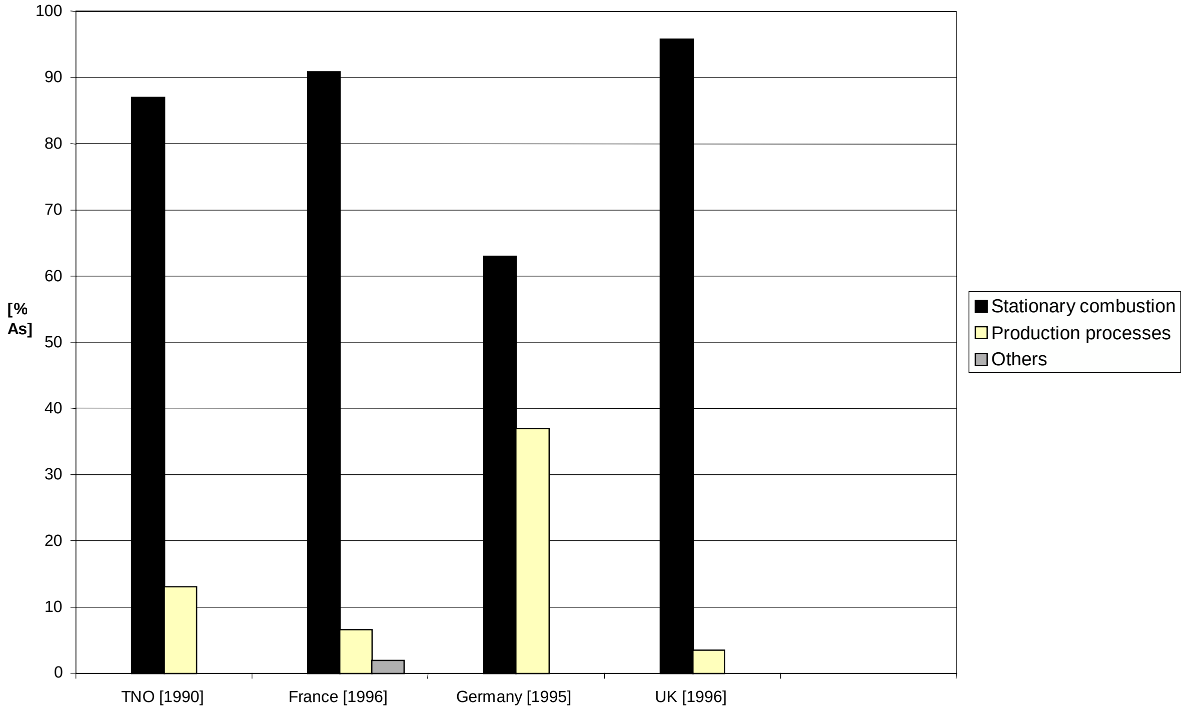


Figure 1.8 a: Anthropogenic arsenic emissions in the 15 Member States 1990 according to TNO [43] and in three individual countries (annex B)

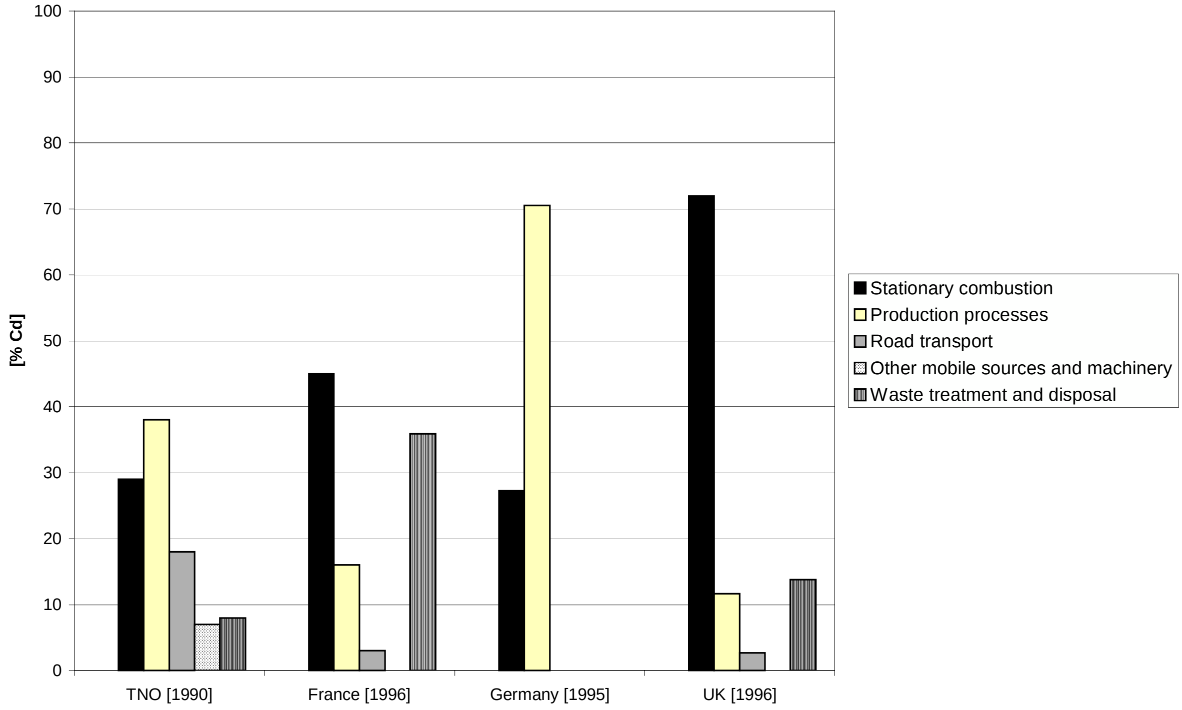


Figure 1.8 b: Anthropogenic cadmium emissions in the 15 Member States 1990 according to TNO [43] and in three individual countries (annex B)

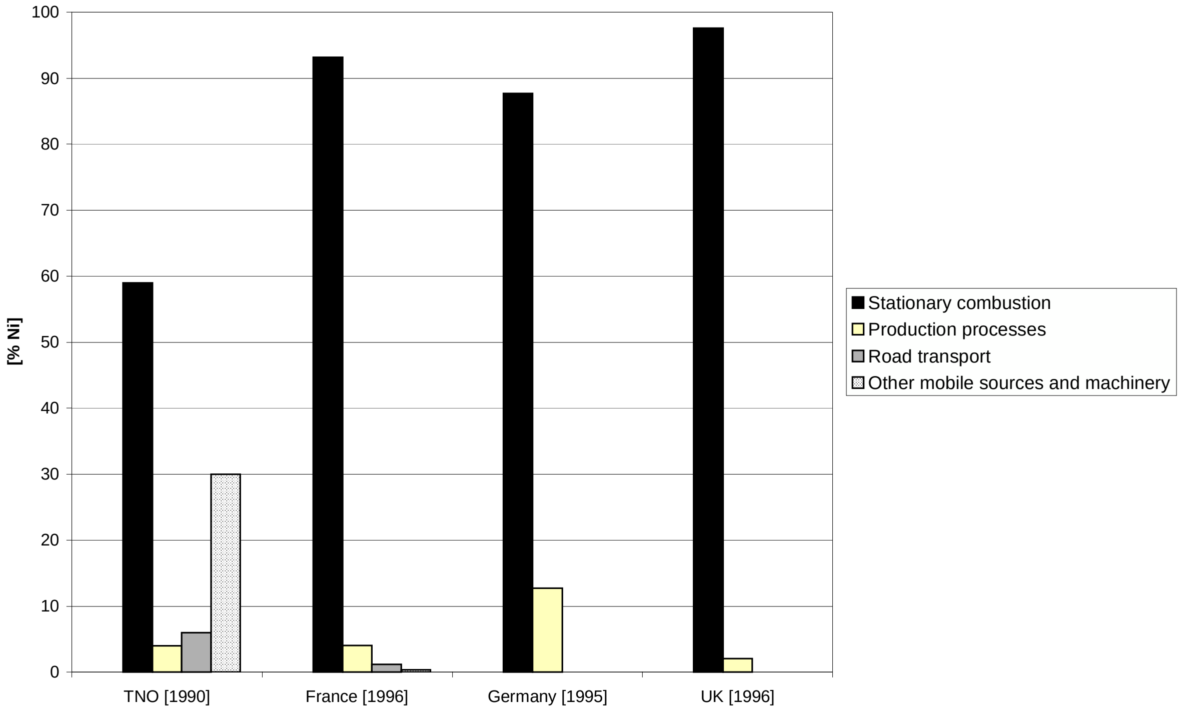


Figure 1.8 c: Anthropogenic nickel emissions in the 15 Member States 1990 according to TNO [43] and in three individual countries (annex B)

1.3.3.2 Emission Activity In The Scope Of The Convention On Long Range Transboundary Air Pollution (LRTAP)

The co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (EMEP) has the main objective to provide more monitoring and modelling data on transboundary fluxes, concentrations and depositions of cadmium, lead and mercury over Europe. In accordance with the Protocol on Heavy Metals (1998) the Parties shall develop and maintain emission inventories and report emission data to the UN ECE Secretariat, encourage research, monitoring and co-operation, in the fields of emissions, long-range transport, deposition levels ect..

It should be noted that for the time being only cadmium is extensively studied in the framework of EMEP activity wheras Ni and As will be considered more thoroughly during the next phase of EMEP. Official data on cadmium emissions submitted by the Parties are collected in the emission data base of the MSC-W (Meteorological Synthesizing Centre West). MSC-E (Meteorological Synthesizing Centre East) , being responsible for modelling of heavy metals , carries out quality control of the emission data and expert estimates in cases when official data are absent. By the end of 1999 emission data on cadmium were submitted by 30 European countries (13 of them are EC members) for a period of at least one year (1990-97). For Portugal and Ireland expert estimates are used [62].

In table 2 of annex B the cadmium emission data are presented. Figure 1.9 shows the spatial distribution of anthropogenic cadmium emissions over the EMEP-region for the year 1996

[62] on the basis of official data and various expert estimates. The highest density of cadmium emissions is observed in industrial regions of Germany, Belgium, Spain, UK and Italy.

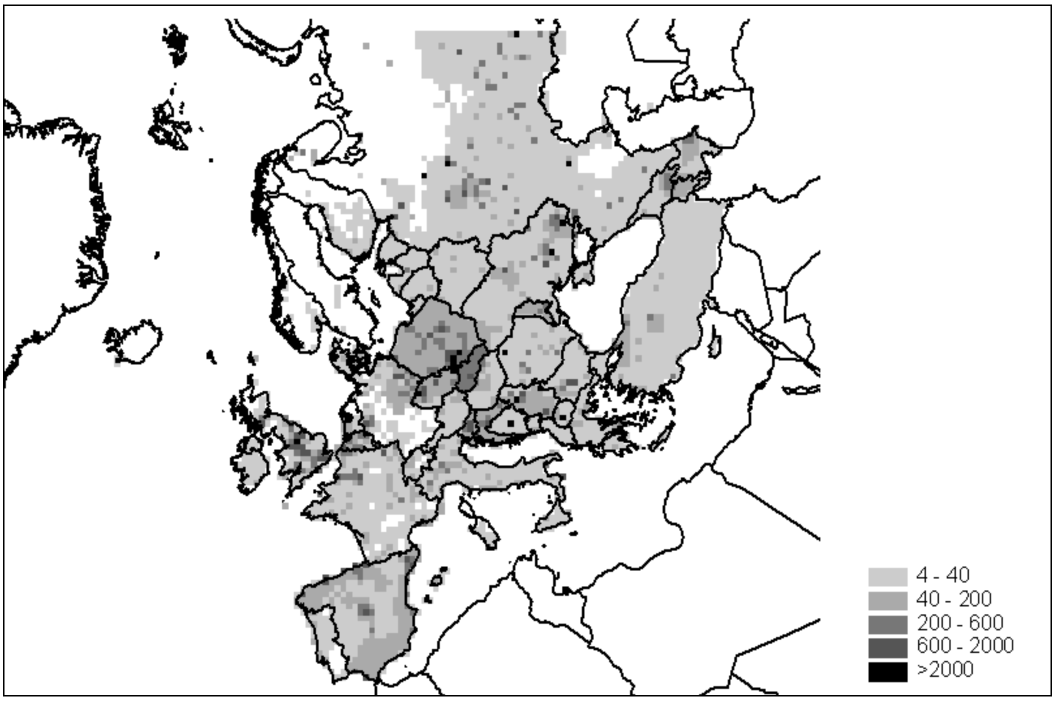


Figure 1.9: Field of anthropogenic emission of cadmium in 1996 with spatial resolution 50x50 km, g/km^2/yr

The uncertainties of heavy metal emissions from individual countries are difficult to assess. It was indicated in the MSC-E report [62] that estimates for cadmium made by various experts differed up to 2.8 times. Within the framework of the ESQUAD project [63] an attempt was made to evaluate the uncertainty range for different countries. According to these data cadmium estimates can vary within up to a factor of ± 3 for Europe as whole. In the TNO-study [43] the uncertainty of heavy metal emissions is reported to be within the range of 1.5 to 3.5.

1.3.3.3 Marine Exhaust Emissions Research Programme By Lloyd's Register Engineering Services

Within the frame of The Marine Exhaust Emissions Research Programme an assessment of marine diesel engine exhaust components was performed by Lloyds Register Engineering Services [64]. Besides the typical combustion products like nitrogen oxides, carbon monoxide, hydrocarbons and particulates, the emissions of many transition elements and metalloides were investigated. The estimation of heavy metals concentration within the exhaust gas stream was undertaken by analysing the heavy metal content of the oil fuel burnt. It was assumed that the heavy metal content in the oil corresponds to that in the exhaust gas. All trace elements were analysed by plasma emission spectroscopy.

The results of the measurements show that the heavy metal composition of the oil fuels from different vessels reflects the component oil blends. The concentrations of arsenic vary from 0.05 to 1.0 mg/kg, the nickel concentration even ranges from 0.07 to 44 mg/kg. On the basis of the concentration determination of the trace elements in fuel and gas oils, word-wide annual emissions of the elements arsenic, cadmium and nickel were estimated as follows:

Table 1.7: Emissions from marine oil fuel consumption [64]

Substance	World-wide Emissions [t/a]
Arsenic	55
Cadmium	26
Nickel	3043

For this calculation it was assumed that the world-wide marine oil fuel consumption is 100 and 40 million tons for fuel and gas oils, respectively. Comparing these emissions to the emission estimates for natural and anthropogenic sources, it can be concluded that nickel emissions in marine exhaust represent a significant proportion. In contrast to this, arsenic and cadmium emissions only play a minor role.

There are no data available describing the emissions from marine exhaust in Europe at present.

1.3.3.4 National Emission Inventories

National emission inventories are kept by many European countries and emission data have been provided on request of the Working Group by Austria, Belgium (Flanders), Denmark, Finland, France, Germany, Italy, Luxemburg, the Netherlands, Sweden and The United Kingdom (tables 3 - 13 in annex B). The data presented refer to different years (only the most recent data were used) and are partly compiled in a different way. Therefore emission data of individual countries may not be compared to each other in all cases. In addition, no informations were given how these data were obtained. Emissions of heavy metals may be based on the analysis of dust components only, not taking into account that part of the metals can permeate the dust filter material. Therefore an underestimation of the emitted heavy metal concentration may result.

In the figures 1.8a – c the most recent available emission data of As, Cd and Ni from France, Germany and the UK are compared with the data published by TNO for the 15 European Member States. In all countries the major part of the arsenic and nickel emissions is due to the sector “stationary combustion”. However, in Germany the emissions resulting from production processes are clearly higher than in the European average and in the case of cadmium even exceed the share contributed to combustion processes. None of the individual countries has assigned nickel emissions to the sector “mobile sources and machinery” proving that the TNO data are not longer valid for this branch. A remarkably varying percentage is reported for the cadmium emissions from waste treatment and disposal, ranging from 0 % in Germany to 36 % in France.

1.3.4 Trends

The evaluation of the emission inventories from some European Member States shows a trend for decreasing emissions for at least one of the three heavy metals. Some examples are given:

In figure 1.10 the development and future projection of the total cadmium emissions in Austria are shown for the period 1985 to 2010. From 1985 to 1995 a decrease of more than 60 % from 4.77 to 1.79 tons/year can be observed. A further slight downward trend is expected until 2010, mainly due to the reduction of emissions from the sector „stationary combustion“.

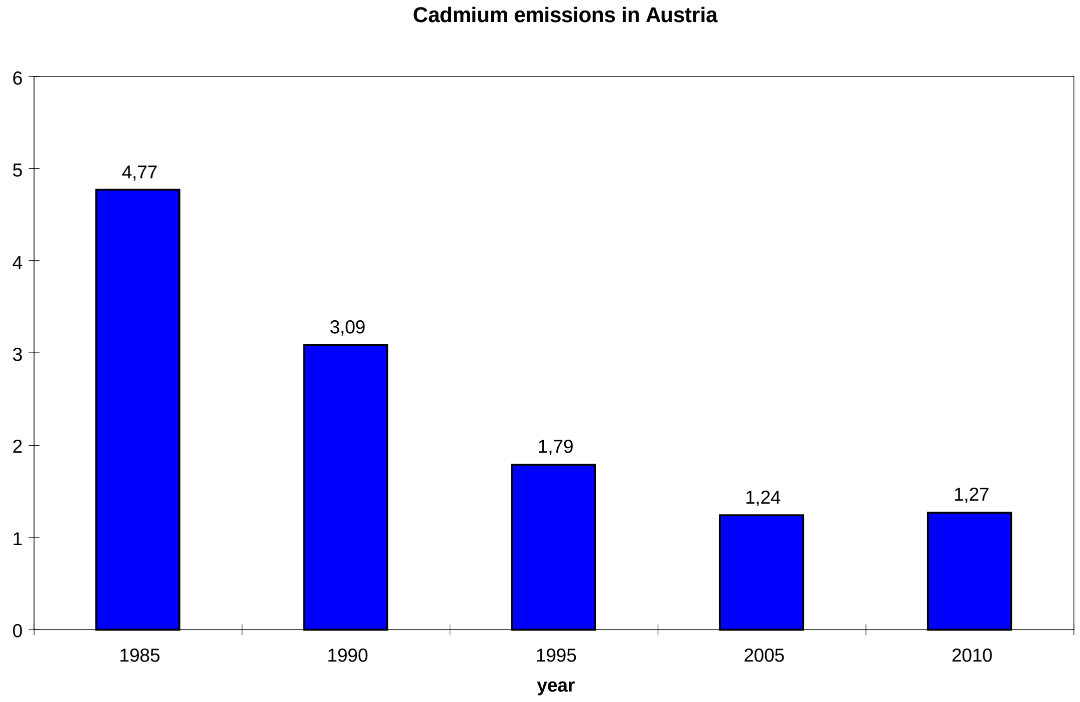


Figure 1.10: Development of cadmium emissions in Austria from 1985 -2010 in tons/year [65]

Also in Italy the annual emissions of the heavy metals concerned could be reduced impressively from 1990 to 1995. The values of arsenic and cadmium dropped by 38 % and 44 % respectively, the nickel emissions even could be more than halved. This development can be explained by the reduction of the emissions in the branch „combustion in energy and tranformation industries“.

According to data published by the German Environmental Agency [66] a pronounced decrease of heavy metal emissions can be noted for Germany as well (table 1.8). In the former Federal Republic of Germany (BRD) the most substantial decrease of heavy metal emissions can be found from 1985 to 1990. This is a result of the application of more effective waste gas cleaning measures which were indispensable to meet the requirements of the 13th ordinance on power stations launched in 1983 and the Technical Instructions on Air Quality Control (1986). Until 1990 in most power plants the necessary dedusting facilities had been installed. For this reason, in the following years only a minor reduction of heavy metal emissions could be observed in this part of Germany. In contrast to this, emissions coming from the former German

Democratic Republic (DDR) were reduced drastically from the beginning of the nineties because many plants were either shut down after the reunification or refitted with more efficient flue gas cleaning.

Table 1.8: Annual emissions of arsenic, cadmium and nickel in Germany [66]

Annual Emissions of Heavy Metalls in Germany from 1985 to 1995 *

	1985			1990			1995 *		
	☐	▨	■	☐	▨	■	☐	▨	■
Arsenic	134	87	221	100	20	120	19	14	33
Cadmium	25	20	45	21	9	30	5	6	11
Nickel	171	269	440	134	143	277	29	130	159

* values estimated for 1995

Source: Environmental Agency 1998

☐ **Former German Democratic Republic**
Neue Bundesländer

▨ **Former Federal Rep. of Germany**
Alte Bundesländer

■ **Germany**

In the United Kingdom a National Emission Inventory has been existing since 1970. From that point emissions of arsenic have declined by 78 % (figure 1.11b). The main source of arsenic emissions in UK is coal combustion with other sources being very small in comparison. Coal use declined over the period considered, in favour of natural gas use. The emissions from coal fired power stations have been revised downwards significantly since the 1995 Inventory.

Also nickel emissions summarized in figure 1.11a declined by more than 75 % since 1970. This is a result of the lower consumption of coal and heavy fuel oil which has been replaced by orimulsion (an emulsion of bitumen in water) in some power stations since 1989. Emissions from power stations have been revised downwards by a factor of two since the previous inventory based on new data from the major power generators [67].

The cadmium emissions have dropped very slowly from a level of about 40 t/a to a value of 20 t/a in 1996 since 1970. The decline in emissions is a result of the general fall in coal combustion, the decline in fuel oil combustion in power generation and recent improvements in waste incineration plants.

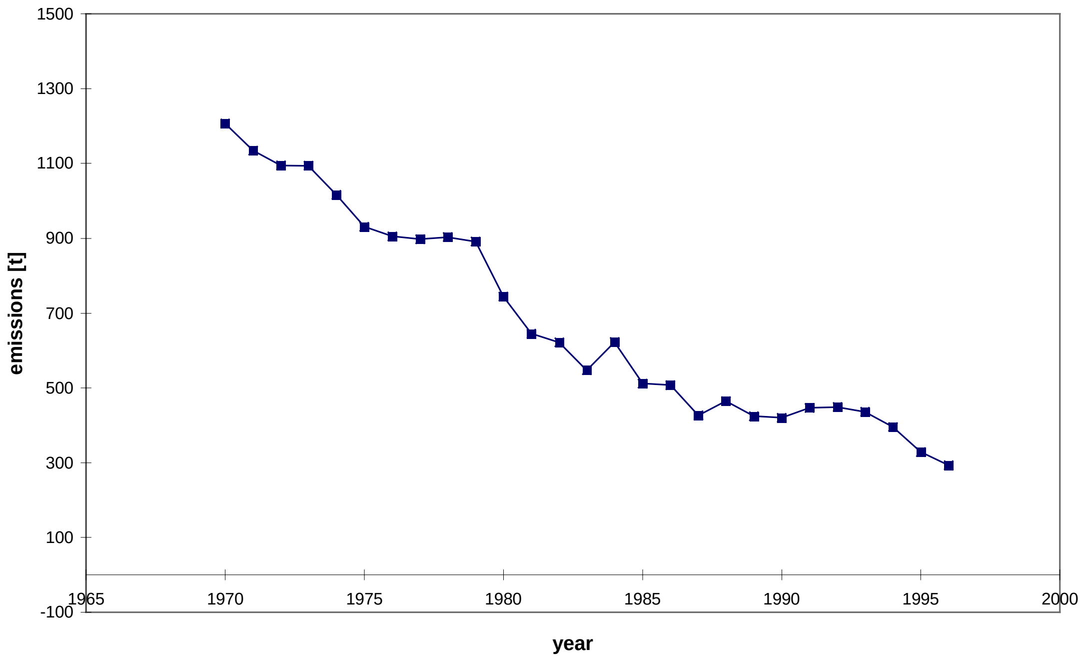


Figure 1.11a: Nickel Emissions from the UK

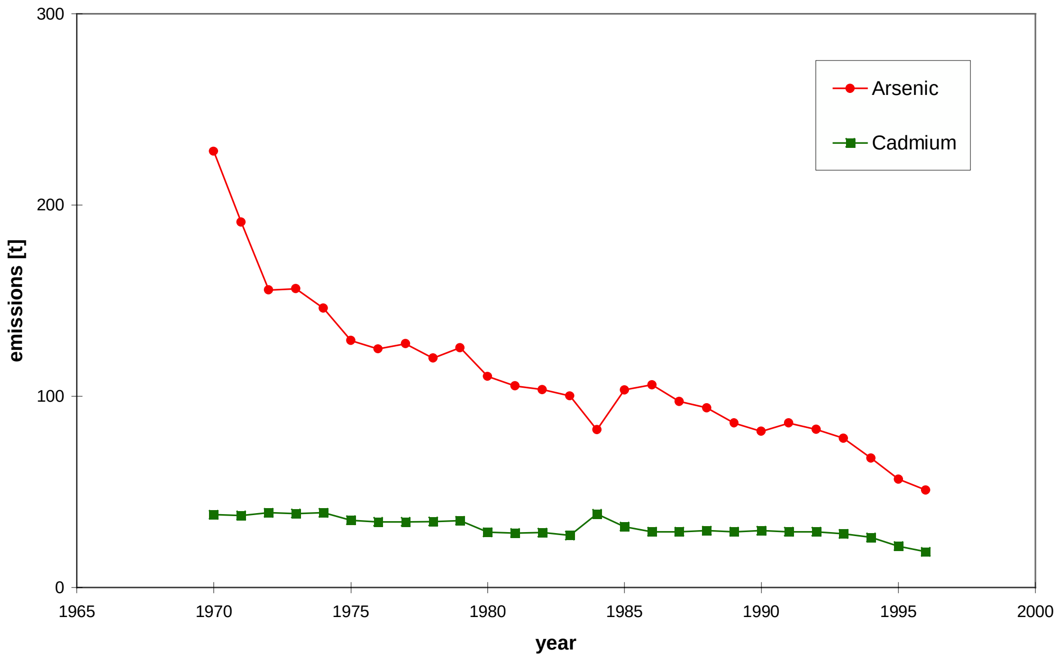


Figure 1.11b: Heavy metals Emissions from the UK

Within the framework of EMEP an assessment of the reduction of cadmium emission in Europe was performed by the Meteorological Synthesizing Centre–East (MSC-East). On the basis of official emission data submitted by the countries to the UN ECE Secretariat a reduction was calculated for the period 1990-95 as follows: about 20 % per year for Sweden and Luxembourg, 15 % per year for Italy, 10 % per year for Finland, 7 % per year for the Netherlands and 3 % per year for Denmark.

An important reason for the decreasing emissions of heavy metals observed in the last years is the introduction of effective abatement techniques. The following example shows the development of emissions from the production plant in Harjavalta, Finland comprising a primary copper smelter, a primary nickel smelter and a nickel refinery (table 1.9). Since 1990 the arsenic and cadmium emissions have been decreased by an order of magnitude, the nickel emissions by a factor of about 3. In the draft of the BREF notes the technology used in Harjavalta is described to be the “Best Available Technology”. Considering the nickel production the specific load could be reduced from 1,71 kg/ton produced nickel in 1990 to 0.05 kg/ ton produced nickel in 1998 [68].

Table 1.9: Development of As, Cd and Ni emissions in Harjavalta, Finland

Year	As [tons]	Cd [tons]	Ni [tons]
1990	15	4.2	3.1
1998	10	0.425	1.7
1999 (estimation)	2	0.299	0.87

1.4 Ambient Air Levels In Europe

1.4.1 Ambient Air Concentrations

Ambient air concentrations of arsenic, cadmium and nickel compounds in Europe are compiled in tables 1.10. - 1.12. In order to make them comparable, the data are arranged according to different important microenvironments: remote areas, rural und urban background, traffic related sites and industrial sites (for a definition see table 3.1). Before using the data sets for intercomparisons, the following comments should be borne in mind:

- The concentration data refer to total contents in suspended particulate matter (TSP), if not indicated otherwise in the tables. If size fractions of the aerosol were measured (e.g. PM10), this was marked under the column "measurement technique" of the tables.

- There are no species specific analyses within this data set.

- It could be argued that TSP data should not be compared with ambient air quality standards based on PM10 sampling, as they will be proposed in later chapters of the position paper (compare, for example, chapters 2.6 and 3.3.4). However, it has been demonstrated by the size distributions and measurement results in chapter 1.2 that TSP and PM10 based data are more or less comparable for arsenic and cadmium, as these metals are enriched in the fine modes. Data based on TSP sampling thus overestimate PM10 based concentrations only by about 10 % or less at rural and urban background stations and about 20 % or less at industrial sites.

- These differences are well within the uncertainties which are inevitable when comparing data measured in different countries by various laboratories, applying a variety of sampling, digestion and analytical methods without prior harmonization (compare column "measurement technique" in the tables).

- Problems may arise for nickel sampled at industrial sites. The size distributions in chapter 1.2 clearly point to the importance of the coarse particle mode in the case of nickel compounds. This effect can be particularly relevant near industrial sites (compare, for example, the big difference of PM10 and TSP based nickel concentrations measured at Harjavalta in 1997, table 1.12). Unfortunately, only few data sets exist in Europe where nickel compounds have been measured simultaneously in the PM10 and TSP mode. From the data presented in table 1.12 (Rome, Harjavalta) and in chapter 1.2 (size distributions, Stolberg), it can be assumed as first guess that nickel concentrations based on PM10 sampling are typically lower by about 30 % than TSP based data at urban locations, whereas even greater differences may occur near industrial sites.

- If not marked otherwise in the tables, all ambient air concentrations are given as annual means. Data from shorter sampling intervals (for example daily or weekly means) can be higher by orders of magnitude. Consequently, they are not comparable with annual or at least half yearly means.

Table 1.10: Arsenic concentrations (ng/m³) at different sites in Europe (annual means and TSP data, if not indicated otherwise)

Location, environment	Sampling period	Concentration	Notes	Measurement technique	Reference
remote					
Spitzbergen, N	1996	0.05			[69]
rural					
Pallas, FIN	1996	0.19			[70]
Schwäbische Alb, D	1998	0.3			[71]
Kollumerwaard, NL	1998	0.64		MVS,ICP-MS	[72]
Biest, NL	1998	1.10		MVS,ICP-MS	[72]
Denmark	1998	0.4 – 1.0			[73]
United Kingdom	1996	0.32 – 1.2	5 different sites, range	Harwell type	[74]
United Kingdom	1997	0.40 – 0.97	5 different sites, range	sampler (~8µm)	[74]
United Kingdom	1998	0.31 – 0.76	5 different sites, range	monthly av.	[74]
Styrrup, Notts., UK	1996-98	4.2 – 3.0			[74]
Löcknitz, D	1997	1.4		AAS	[74]
Knokke	1998	1.4		AAS, LVS	[84]
urban					
Koge, DK	1998	1.3			[73]
Niedersachsen, D	1997	1.2 – 1.6			[76]
Rhine-Ruhr area, D	1997	1.0 – 2.8	range from 39 stations	MVS, AAS	[77]
Rhine-Ruhr area, D	1998	0.8 – 3.1	range from 39 stations	MVS, AAS	[78]
Baden-Württemberg, D	1997	0.8 – 2.3	PM10	HVS,ICP-MS	[79]
Baden-Württemberg, D	1998	0.4 – 1.5	PM10	HVS,ICP-MS	[80]
Bilthoven, NL	1998	0.85		MVS,ICP-MS	[72]
traffic					
Denmark	1998	1.0 – 1.5			[73]
Rostock, D	1997	0.69		AAS	[75]
Neubrandenburg, D	1997	1.5		AAS	[75]
Essen-Ost, D	1997	2.0		MVS, AAS	[77]
Vlaardingen, NL	1996	1.54			[72]
Spain	1996	0.05 - 4			[81]
Perafort, E	1996	0.76	influenced by petrochemical	AAS, HVS	[82]
Martorell, E	1996	1.06	industry	AAS, HVS	[82]
Antwerp (urban/traffic), B	1998	4.1		AAS, LVS	[84]

Table 1.10 (continued): Arsenic concentrations (ng/m³) at different sites in Europe (annual means and TSP data, if not indicated otherwise)

Location, environment	Sampling period	Concen-tration	Notes	Measurement technique	Refe-rence
industrial					
Hamburg, D	1997/98	5 and 13	secundary copper smelter,	LVS, AAS	[83]
			dis-		
Datteln, D	1997	9	tance: 1000 m, windward/lee	MVS, AAS	[77]
Datteln, D	1998	14.3	vicinity of a zinc smelter	MVS, AAS	[78]
Stolberg, D	1997	4	vicinity of a zinc smelter	MVS, AAS	[77]
Stolberg, D	1998	2.3	lead smelter	MVS, AAS	[78]
Kokkola, FIN	1993	1.7	distance: 600 m		[70]
Kokkola, FIN	1993	1.2	zinc industry; distance 1500	PM 10	[70]
Raahe, FIN	1998	1.2	m		[70]
Harjavalta, FIN	1995	27	zinc industry; distance 4000		[70]
Harjavalta, FIN	1996	24	m		
Harjavalta, FIN	1997	20	near iron and steel plant		
Harjavalta, FIN	1995	21	copper/nickel smelter	PM 10	[70]
Harjavalta, FIN	1996	16	distance: 1000 m	PM10	
Harjavalta, FIN	1997	16		PM10	
Hoboken, B	1998	10 - 50	copper/nickel smelter	XRF, LVS	[84]
			distance: 1000 m		
Hoboken, B	1998	97	lead-copper smelter, range of	AAS, LVS	[84]
			several sampling points,		
Duisburg, D	1999	11	distance up to 250 m	AAS, MVS	[85]
Duisburg-Bruckhausen, D	1999	4	lead-copper smelter	AAS, HVS	[85]
			(industrial hot spots)		
			150 m from non ferrous		
Beverwijk, NL	1998/99	0.9	industry, half yearly av.	PM10,Partisol	[72]
Hoek van Holland, NL	1998/99	0.98	700 m windward of steel mill,	HVS,ICP-OES	[72]
			1/99-10/99		
			near steel mill		
			petrochem. industry		

Abbreviations:

HVS, MVS, LVS:	high, medium, low volume sampler
AAS:	Atomic Absorption Spectroscopy
ICP-MS:	Inductively Coupled Plasma-Mass Spectrometry
XRF:	X-Ray Fluorescence
	(for a description of monitoring methods, see chapter 3.3)
ICP-OES:	Inductively Coupled Plasma - Optical Emission Spectrometry

Table 1.11: Cadmium concentrations (ng/m^3) at different sites in Europe (annual means and TSP data, if not indicated otherwise)

Location, environment	Sampling period	Concen-tration	Notes	Measurement technique	Refe-rence
Remote					
Arctic and Pacif. Ocean		0.003			[86]
Jungfraujoch, CH	1998	<0.03			[124]
Rural					
Pallas, FIN		0.032			[70]
Denmark	1998	0.2 – 0.3	different sites		[73]
Schauinsland, D	1998	0.12			[88]
Neuglobsow, D	1998	0.28			[88]
Löcknitz, D	1997	0.31		AAS	[75]
Hessen, D	1998	≤0.2			[89]
Kollumerwaard, NL	1998	0.21		MVS,ICP-MS	[72]
Biest, NL	1998	0.39		MVS,ICP-MS	[72]
Rigi, CH	1998	0.13		PM10	[124]
Tänikon, CH	1998	0.23		PM10	[124]
United Kingdom	1996	0.06 – 0.36	6 different sites, range	Harwell type	[74]
United Kingdom	1997	0.06 – 0.29	6 different sites, range	sampler (~8μm)	[74]
United Kingdom	1998	0.05 – 0.2	6 different sites, range	monthly av.	[74]
Knokke, B	1998	0.7		AAS, LVS	[84]
Urban					
United Kingdom	1998	0.84 – 1.05	five sites		[90]
Helsinki, FIN	1996/7	0.11 – 0.13	two sites, PM 15		[70]
Zürich, CH	1998	0.29		PM10	[124]
Lugano, CH	1998	0.45		PM10	[124]
Hamburg, D	1993	1.2		LVS, AAS	[91]
Niedersachsen, D	1997	0.2 – 0.5			[76]
Rhine-Ruhr area, D	1998	0.5 – 2.9	range from 39 stations	MVS, AAS	[78]
Hessen, D	1998	0.3 – 0.5	range from 6 stations	MVS, AAS	[89]
Stuttgart, D	1996	0.9	PM10	HVS,ICP-MS	[79]
Koge, DK		<1.5			[73]
Bilthoven, NL	1998	0.30		MVS,ICP-MS	[72]
Montalto di Casto, I	1996	0.42	May - September		[126]

Table 1.11 (continued): Cadmium concentrations (ng/m³) at different sites in Europe (annual means and TSP data, if not indicated otherwise)

Location, environment	Sampling period	Concentration	Notes	Measurement technique	Reference
Traffic					
Magdeburg, D	1998	0.3			[92]
Halle, D	1998	0.6			[92]
Essen-Ost, D	1997	1.0			[77]
Düsseldorf-Mörsenb., D	1997	1.2		MVS, AAS	[77]
	1998	0.3 – 0.5	3 stations	MVS, AAS	[89]
Hessen, D	1998	0.21 – 0.44		MVS, AAS	[80]
Baden-Württemberg, D	1998	0.31		PM10	[124]
Dübendorf; CH	1998	0.41; 0.36		PM10	[124]
Lausanne und Bern, CH	1998	1.0			[90]
London, UK (Cromwell Road)	1990	2			[93]
Paris, F	1995/6	0.4	TSP concentrations similar	PM10,HVS,AAS	[94]
Rome, I	1999	0.46	PM10, two months		[125]
Rome, I	1998	2.4		AAS, HVS	[82]
Tarragona/Martorell, E	1998	1.3	urban traffic	AAS, LVS	[84]
Antwerp, B					
industrial					
Harjavalta, FIN	1995	3.5	copper/nickel smelter/refinery		[70]
Harjavalta, FIN	1996	2.1	distance: 1000 m		[70]
Harjavalta, FIN	1997	1.0			[70]
Harjavalta, FIN	1995	2.3		PM 10	[70]
Harjavalta, FIN	1996	1.2		PM 10	[70]
Harjavalta, FIN	1997	0.7		PM 10	[70]
Kokkola, FIN	1993	0.2	1,5-4 km from zinc smelter		[70]
Datteln, D	1997	23.7	next to a zinc smelter	MVS, AAS	[77]
Datteln, D	1998	7.7	next to a zinc smelter	MVS, AAS	[78]
Stolberg, D	1997	3.4	600 m from a lead smelter	MVS, AAS	[77]
Stolberg, D	1998	2.7	600 m from a lead smelter	MVS, AAS	[78]
Duisburg-Meiderich, D	1998	16.8	vicinity of steel industry	MVS, AAS	[78]
Hamburg, G	1997/8	1.3 and 6.4	next to metal processing plant	LVS, AAS	[83]
Hoboken, B	1998	10 –20	distance: 1000 m windward/lee non-ferrous industry	LVS, XRF	[84]
Hoboken, B	1998	13	distance: 10 – 600 m		[84]
Treibach, A	1998	1- 4	non-ferrous industry	AAS, LVS	[97]
Duisburg, D	1999	20.2	vicinity of chemical industry	AAS, MVS	[85]
Duisburg-Bruckhausen, D	1999	1.6	150 m from non-ferrous plant, half yearly average	AAS, HVS	[85]
Bewerwijk, NL	1998/9	0.57	700 m windward of steel mill, 1/99-10/99	PM10, Partisol	[72]
Hoek van Holland, NL	1998/9	0.57	near steel mill petrochem. industry	HVS,ICP-OES	[72]

Abbreviations: see table 1.10

Table 1.12: Nickel concentrations (ng/m³) at different sites in Europe (annual means and TSP data, if not indicated otherwise)

Location, environment	Sampling period	Concen-tration	Notes	Measurement technique	Refe-rence
Remote					
North Sea		0.03			[95]
rural					
Denmark	1998	1.1 - 2.1			[73]
Pallas, FIN	1996	0.52			[70]
Brotjacklriegel; D		0.4			[88]
Neuglobsow, D		1.3			[88]
Hessen, D	1998	1.1 – 1.5		AAS	[89]
Eifel, D	1997	1.7			[77]
United Kingdom	1996	0.61 – 2.2	5 different sites, range	Harwell type	[74]
United Kingdom	1997	0.95 – 2.2	5 different sites, range	sampler (~8µm)	[74]
United Kingdom	1998	<0.1-1.4	5 different sites, range	monthly av.	[74]
Styrrup, Notts., UK	1996-98	3.5 – 1.6			[74]
Kollumerwaard, NL	1998	2.1		MVS,ICP-MS	[72]
Biest, NL	1998	2.3		MVS,ICP-MS	[72]
urban					
Koge, DK	1998	2.2			[73]
Helsinki, FIN	1996/97	2.6 – 3.5			[70]
Magdeburg, D	1998	2.3			[92]
Stendal, D	1998	8.8			[92]
Niedersachsen, D	1997	1.6 – 3.2			[76]
Hessen, D	1998	1.8 – 2.9	range from 6 stations	AAS	[89]
Rhine-Ruhr area, D	1998	2.3 – 12.1	range from 39 stations		[78]
United Kingdom	1998	7.6 – 9.6	five sites, range		[90]
Rome, I	1995/6	13		HVS, AAS	[94]
Rome, I	1995/6	8	PM 10	HVS, AAS	[94]
Bilthoven, NL	1998	2.3		MVS,ICP-MS	[72]
Montalto di Castro, I	1996	4.6	May - September		[126]
traffic					
Denmark	1998	2.4 - 3.8			[73]
France	1998	4			[93]
United Kingdom	1998	10.1			[90]
Dessau, D	1998	3.1			[92]
Halle, D	1998	5.7			[92]
Hessen, D	1998	2.5 – 2.9	3 stations	AAS	[89]
Rostock, D	1996	3.3		AAS	[71]
Neubrandenburg, D	1996	4.1		AAS	[71]
Düsseldorf-Mörsenb.,	1998	6.7		MVS, AAS	[77]
D	1998	7.0		MVS, AAS	[77]
Essen-Ost, D	1998	7	influenced by industry	HVS, AAS	[82]
Perafort, E	1998	21	influenced by industry	HVS, AAS	[82]
Martorell, E	1998	15	urban-traffic	LVS, AAS	[84]
Antwerp, B					

Table 1.12 (continued): Nickel concentrations (ng/m³) at different sites in Europe (annual means and TSP data, if not indicated otherwise)

Location, environment	Sampling period	Concen-tration	Notes	Measurement technique	Refe-rence
industrial					
Genk, B	1997	40	influenced by steel factory and power plant	LVS/XRF	[96]
Hoboken, B	1997	30 - 50	industrial sites, non ferrous industry	LVS/XRF	[96]
Hoboken, B	1998	36	non-ferrous industry	AAS, LVS	[84]
Harjavalta, FIN	1997	102	copper/nickel smelter distance:1000 m		[70]
Harjavalta, FIN	1997	20	copper/nickel smelter distance:1000 m	PM10	[70]
Siegen, D	1997	36.4	vicinity of steel plant		[77]
Duisburg-Meiderich, D	1998	19.4	vicinity of steel plant		[78]
Treibach, A	1998	20 - 32	vicinity of chemical industry		[97]
Duisburg-Bruckhausen, D	1999	18.0	700 m windward of steel mill, 1/99-10/99	AAS, HVS	[85]
Beverwijk, NL	1998/99	2.2	near steel mill	PM10,Partisol	[72]
Hoek van Holland, NL	1998/99	8.6	petrochem. industry	HVS,ICP-OES	[72]

Abbreviations: see table 1.10

- Only recent data (generally from 1995 onwards) have been taken on board. The reason for this is the distinct downward trend for time series of metal and metalloid compounds observed at many locations in Europe (see chapter 1.4.3), which make older data outdated and often impossible to compare with data measured in the ninetees. That is the reason why reviews of older monitoring data even in recent reports and compilations as, for example, the IPCS document on arsenic (1999) have not been referenced and used in this position paper, as they may give misleading impressions of current concentrations in Europe.

1.4.1.1 Arsenic In Ambient Air

Concentrations of arsenic compounds at various locations from 6 Member States have been compiled in table 1.10. In agreement with expectations, arsenic levels can be arranged in the following order: remote ≪ rural < urban ~ traffic ≪ certain industrial locations. Whereas levels of arsenic generally do not exceed 1.5 ng/m³ at rural sites, data from Styrrup, Nottinghamshire are somewhat higher. This may reflect some input from local sources.

Urban background levels show a quite narrow range of 0.5 - 3 ng/m³. Within this range are also data from traffic related sites. Consequently, there is no indication that considerable amounts of arsenic are emitted by traffic, which nicely compares with the emission data (see preceding chapter). Arsenic concentrations from industrial sites span a wide range from urban background or even rural levels (e.g. Kokkola, Finland; Beverwijk, Netherlands) up to concentrations which are one order of magnitude higher than at urban locations without direct industrial impact. Several factors can be identified which will influence these concentration levels strongly:

- The type of industrial facility (e.g. non ferrous smelter with potentially high arsenic emissions, iron and steel plant with lower emissions).
- The type of flue gas cleaning (mostly not indicated in reports on ambient air quality) and the type of the process involved (for example QLS process with comparably low emissions).
- The distance and the position of the sampling point in relation to the facility (for example windward or to the lee).

Particularly the distance from the facility plays a decisive role. Generally, concentration levels are highest in the immediate vicinity of the factory, with near background levels being reached two or three kilometers apart. All these factors make it difficult to compare data measured at industrial sites. Consequently, these additional informations have been added to the table, as far as they could be extracted from the reports. They can at least partly explain the wide concentration ranges observed. It has to be mentioned that the industrial facilities (for example, the smelters at Hoboken and Harjavalta) generally apply best available techniques as described in the IPPC draft BREF note (see chapter 1.5.2).

The big concentration gap of about one order of magnitude between urban areas and the surroundings of certain industrial facilities clearly points to an important problem for standard setting: limit values which will be easily met in the urban background may be very difficult to reach at certain industrial hot spots. On the other hand, it is hard to accept that people living near industrial sites should be permanently less protected by frequent breaches of effect based limit values than people living elsewhere. As can be taken from the tables, this comment is valid for all three metals.

1.4.1.2 Cadmium In Ambient Air

Much what has been said for arsenic also applies for cadmium concentrations in ambient air, so that it is sufficient to comment on some peculiar features.

The cadmium burden in rural areas is even lower than for arsenic (see table 1.11). This may reflect the difference in the shares of the main sources: combustion processes are ubiquitous, whereas production processes are concentrated in industrial areas. Also urban background levels in some cities without relevant industrial input are quite low (for example Rome, Helsinki, Zürich or cities in Hessen) and only slightly above rural levels. On the other hand, the concentration gradient of one or two orders of magnitude between rural areas in Central or Western Europe and remote regions point to the important input by long range transport.

Again, concentrations at traffic exposed sites are in the same range as urban background levels. This is a clear argument against relevant cadmium emissions from traffic, as assumed by the TNO inventory (compare chapter 1.3), and supports the more recent data from the national inventories. This is also supported by cadmium levels simultaneously measured at a traffic exposed site in Rome at two different heights (street level and 30 m high) in spring 1999. Street levels (0.53 µg/m^3, PM10) were insignificantly elevated compared with background levels at 30 m (0.47 µg/m^3) [125].

As in the case of arsenic, cadmium levels are higher by about one order of magnitude compared with urban concentrations in the surroundings of certain types of industrial facilities, particularly non ferrous smelters (which often coemit arsenic and cadmium compounds), but also near certain steel works with significant input of scrap-metal.

1.4.1.3 Nickel In Ambient Air

Nickel concentrations in urban areas (see table 1.12) are considerably higher than arsenic and cadmium levels, which corresponds to the European emissions, which are about one order of magnitude higher for nickel, compared to cadmium and arsenic emissions (see chapter 1.3). They can reach annual averages of 10 - 15 ng/m^3, at some locations with widespread industrial input about 20 ng/m^3 (for example at Martorell in Spain, an urban area with petrochemical industry some kilometers apart). Again, nickel levels at traffic exposed sites are within the range of urban background concentrations. Consequently, there is no indication from monitoring data road traffic being a major source of nickel compounds.

As has already been mentioned for cadmium and arsenic compounds, nickel levels near certain industrial facilities can exceed urban background concentrations by nearly one order of magnitude, particularly in the case of copper/nickel smelters and steel plants. The very high annual mean of 102 ng/m^3 reported for the smelter at Harjavalta in 1997 was probably due to disturbances in the flue gas cleaning (breakthrough of a filter). Preliminary data for 1999 are in a more typical range of about 20 ng/m^3.

1.4.1.4 Typical Levels In Europe

Following conclusions can be drawn from the concentration data presented so far:

- Whereas several Member States provide a rather comprehensive picture of their ambient air levels in respect to metals and metalloids, there are some Member States with only few or no data at all. Consequently, the picture emerging for the European union is far from complete. Particularly the situation in Southern Europe is poorly represented in the available data set.

- Nevertheless, the data allow for extracting typical concentration ranges for the microenvironments considered:

  rural areas
  arsenic: 0.2 - 1.5 ng/m^3
  cadmium: 0.1 - 0.4 ng/m^3
  nickel: 0.4 - 2 ng/m^3

  urban background (incl. traffic related sites)
  arsenic: 0.5 - 3 ng/m^3

cadmium:	0.2 - 2.5 ng/m³
nickel:	1.4 - 13 ng/m³
industrial sites	
arsenic:	2 - 50 ng/m³
cadmium:	2 - 20 ng/m³
nickel:	10 - 50 ng/m³

1.4.2 Deposition

Depending on the main transfer process from the atmosphere to surfaces, deposition can be measured as wet deposition, dry deposition or bulk deposition (the sum of dry and wet deposition, including interception and transfer by dew and fog). A short description of these processes and a definition of the concepts is given in chapter 3.3.2.

Routine measurements refer to either wet deposition (predominantly in rural areas, see chapter 3.3.2) or bulk deposition. Dry deposition is only rarely monitored (see, for example, [108]). In the tables 1.13 - 1.15, where recent deposition data from Member States and from Switzerland are presented, it is indicated under the column "notes" by "w" (wet) and "b" (bulk), which kind of deposition has been measured. As the results from deposition measurements of heavy metals and metalloids are usually reported either in the unit [µg/m²day] or [µg/m²year], both units have been included in the tables.

Most deposition measurements refer to single measurement sites (spots). In some countries, the results from deposition measurements are reported as averages over a certain area (e.g. 1 km²). If this is the case, it has been mentioned under the column "notes", to make data comparable as far as possible. When comparing the data, it should also be borne in mind that different measurement methods can give rise to results which may differ up to a factor 2, compare chapter 3.3.2.

The deposition data by and large follow the same pattern as the concentration measurements, so that we can confine ourselves to some remarks and particular features, in order to avoid repetitions. For the same reason, arsenic, cadmium and nickel compounds can be discussed together.

Unfortunately, the deposition data base is even more incomplete than that for concentrations presented in the preceding subchapter, particularly for urban and industrial areas. Apparently, deposition levels in these microenvironments are routinely monitored by only three Member States (Austria, Belgium and Germany). Consequently, the data presented in the tables can only give rough indications of deposition levels in Europe. The data base for rural depositions is slightly better, with additional data provided by Sweden, Finland and the United Kingdom, due to measurements in the framework of the UN ECE protocol on heavy metals (see chapter 1.5.3).

Rural depositions in Scandinavia, Scotland and in alpine regions (Davos) are generally lower by several factors than depositions in rural areas of Central and Western Europe. Obviously, deposition decreases with the distance from densely populated areas. On the other hand, the deposition burden in several less industrialized cities is comparable with rural levels in Central and Western Europe.

Table 1.13: Arsenic deposition at different sites in Europe

Location, environment	Sampling period	Deposition [µg/m^{2}d]	Deposition [µg/m^{2}y]	Notes	Reference
rural					
Deuselbach, D	1997	0.24	87	w	[88]
Waldhof, D	1997	0.29	106	w	[88]
Bredkälen, S	1997	0.082	32	w	[91]
Svaertedalen, S	1997	0.42	153	w	[91]
Davos, CH	1997	0.06	22	b	[87]
Lägeren, CH	1997	0.43	157	b	[87]
Vuoskojärvi, FIN	1997	0.087	32	b	[70]
Virolahti, FIN	1997	0.39	143	b	[70]
Löcknitz, D		0.2	73	b	[71]
Gülzow, D		0.23	84	b	[71]
Knokke, B	1990-98	1 - 8	364 - 2912	b, range of several years, NILU	[84]
urban					
Innsbruck, A	1998	0.22	80	b	[98]
Velbert, D	1995	0.9 - 1.6	329 – 584	b,range from 48 areas of 1 km^2	[99]
Hamburg-Bahrenfeld, D	1996	2 - 5	730 - 1825	b,range of 12 areas of 1 km^2	[100]
Lugano, CH	1997	0.27	99	b	[87]
Zürich, CH	1997	0.39	142	b	[87]
Ghent, B	1996	6	2184	b	[84]
De Zilk,Rotterdam,NL	1996-98	0.2 - 0.7	80 - 240	w	[72]
traffic					
Neubrandenburg, D	1997	0.36	131	b	[71]
Schwerin, D	1997	0.73	266	b	[71]
Bern, CH	1997	0.42	153	b	[87]
Lausanne, CH	1997	0.53	194	b	[87]
industrial					
Arnoldstein, A	1995	3.0 - 6.9	1077–2508	b	[97]
Arnoldstein, A	1996	2.2 – 7.5	801-2715	b	[97]
Arnoldstein, A	1997	2.0 – 7.3	728-2660	b	[97]
Arnoldstein, A	1998	2.3 – 4.3	834-1565	b, 10 measurement sites next to a metalworking plant	[97]
Wietersdorf, A	1997	around 2	around 728	b	[97]
Wietersdorf, A	1998	2.2 – 3.1	801 – 1128	b, several measurement sites near a cement plant	[97]
Frantschach, A	1997	1.8 – 4.3	655 - 1565	b	[97]
Frantschach, A	1998	2.2 – 2.8	801 - 1019	b, several measurement sites near a cellulose plant	[97]
St. Veit; A	1998	2.0 – 3.1	728 –1128	b, eight measurement sites near a fibre panel production	[97]
Hamburg, D	1996	4 – 69	1460-25185	b, range of 16 areas of 1 km^2 near a metal processing plant	[100]
Hoboken, B	1997	23	8372	b, (distance : 1000 m)	[96]
Hoboken, B	1997	430	156520	b, (distance: 10 m)	[96]
Hoboken, B	1998	8	2912	b, (distance : 1000 m)	[96]
Hoboken, B	1998	206	74984	b, (distance: 10 m) near non-ferrous industry	[96]
Belgium	1998	8 -708	2912-257712	b, different industrial sites	[84]
Duisburg, D	1996	13.4	4891	b,1 km^2, near non ferrous industry	[99]

Table 1.14: Cadmium deposition at different sites in Europe

Location, environment	Sampling period	Deposition [µg/m²d]	Deposition [µg/m²y]	Notes	Reference
rural					
Leba, P	1996	0.1	37	w	[101]
Zingst, D	1996	0.052	19	w	[101]
Deuselbach, D	1997	0.35	128	w	[88]
Waldhof, D	1997	0.52	188	w	[88]
Bredkälen, S	1997	0.049	18	w	[102]
Arup, S	1997	0.15	54	w	[102]
Scotland, UK	1995	0.079	29	w	[103]
Vuoskojärvi, FIN	1997	0.011	4	b	[70]
Virolahti, FIN	1997	0.074	27	b	[70]
Davos, CH	1997	0.06	22	b	[87]
Lägeren, CH	1997	0.043	16	b	[87]
Löcknitz, D	1997	0.12	44	b	[71]
Gülzow, D	1997	0.14	51	b	[71]
Knokke, B	1990-98	1 - 2	364 – 728	b, different years, NILU	[84]
urban					
Ghent, B	1996	1	364	b	[84]
Innsbruck, A	1998	0.16 and 0.2	59 and 73	b	[98]
Hamburg-Bahrenfeld, D	1996	0.4-0.8	330	b, range of 12 areas of 1 km²	[100]
Bottrop/Gladbeck, D	1995	0.5 – 1.3	183-475	b, range of 125 areas of 1 km²	[99]
Netherlands, background stations (urban, rural)	several years	0.2 - 0.7	80 - 240	w, range of several stations	[72]
Montalto de Castro,I	1998/99	0.2 and 0.3	73 and 101	b	[126]
traffic					
Neubrandenburg, D	1997	0.22	80	b	[71]
Schwerin, D	1997	0.36	131	b	[71]
Innsbruck, A	1998	0.13 and 0.21	49 and 77	b	[98]

Table 1.14 (continued): Cadmium deposition at different sites in Europe

Location, environment	Sampling period	Deposition [µg/m^{2}d]	Deposition [µg/m^{2}y]	Notes	Refe-rence
industrial					
Arnoldstein, A	1995	0.61 – 8.3	222 - 3014	b	[97]
Arnoldstein, A	1996	1.04 – 7.5	379 - 2726	b	[97]
Arnoldstein, A	1997	0.55 – 5.5	200 - 1987	b	[97]
Arnoldstein, A	1998	0.5 – 4.0	182 - 1467	b, ten measurement sites next to a metalworking plant	[97]
St. Kosmas, A	1995	0.17 – 1.03	62 - 375	b	[97]
St. Kosmas, A	1996	0.17 – 1.68	62 - 593	b	[97]
St. Kosmas, A	1997	0.14 – 0.85	51 - 309	b	[97]
St. Kosmas, A	1998	0.12 – 0.43	44 -157	b, ten measurement sites next to a chemical plant	[97]
Radenthein, A	1995	0.21 – 0.50	76,4 - 182	b	[97]
Radenthein, A	1996	0.14 – 0.72	51 - 262	b, four measurement sites	[97]
Treibach, A	1995	0.34 – 12.1	123,8–4404	b	[97]
Treibach, A	1996	0.38 – 1.3	138 – 473	b	[97]
Treibach, A	1997	0.27 – 5.6	98 – 2038	b	[97]
Treibach, A	1998	0.13 – 0.75	47 – 273	b, several measurement sites near a chemical plant	[97]
Wietersdorf, A	1996	0.21 – 1.1	76 –400	b	[97]
Wietersdorf, A	1997	0.2 – 0.5	73 – 182	b	[97]
Wietersdorf, A	1998	0.12 –0.4	44 – 146	b, several measurement sites near a cement plant	[97]
Frantschach, A	1997	0.2 – 0.4	73 -146	b	[97]
Frantschach, A	1998	0.2	73	b, several measurement sites near a cellulose plant	[97]
St. Veit, A	1998	0.17 – 0.3	62 – 109	b, eight measurment sites near a fibre panel production	[97]
Brixlett, A	1998	4.6	1670	b, (distance: 1000 m)	[98]
Brixlett, A	1998	0.42/0.15	153/153	b, (distance: 2/3 km) copper processing plant	[98]
Duisburg, D	1996	8.5	3103	b, 1 km^2 close to steel industry	[99]
Hamburg, D	1996	1.2 – 5.0	438-1825		[100]
				b, range of 16 areas of 1 km^2	
Hoboken, B	1997	19	6916	near metal processing plant	[96]
Hoboken, B	1997	122	44408	b, (distance : 1000 m)	[96]
Hoboken, B	1998	3	1092	b, (distance: 10 m)	[96]
Hoboken, B	1998	98	35672	b, (distance : 1000 m)	[96]
				b, (distance: 10 m) near non-	
Belgium	1998	1 - 49	364–17836	ferrous industry	[84]
				b, (different industrial sites)	

Table 1.15: Nickel deposition at different sites in Europe

Location, environment	Sampling period	Deposition [µg/m²d]	Deposition [µg/m²y]	Notes	Reference
rural					
Deuselbach, D	1997	2.1	766	w	[88]
Waldhof; D	1997	3.1	1151	w	[88]
Bredkälen, S	1997	0.26	96	w	[102]
Svartedalen, S	1997	0.69	253	w	[102]
Scotland, UK	1995	0.02	7,6	w	[103]
Löcknitz, D	1997	2.5	912	b	[71]
Gülzow, D	1997	4.3	1570	b	[71]
Vuoskojärvi, FIN	1997	0.029	11	b	[70]
Virolahti, FIN	1997	0.66	241	b	[70]
urban					
Innsbruck, A	1998	0.16/0.2	59/73	b	[98]
Velbert, D	1995	0.4 – 1.9	146-694	b,range from 48 areas of 1 km²	[99]
Rotterdam, NL	1996-98	ca. 2.8	ca. 1000	w	[72]
Montalto di Castro,I	1998/99	0.9 and 3.8	327 and 1382	b	[126]
traffic					
Neubrandenburg, D	1997	0.22	80	b	[71]
Stralsund, D	1997	0.36	131	b	[71]
Innsbruck, A	1998	0.13/0.21	49/77	b	[98]
industrial					
Arnoldstein, A	1996	1.9 – 6.5	681 - 2366	b	[97]
Arnoldstein, A	1997	1.9 – 10.2	706 - 3713	b	[97]
Arnoldstein, A	1998	2.3 – 7.0	834 - 2563	b, ten measurement sites next to a metalworking plant	[97]
St. Kosmas, A	1995	13.1 – 50.1	4768–18236	b	[97]
St. Kosmas, A	1996	2.4 – 38.6	874–14050	b	[97]
St. Kosmas, A	1997	2.1 – 40.7	869–14815	b	[97]
St. Kosmas, A	1998	2.8 – 21.6	1019–7862	b, ten measurement sites next to a chemical plant	[97]
Radenthein, A	1995	6.3 – 11.3	2293-4113	b	[97]
Radenthein, A	1996	1.8 – 4.2	655-1529	b, four measurement sites	[97]
Treibach, A	1995	36.8 - 126	13395–45864	b	[97]
Treibach, A	1996	31.2 – 129	11356-46956	b	[97]
Treibach, A	1997	1.9 – 55.8	692-20311	b	[97]
Treibach, A	1998	3.4 – 51	1238-18564	b, several measurement sites near a chemical plant	[97]
St. Veith, A	1998	2 - 3.7	728-1346		[97]
Wietersdorf, A	1996	1.2 – 3.5	437 – 1274	b	[97]
Wietersdorf, A	1997	1.7 – 3.6	619 – 1310	b	[97]
Wietersdorf, A	1998	2 – 3.1	728 – 1128	b, several measurement sites near a cement plant	[97]
Frantschach, A	1997	1.7 – 2.6	619 – 946	b	[97]
Frantschach, A	1998	2.1 – 2.2	764 – 801	b, several measurement sites near a cellulose plant	[97]
Duisburg, D	1995	76	27740	b, area of 1 km² close to steel industry	[99]

Depositions at traffic exposed sites fall within the range of typical urban levels. The conclusions drawn in the previous subchapter from concentration data that traffic is not an important source for heavy metals and metalloids is thus confirmed.

Monitoring sites near certain industrial facilities measure very high depositions, which can exceed urban background levels by up to three orders of magnitude. The spatial gradients of depositions near sources are even more pronounced than those from concentrations. This seems plausible, as deposition near sources is dominated by coarse particles with high deposition velocities. There are several examples in the tables for this steep deposition gradient. From table 1.14, for example, it can be taken that cadmium deposition very close to the source in Hoboken, Belgium (10 m) exceeds the deposition 1000 m apart by about one order of magnitude. Whereas deposition near an industrial source in Brixlett (1000 m) still exceeds background levels by more than one order of magnitude, deposition levels in 2 km distance have decreased by a factor of ten, and in 3 km distance they have reached rural background levels.

It can be concluded that high deposition levels are local problems near certain industrial sources. However, within a perimeter of 1 -2 km around those sources, deposition of heavy metals and metalloids may pose significant risks to the soil and to agricultural crops (see chapter 2.4 and 2.5).

1.4.3 Trends In Ambient Air Levels

The following subchapters give a trend analysis of the development of the concentrations of arsenic, cadmium and nickel compounds in ambient air. Some selected long-term measurement results of the recent years are plotted for each metal in the figures 1.12, 1.13 and 1.16. Linear regression analysis of the time series was performed in order to find out, whether or not a long term trend for the metal concentrations can be observed. The slope of the regressional analysis was calculated and the significance of a negative value was tested at the 95 % level. A negative slope indicates a decrease of ambient air concentrations within the respective years.

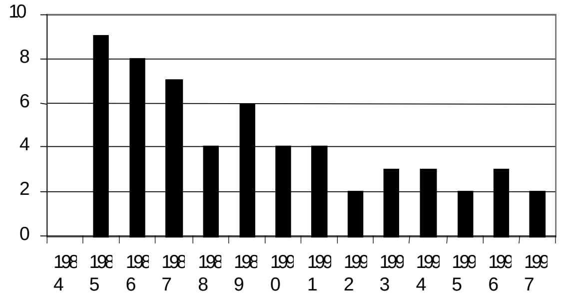
1.4.3.1 Trends In Ambient Air Levels – Arsenic

Figure 1.12 represents the results of six different measurements of arsenic in suspended dust (TSP), wet and bulk deposition carried out in recent years, between 1984 and 1997 and 1996 and 1998, respectively. The data analysis of nearly all performed measurements shows a negative slope and therefore proofs a decreasing trend. Only two of the five Swedish measurements do not have a significant negative slope at the 95 % level, but there is at least a hint for decreasing concentrations of arsenic in ambient air.

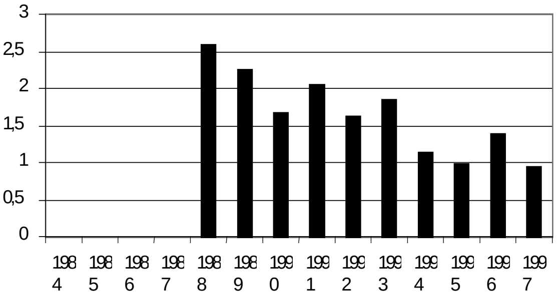
In Germany the most effective reduction of heavy metals in ambient air had been achieved between 1984 and 1990 as a result of the introduction of dust abatement techniques in many plants. For example, in the Rhine-Ruhr area a decrease of 80 % could be reached within this period. A comparable drop of 73 % between 1984 and 1993 was also found in other parts of Germany [104].

Since 1992 the German measurement data have shown a slowdown of the annual reduction of arsenic concentrations. This is also confirmed by Swedish and Dutch data, where the concentration changes between 1994 and 1997 show a similar course. This trend is indicated by the most recent measurement results for the Rhine-Ruhr area where values of 2.31 (1995), 2.72 (1996), 1.75 (1997) and 1.5 (1998) were determined. A similar development can be observed for all measurement stations in Baden-Württemberg for the period from 1996 to 1998 [80]. In the Netherlands a decrease of 64% was observed in the years from 1988 to 1997 [72].

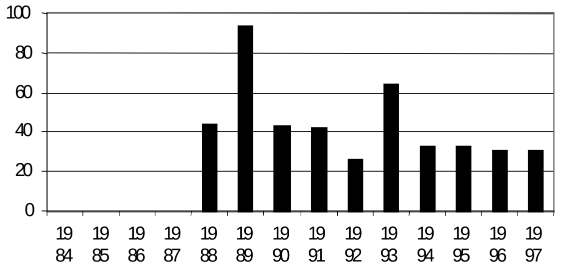
Germany [77], Rhein-Ruhr-Area, urban, TSP, As [ng · $\mathrm{m^{-3}}$]



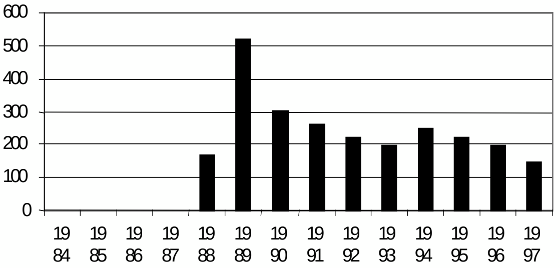
Netherlands [72], mean of 4 st., rural/urban/traffic, TSP, As [ng · $\mathrm{m^{-3}}$]



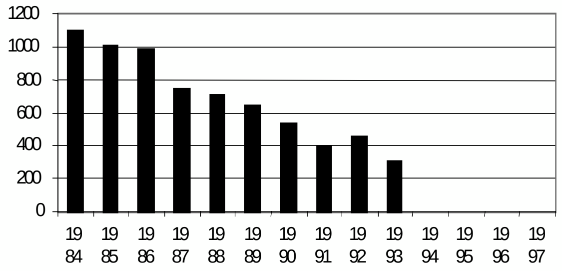
Sweden [102], Bredkälen, rural, wet deposition As [µg·$\mathrm{m^{2}}$·$\mathrm{y^{-1}}$]



Sweden [102], Arup, rural, wet deposition As [µg·$\mathrm{m^{2}}$·$\mathrm{y^{-1}}$]



Germany [104] mean of 6 st., rural/near to city, bulk deposition, As [µg·$\mathrm{m^{-2}}$·$\mathrm{y^{-1}}$]



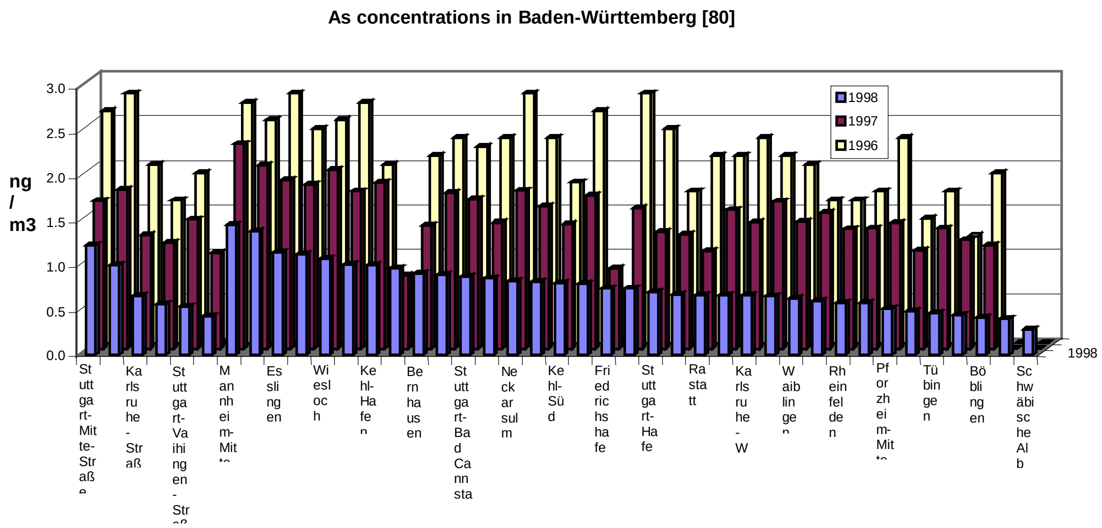


Figure 1.12: Arsenic in ambient air - trends

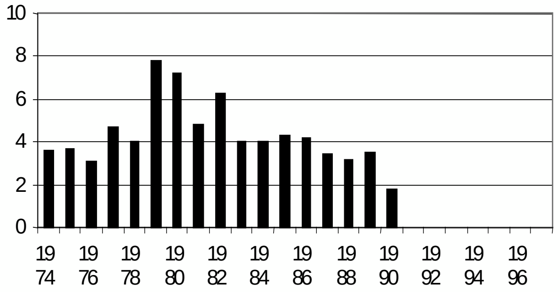
1.4.3.2 Trends In Ambient Air Levels – Cadmium

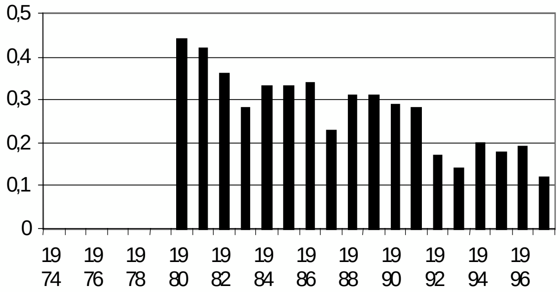
In figure 1.13, eight diagrams are presented which show the development of cadmium concentrations in total suspended matter, wet deposition and bulk deposition in different countries in recent years.

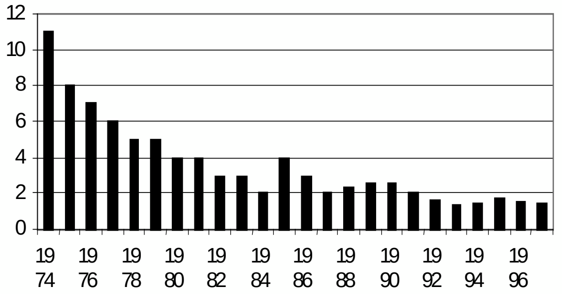
In all cases a decrease of the cadmium concentrations can be obseved. Only at two measurement stations (Champs Elysées, France, [93] and Aspvreten, Sweden, [102]) the decrease is not significant at a 95 % level. Especially in the Rhine-Ruhr area a very impressive drop of the cadmium concentration of 82 % took place between 1974 and 1984. (It should be noted that the slightly increased levels after 1984 are due to the fact that measuring sites in more polluted areas were chosen.) Other German measurement series [88] showed reductions of 73 % in TSP between 1990 and 1997, the Dutch TSP values declined by 47% (1988 - 1997 [72]) and for the bulk deposition a drop of 41 % (1984 - 1993) was observed. The concentration data for the United Kingdom have stabilized at values of about 1 ng m^{-3}.

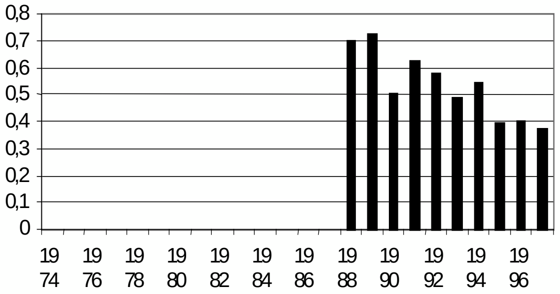
As already observed for the arsenic trend data, the decrease of the cadmium concentration stopped or slowed down around 1992. The values in the Netherlands have been stagnating since 1995. However, measurement results for all sites in Baden-Württemberg still show a slight decrease of cadmium ambient air concentrations for the years 1996 -1998.

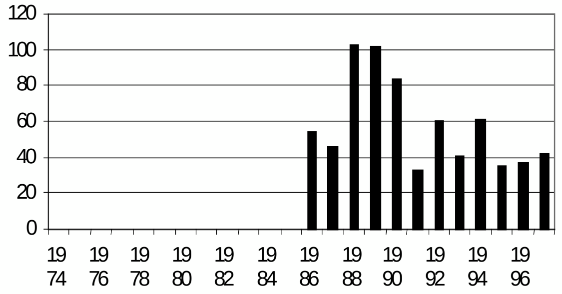
Moss studies show that the deposition of Cd over Sweden has decreased substantially during the period 1975-1990. The reduction was 48 % from 1975 to 1985 [105] and 15 % from 1985 to 1990 [106].

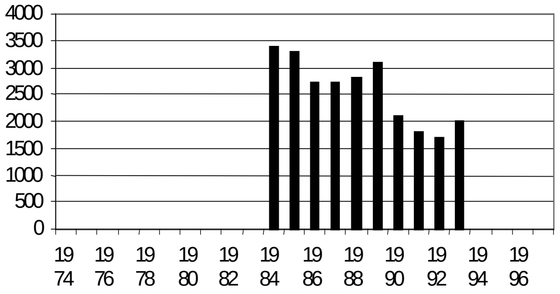

France [93], Paris-Champs Elysées, traffic, TSP, Cd [$ng \cdot m^{-3}$]


Germany [88], Schauinsland, rural TSP, Cd [$ng \cdot m^{-3}$]


Germany [77], Rhein-Ruhr-Area, urban, TSP, Cd [$ng \cdot m^{-3}$]


Netherlands [72], mean of 4 st., rural/urban/traffic, TSP, Cd [$ng \cdot m^{-3}$]


Sweden [102], Aspvreten, rural wet deposition, Cd [$\mu g \cdot m^{-2} \cdot y^{-1}$]


Germany [107], mean 25 stations, rural/near to city, bulk deposition, Cd [$\mu g \cdot m^{-2} \cdot y^{-1}$]

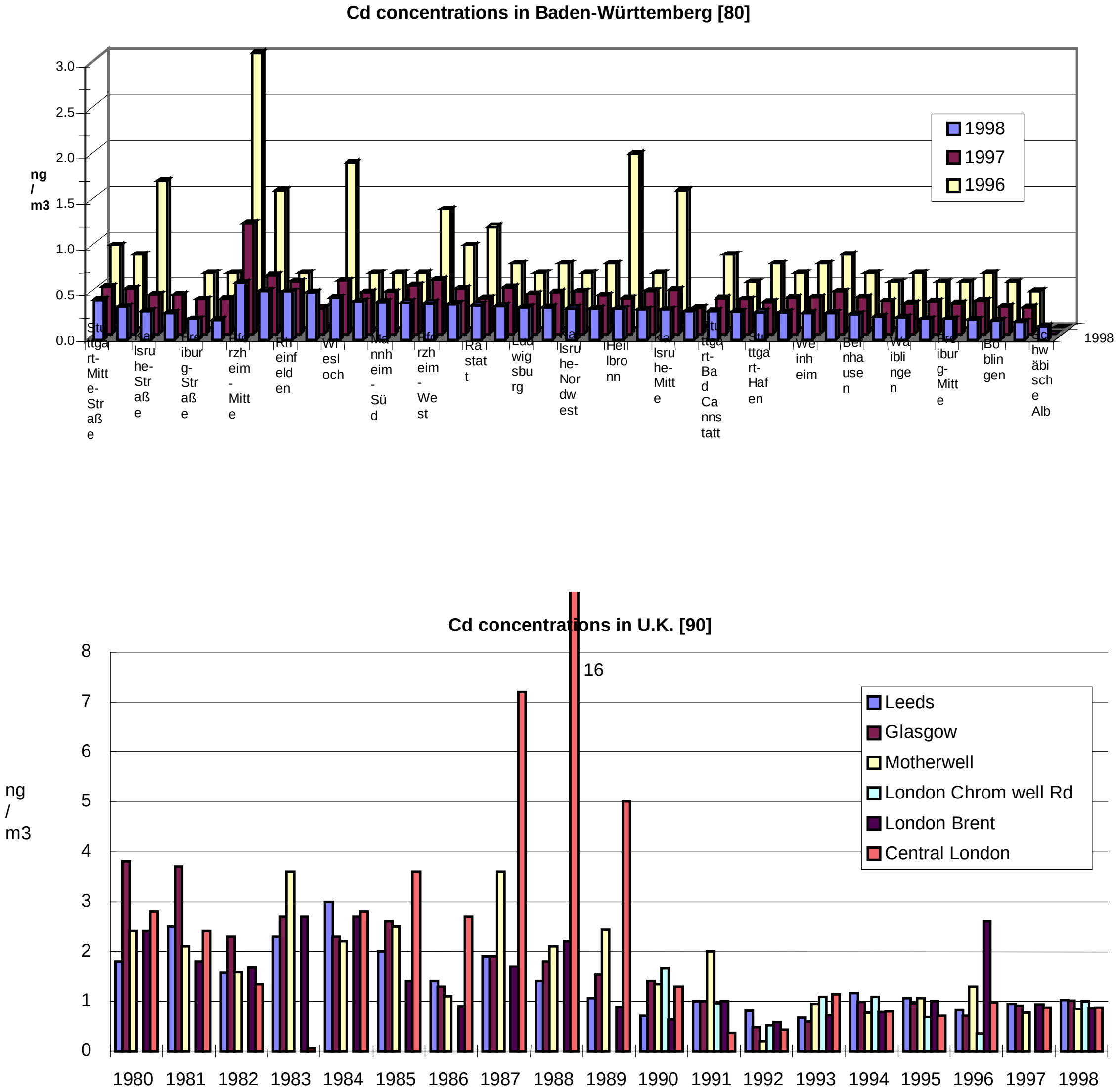


Figure 1.13: Cadmium in ambient air - trends

Within the EMEP region there is only a limited number of stations where multi-annual series of cadmium measurements are performed. Data on temporal variations of Cd pollution levels at several EMEP measurement sites [69] are prepared by MSC-E/EMEP and given in figure 1.14 (mean annual Cd air concentrations (ng/m^3) for the period 1987-96) and in figure 1.15 (annual Cd wet depositions (µg/m^2•yr.) for 1990-96) (see list of EMEP HM and POP monitoring sites in Appendix C and map of their locations in figure 3.4 of chapter 3). Air concentration data are presented for Germany and Slovakia, wet deposition ones are given for various regions near the Baltic Sea. As seen from the graphs, there is no distinct time trend with respect to both parameters at those locations. However, these sites may not be representative for the whole EMEP region.

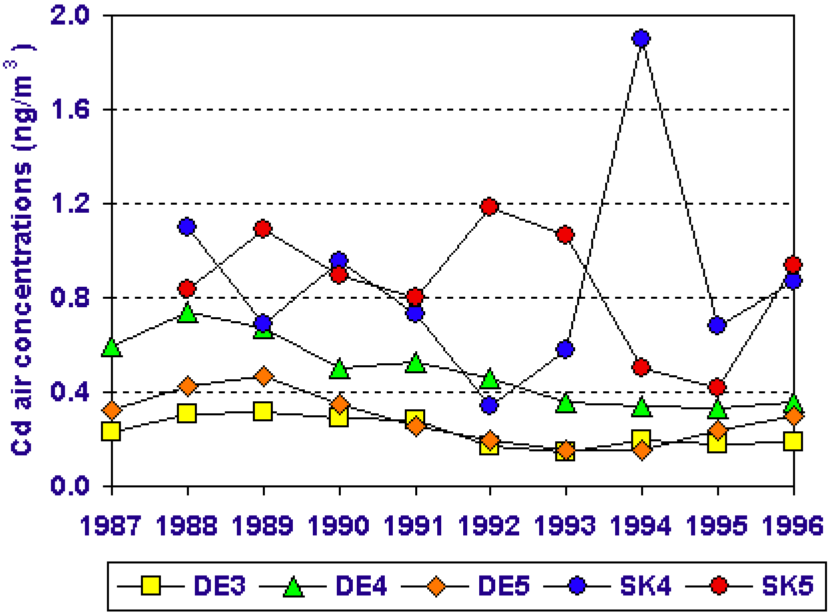


Figure 1.14: Temporal variations of Cd air concentrations measured at several EMEP monitoring sites (ng/m^3)

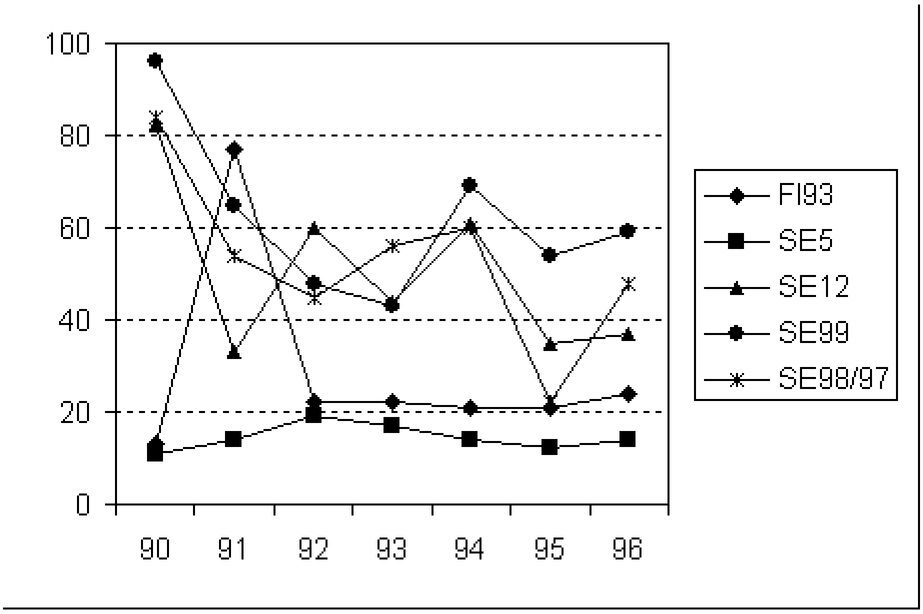


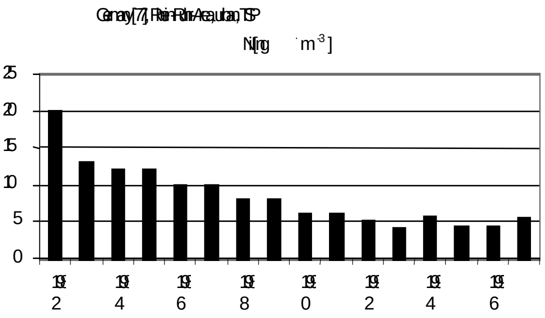
Figure 1.15: Temporal variations of Cd wet deposition at several EMEP monitoring sites (µg/m^2•yr.)

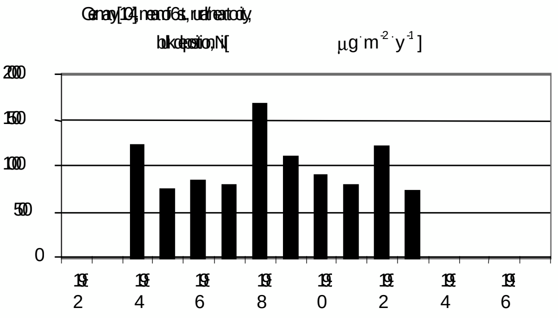
1.4.3.3 Trends In Ambient Air Levels - Nickel

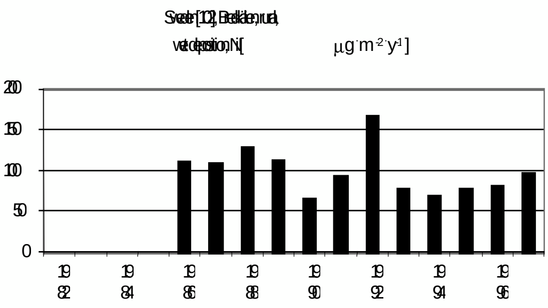
Figure 1.16 shows six diagrams of measurement series performed in Sweden, Germany and the United Kingdom between 1982 and 1997.

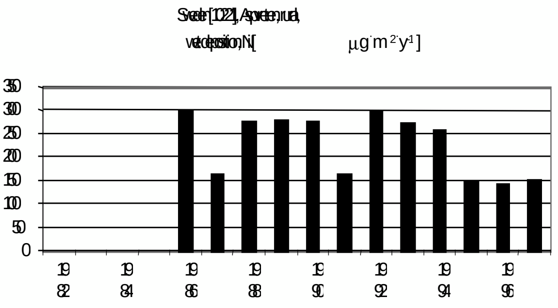
The data indicate that in highly industrialized areas like the Rhine-Ruhr area the most efficient reductions occurred, whereas in rural regions only a very small or none decrease of Nickel concentrations could be observed.

A reduction of 65 % of nickel concentrations took place in the Rhine-Ruhr area between 1982 and 1990 [77]. On the other hand this high decrease has not been observed in other German regions not so heavily industrialized. Also only a small decrease can be observed for the data measured in the United Kingdom [90] where a stabilisation of the values took place within the last years.









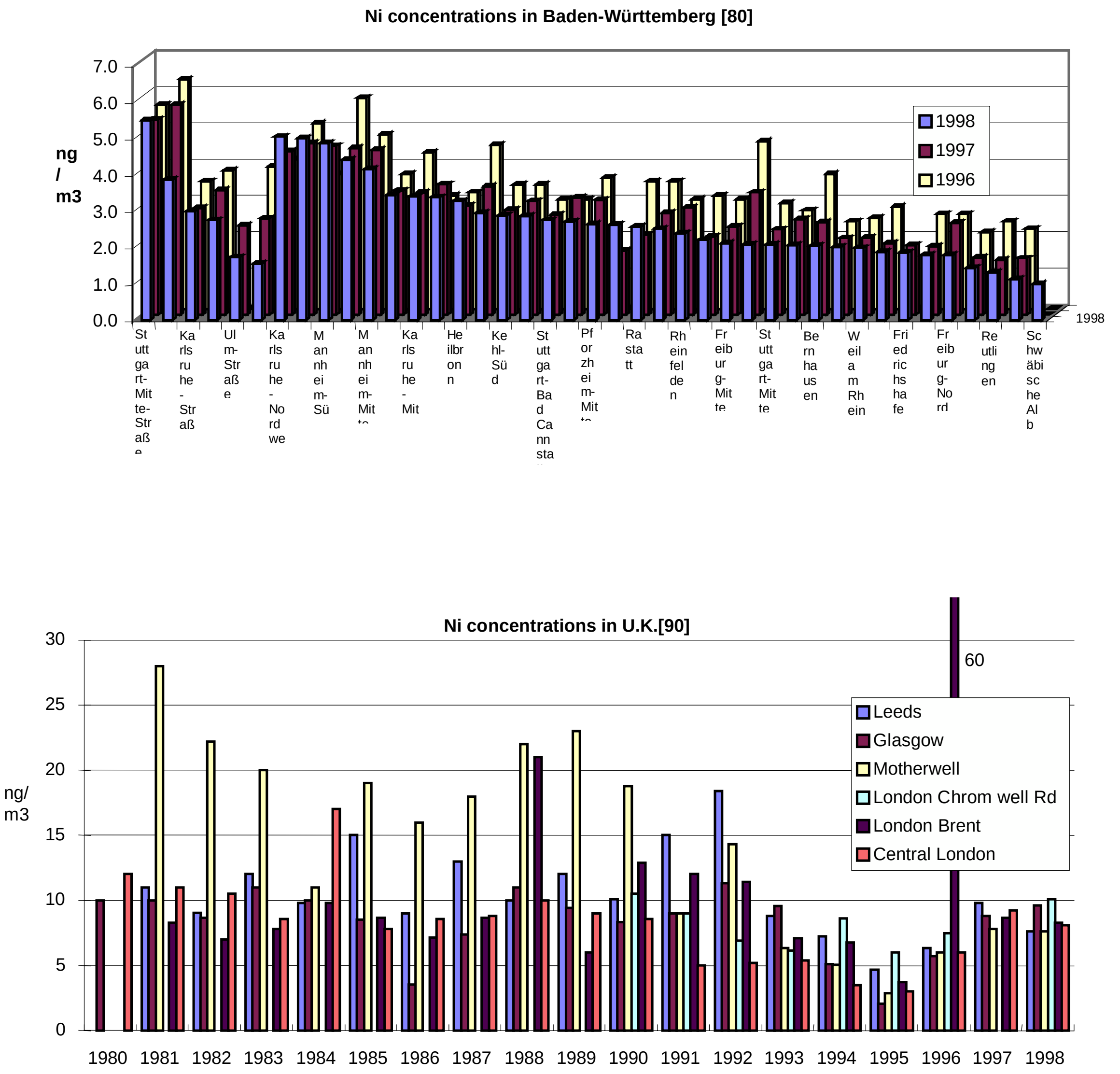


Figure 1.16: Nickel in ambient air - trends

1.5 European And National Legislation

1.5.1 National Standards And Guidelines

At present only few Member States have introduced ambient air quality standards in their national legislation. Up-to-date information on the existence of standards has been collected by a questionnaire, and an overview is presented in table 1.16. Legally binding ambient air quality standards have only been introduced in Austria, Belgium (Flanders) and Germany (compare table 1.17). It has to be mentioned that the ambient air quality standards in Germany and Flanders are combined with specific monitoring requirements, e.g. an averaging over 1 km² in Germany or calculating the mean from several samplers for deposition in Flanders (for details see chapter 3).

Table 1.16: Setting of standards in the national legislation of the Member States for at least one of the elements As, Ni and Cd [110]

Member state	AAQ Standards		Emission Standards
	Concentration	Deposition	
Austria	-	+ (Cd)	+
Belgium (Flanders)	+ (Flanders) (Cd)	(+)[a] (Flanders) (Cd)	+ (Flanders)
Denmark	-	-	-
Finland	-	-	(-)[b]
France	-	-	+
Germany	+ (Cd)	+ (Cd)	+
Greece	*(still missing)*		
Ireland	-	-	+
Italy	-	-	+
Luxemburg	-	-	+
Netherlands	(+)[a] (As, Ni)	(+)[a] (Cd)	(+)[a][b]
Portugal	-	-	+
Spain	-	-	(+)[a][c]
Sweden	-	-	(-)[b]
United Kingdom	-	-	(-)[b]

a) not legally binding
b) emission limits have been set for specific sources in environmental permits
c) only for incineration activities

Table 1.17: Ambient air quality standards (concentration and deposition) in some Member States [110]

Member state	Austria	Belgium (Flanders)	Germany
Concentrations (annual means ng/m³)			
Cd	-	40	40
Depositions			
Cd	2 µg $m^{-2}d^{-1}$	-	5 µg $m^{-2}d^{-1}$

For comparison, legally binding limit values of Switzerland are shown in table 1.18. Other industrialized countries like USA, Canada or Japan do not have at present legally binding air quality standards for cadmium, arsenic or nickel compounds, but they have established or are preparing guide values or reference exposure levels (see below).

Table 1.18: Ambient air quality standards (concentration and deposition) in Switzerland, annual means

Country	Concentrations (ng•m^{-3})			Depositions (ng•m^{-3})		
	Cd	As	Ni	Cd	As	Ni
Switzerland [111]	1.5	-	-	2	-	-

Several Member States apply non legally binding target or guide values for the assessment of heavy metals and metalloids in ambient air. Belgium (Flanders) [84] uses target values of 5 ng/m³ (annual means) to assess the concentrations of arsenic and nickel as well as a deposition target value of 20 µg m^{-2}d^{-1} for cadmium. The Netherlands [72, 112] have two sets of concentration target values, the first one defining the maximum acceptable risk level, the second one (in brackets) the level to be strived at. They are as follows: arsenic 0.5 ng/m³ and nickel 0.25 ng/m³. For cadmium deposition, the Netherlands use a target value of 1.0 g hectare^{-1} year^{-1}, corresponding to 0.27 µg m^{-2}d^{-1}.

In 1991, the ministers for the environment of the German states have recommended guide values of 5 ng/m³ for arsenic and 1.7 ng/m³ for cadmium to be striven at in air quality management plans [113]. These guide values are not legally binding and were until now not transferred into national legislation. Some German states apply these guide values also as thresholds for further examinations in the licence procedure for industrial facilities. Other states use higher thresholds of 12.5 ng/m³ for arsenic and 4.25 ng/m³ for cadmium.

The model underlying the proposed guide values takes into consideration the existence of seven carcinogens with major importance for ambient air and aims at the limitation of the total (summed up) risk caused by these carcinogenic compounds (Länderausschuss für Immissionsschutz, 1992 [114]. Together with certain reserves (with a quota of 31 %) for the carcinogenic air pollutants, which may have possibly to be regulated at a later stage, the additive (total) risk for all seven compounds corresponds to 1 : 2500. Unit risks of 4 x 10^{-3} for arsenic and 1.2 x 10^{-2} for cadmium were used for this cumulative risk assessment [114].

Based primarily on non-carcinogenic effects, the Länderausschuss für Immissionsschutz proposed a guide value for nickel compounds of 10 ng/m³ (annual mean) [115 in 1997], which has not been implemented yet into national law, but is applied in the permit procedure by some German states.

Seven Member States [110] have introduced emission limit values in their national legislation, whereas some more Member States use emission limit values in the authorization procedure for specific industrial installations on a case by case basis (compare also the following section on IPPC directive and BREF notes).

As mentioned above, guidelines or reference exposure levels will be or have been established by the US EPA, by US state agencies and by Ontario, Canada. Table 1.19 presents the current state of discussion for nickel. However, reference exposure levels must not be confounded with binding limit values. In addition, a comparison with standards or guide values from other countries is made even more difficult by the fact that the practise and implications when applying those values can vary widely from country to country. The guideline published by the EPA of California has been critized by NIPERA.

Table 1.19: Ambient air guidelines or reference exposure levels for nickel compounds in the USA and Canada

Agency (effective date)	Compound	Air concentration (ng/m^3) associated with a 10^{-6} cancer risk	Ambient air guidelines (ng/m^3) or reference exposure level
US EPA [1991]	Nickel refinery dust Nickel subsulfide	4.17 2.08	- -
Canada, Ontario [1996]	Nickel	4.0	40
US Agency for Toxic Substances and Disease Registry [1997]	Nickel	3.85	-
California EPA [1993, cancer risk, 2000 reference exposure levels, still under review]	Nickel compounds (except oxide) Nickel oxide	- -	50 100

1.5.2 EC Legislation To Abate The Emissions Of Heavy Metals And Metalloids

New and upcoming EC legislation on the control of emissions will further reduce the present pollution by heavy metals and metalloids. This will be of relevance for the setting of AQS standards and for the economic evaluation. To discuss this legislation in detail would certainly be out of the scope of this position paper, but a short summary of present activities in this neighbouring field may be of interest.

The EC directive 96/61 EC on Integrated Pollution Prevention and Control (IPPC-directive) [116] had to be transferred into national law until october 31, 1999. Inter alia, it requires the Member States to base the permit for industrial facilities given in annex I on best available techniques (BAT, art. 9), and to lay down emission limit values in the permit for pollutants mentioned in annex III (inter alia metals and metallic compounds, arsenic and arsenic compounds [114]. In accordance with art. 16 establishing an exchange of information on BAT and emission limit values between commission and Member States, documents describing BAT for certain types of facilities (BREFs) are currently established by the IPPC bureau in Sevilla in cooperation with Member States and principal stake holders. 8 drafts for BREFS have been presented so far, including BREFs on iron and steel, production of non-ferrous metals and glass industry. The BREF on iron and steel has been approved by the Information Exchange Forum (IEF) from Member States and principal stake holders and will be published soon by the commission. Upcoming BREFs will cover primary and secondary production of non-ferrous metals (inter alia for cadmium and nickel), refineries, foundries and large combustion plants. The BREF notes presented so far are of high technical quality and rather demanding, so that significant emission reductions in the next decade can be expected.

Whereas the majority of industrial installations will be dealt with under the IPPC directive and BREFS, certain groups of facilities are or will be covered by particular directives. Examples are the directive on the incineration of hazardous waste (94/67/EC [117]) and the directive on the incineration of waste, where a common position has been reached in June 1999 [118]. This common position contains, inter alia, limit values for cadmium, arsenic and nickel in annexes II (coincineration) and V (waste incineration). Finally, the commission has come forward with a proposal for a new directive on large combustion plants [119], which is currently discussed in the Council. The present directive on large combustion plants 88/609/EEC does not contain emission limits for metal and metalloid compounds. However, their emissions are indirectly controlled to some extent by emission limits for dust.

Also the directive 1999/30/EC relating to limit values, inter alia, for particulate matter and lead, the so called first daughter directive on ambient air quality [120], will indirectly help to reduce the emissions. The tough ambient air quality standards for particulate matter prescribed therein can only be met by further reductions of dust emissions, which will also control the emissions of heavy metals and metalloids to a certain extent.

1.5.3 UN ECE Protocol To The Convention On Long-Range Transboundary Air Pollution On Heavy Metals And OSPAR Decision/Recommendation On Limits For Emissions From The Primary Non-Ferrous Metal Industry

UN ECE Protocol

Within the framework of the Convention on long-range transboundary air pollution in Europe (Geneva 1975), the Member States of the UNECE (United Nations Economic Commission for Europe) have consented on a protocol on heavy metals during their meeting in Aarhus in June 1998 [121].

From the heavy metals contained in annex I of the Framework directive [1] lead, cadmium and mercury are covered by the protocol [121].

The protocol will enter into force 90 days after 16 (out of about 45) Member States of UNECE will have deposited their documents on adoption or ratification with the Secretary-General of the United Nations (UN). At present, only Canada has done so. If ratification runs smoothly, the protocol may come into force in the year 2000.

The protocol aims at controlling the emissions of anthropogenic emissions of heavy metals, which may be subject to transboundary transport and may endanger human health or the environment as a whole (art. 2 of the protocol).

The Member States which will have adopted the protocol shall

- reduce their overall annual emissions in relation to 1990 or any other year in the decade from 1985 - 1995, specified by the Member State at the adoption of the protocol (art. 3 of the protocol);

- use best available technologies laid down in annex III for new installations laid down in annex II and for existing facilities;

- apply emission limit values (referring to particulate emissions, annex V) for certain specified new installations and for existing facilities, as far as technically and economically feasible;

- take additional measures for product management (e.g. Hg content in batteries, annex VII);

- establish and maintain an emission inventory taking into account the EMEP standards for inventories;

- facilitate the exchange of informations, of techniques to abate the emissions of heavy metals und of technical aid.

Member states may use economic instruments and voluntary agreements with industry to reduce their heavy metal emissions. They shall advance research on emissions, transport, concentration levels and deposition of heavy metals as well as on abatement measures and alternative products. They are requested to report to UNECE regularly on their emissions and the abatement actions taken.

EMEP (Cooperative programme for monitoring and evaluation of long-range transmission of air pollutants in Europe) shall supply annually monitoring data and modelling results on depositions and transboundary fluxes of heavy metals to the executive committee of UNECE.

It can be expected that the UNECE protocol on heavy metals will reduce the long range transport and the widespread input of heavy metal compounds especially into ecosystems. Because of the large scale considered within EMEP and important for transboundary transport, the protocol will not primarily aim at the reduction of ambient air levels of cadmium and other heavy metals in urban areas and hot spot situations, although the application of best available techniques and other abatement measures will also improve the situation on this scale. However, the emission reductions by the signatories agreed upon in art. 3 have not been quantified (e.g. by percentages of reduction or emission ceilings) and are thus left to the signatories.

The future monitoring and modelling work program of EMEP will be concentrated also on nickel and arsenic compounds, which belong to a set of eight priority elements (Pb, Hg, Cd, Cr, Ni, Zn, Cu and As) [122].

Draft OSPAR Decision/Recommendation

Based on article 2 of the Convention for the Protection of the Marine Environment of the North-East Atlantic („OSPAR Convention“), work is in progress to establish a decision or recommendation on limits for emissions from the primary non-ferrous metal industry (zinc, copper, lead and nickel works) [123]. The draft which is currently discussed by the involved parties applies to the primary metallurgical industry producing one or more of the metals zinc, copper, lead and nickel or co-products containing these metals. Inter alia, the draft contains limit values for the emissions into the air of particulate matter, of nickel and its compounds, of cadmium compounds (together with mercury and thallium), and of arsenic compounds (together with selenium). In addition, limit values for the discharge of these and other compounds into water will be set, together with monitoring requirements. The emission limit values shall apply to new installations after the entry into force and to existing installations within five years. The entry into force was originally planned for January 2000, but will be delayed considerably, as negotiations of the draft are still going on.

1.6 Summary Of Key Points, Chapter 1

Chapter 1 compiles the available knowledge on the chemical characterization of arsenic, cadmium and nickel compounds in the atmosphere, on sources and emissions, on ambient air levels and on current national and international legislation.

Arsenic, cadmium and nickel compounds are present as different chemical species within the airborne aerosol. The species differ considerably in respect to their toxicity, carcinogenic potency and other properties influencing their bioavailability like, for example, their water solubility, particle size distributions and specific surface areas. Unfortunately, only few measured data from species specific analysis exist in ambient air. Likewise, species specific measurements of the effluents of the most important sources are scarce. Hence, the assessment of effects will be stricken with considerable uncertainties.

Arsenic compounds predominantly exist as variable mixtures of arsenites and arsenates in ambient air. Ratios (As(III) to As(V)) between 27 % (rural) and more than 50 % in urban areas have been reported.

There are no ambient air data for cadmium compounds. From emission measurements it can be assumed that the most abundant species are oxides, sulfate, chloride and elemental cadmium.

Emissions of nickel species heavily depend on the kind of emitting sources. Combustion sources are predominantly emitting nickel sulfate and oxidic nickel, whereas industrial processes may also emit metallic nickel, nickel alloys and in the case of two nickel refineries in Europe, nickel subsulfide. First ambient air measurements have resulted in oxidic nickel as main fraction (about 50 %), followed by soluble compounds (20 - 40 %) and smaller portions of metallic and sulfidic nickel (5 - 8 %).

Measurements of size distributions in several Member States (Finland, France, Germany, Spain) have shown that arsenic and cadmium compounds are mainly concentrated in the fine mode (< 2.5 µm) of the aerosol. This fraction can be transported over long distances and can penetrate deeply into the respiratory system. Nickel compounds have a share of up to 30 % in the coarse mode (about or above 10 µm).

On a global and even more European scale, anthropogenic sources considerably outweigh the natural ones, estimates for global natural shares being 25 - 60 % for arsenic, 10 % for cadmium and 35 % for nickel.

Several scientific organisations (TNO (1990), EMEP (1997)) have published European emission inventories. In addition, recent national emission inventories exist from 11 Member States, which are compiled in the annexes.

87 % of arsenic is emitted by stationary combustion (heavy fuel, coal). The remaining is emitted by the non-ferrous metal industry, particularly copper and zinc smelters. Based on the TNO inventory (1990), around 40 % of cadmium is emitted by the non-ferrous metal industry and 29 % is emitted by stationary combustion. A significant part is attributed to road transport. Data on the share of road transport are conflicting. Whereas the TNO inventory assigns 18 % of European cadmium emissions to this sector, this figure is neither confirmed by the recent national inventories (between 1 and 4.5 %), nor by monitoring data in ambient air.

Based on recent national inventories, 87 to 97 % of nickel is emitted by stationary combustion (heavy fuel, coal). These figures are in conflict with the TNO report, which assigns only 53 % to this sector. The same situation occurs for "Mobile sources and machinery" which represents 30 % of the nickel emissions reported by TNO, whereas national inventories place this share at few percents.

Regions with the highest emission densities for cadmium according to EMEP data are north-western Germany and Belgium, northern Italy and parts of Spain.

Several Member States have established emission trends. Data from Austria, Italy, Germany and the United Kingdom show large reductions in the eighties and early nineties and lower or no reduction afterwards. This is also reflected by the monitoring data which generally show decreasing trends in the eighties and before, and only small or no decreases in the nineties. This holds also true for trends in deposition near sources as well as in background areas.

In contrast to the virtually not existing species specific data, measurements of the total arsenic, nickel or cadmium content in ambient air (TSP and PM10) are abundant, from which typical levels in different micro environments can be derived. Typical levels for arsenic are 0.05 ng/m^3 (remote areas), 0.2 - 1.5 ng/m^3 (rural), 0.5 - 3 ng/m^3 (urban background and traffic related) and up to 50 ng/m^3 at industrial sites. Typical concentration ranges for cadmium are 0.1 - 0.4 ng/m^3 (rural), 0.2 - 2.5 ng/m^3 (urban background and traffic related sites), and up to 20 ng/m^3 at industrial sites, whereas typical nickel levels are somewhat higher (0.4 - 2 ng/m^3 in rural areas, 1,4 - 13 ng/m^3 at urban background and traffic related sites) (in Spain up to 20 ng/m^3), and a range of 10 to 50 ng/m^3 near industry. There is no clear indication of higher cadmium levels at traffic related sites. The same pattern is shown by deposition data, where the gradient between industrial sources and the urban background is even more distinct (about one order of magnitude or more). The big concentration gap of about one order of magnitude between urban areas and the surroundings of certain industrial facilities clearly points to an important problem for the risk manager: Limit values attained in the urban background may be very difficult to reach at certain industrial hot spots.

The recent European values are significantly lower than somewhat older and worldwide data cited in the IPCS document for arsenic.

Data on current national legislation were collected by a questionnaire. Legally binding air quality standards for cadmium exist in three Member States, whereas the majority of Member States limit the emissions, some in individual permits. Three Member States apply target or guide values.

The USA, Canada and Japan have not regulated ambient air levels of arsenic, cadmium, and nickel so far. However, the US EPA and some state agencies in the USA and Canada have established guidelines for ambient air levels.

EC legislation regulates the emissions of the most important industrial sources either directly or indirectly (by means of emission limits for dust). Important directives are the IPPC directive in combination with BREF notes, the two directives on waste incineration and the directive on large combustion plants. In addition, international agreements like the UNECE protocol on heavy metals (cadmium) or an OSPAR decision/recommendation (draft) on limits for emissions from the primary non-ferrous metal industry are either in the process of ratification (UNECE) or in preparation (OSPAR). These regulations and international agreements will help to further reduce emissions of arsenic, cadmium and nickel compounds and their widespread input into eco-systems.

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2. RISK ASSESSMENT

2.1 Arsenic

2.1.1 Sources And Occurrence In The Environment

Arsenic is ubiquitous in the environment and is present mostly in its trivalent (As(III)) and pentavalent (As(V)) forms with sulfides being the predominant compounds. Depending on the conditions of the media, tri- and pentavalent forms can be converted into one another. Methylation of inorganic arsenic is known to occur in water and soil and minor amounts of methylated species might be present in air as well (WHO, 1987; 1997 [1,2]).

2.1.1.1 Air

As has been explained in more detail in chapter 1.3, arsenic is released into the atmosphere both from natural and anthropogenic sources. Most of the man-made emissions are released from metal smelters and the combustion of fuels. The use of pesticides used to be an important source as well, but has declined since its restriction in various countries (WHO, 1997 [2]; Becher and Wahrendorf, 1992 [3]). Arsenic is present in the atmosphere mostly as a variable mixture of tri- and pentavalent species of inorganic arsenic with the latter being predominant. There is, however, evidence that low concentrations of methylated arsenic might be present in the air of urban areas (WHO, 1987; 1997 [1,2]).

2.1.1.2 Dust

Arsenic in the atmosphere exists as particulate matter, mostly as particles less than 2 µm in diameter. These particles are transported by wind and air currents until they return to the ground by wet or dry deposition. Resuspension may contribute to the concentration of arsenic in air. Dust in the vicinity of copper smelters can contain arsenic in high concentrations (WHO, 1997 [2]).

Data on wet and dry deposition are given in chapter 1.4.

In a study of German households, the amount of arsenic in dust settled on indoor surfaces and the concentration of arsenic in dust samples taken from vacuum cleaner bags was measured (Krause et al., 1991 [4]); the results are given in table 2.1.1.

The arsenic concentration in house dust (median: 1.59 mg/kg) thus seems to be at the lower end of the range of background concentrations in German soils reported above (median: 1-12 mg/kg) and much lower than the average background concentration of 7 mg/kg reported by WHO (1987 [1]).

Table 2.1.1: Arsenic in household dust (Krause et al., 1991 [4])

	Arsenic dust deposition	Arsenic concentration in dust
n	2184	2633
10th percentile	3 ng/(m^2•d)	0.58 mg/kg
50th percentile	10 ng/(m^2•d)	1.59 mg/kg
95th percentile	40 ng/(m^2•d)	4.58 mg/kg
Arithmetic mean	14 ng/(m^2•d)	2.06 mg/kg
Geometric mean	9 ng/(m^2•d)	1.46 mg/kg

2.1.1.3 Water

The arsenic content in water can vary due to geological conditions, industrial emissions and atmospheric deposition. In an oxygenated environment, arsenic(V) predominates as the chemical species, usually as arsenates. Arsenic(III) (arsenites) is found as the most common form in reducing conditions, such as deep lake sediments or groundwaters. Methylation of inorganic arsenicals might occur in some waters, resulting in monomethylarsonate and dimethylarsenite, and some marine organisms are able to convert inorganic arsenicals to complex organo-arsenic compounds, e.g., arsenocholine and arsenobetaine (WHO, 1996; 1997 [5, 2]).

2.1.1.4 Soil

Arsenic is present in soil due to geogenic sources, industrial emissions, and the use of pesticides containing arsenic. In soil, too, arsenic is present mostly in its pentavalent form under oxygenated conditions while trivalent species predominate in a reducing environment. The leaching to groundwater layers is thought to be low because of binding to hydrous oxides of iron and aluminium. Biomethylation of inorganic arsenicals in soil and subsequent volatilisation of the resulting methylarsines may occur (WHO, 1997 [2]).

Natural, i.e. geogenic, background levels of arsenic in soil are usually below 40 mg/kg with a mean of approx. 7 mg/kg (WHO, 1987 [1]). Soil near industrial emission sources and soil on which pesticides containing arsenic were used can contain much higher values of up to 2500 mg/kg (WHO, 1987; 1997 [1,2]). Soil in close vicinity of copper smelters can be heavily contaminated with arsenic, e.g., arsenic concentrations above 90 mg/kg have been found around the Anaconda smelter in USA, and around the smelter in Potosi, Mexico, median concentration of arsenic in soil and dust amounted to 502 and 857 mg/kg (WHO, 1997 [2]).

For background concentration of arsenic in soil in rural areas of Germany, values were found to be 1-12 mg/kg (median) depending on the substrate (LABO, 1995 [6]). For the Netherlands, an average value of 12 mg/kg dry matter (90th percentile 22 mg/kg) for agricultural and horticultural land has been determined (Slooff et al., 1990 [7]).

2.1.1.5 Other

Arsenic compounds have a long history of use in medicine, e.g., in the treatment of syphilis, yaws, amoebic dysentery and trypanosomiasis. Several arsenic compounds are still used to treat certain severe parasitic diseases. Chinese herbal medicines may contain high amounts of inorganic arsenic (ATSDR, 1998 [8]). Since these sources of arsenic exposure may only be relevant to individual cases, but are of negligible importance for the general population, these sources will not be further evaluated here.

2.1.2 Human Exposure, Uptake And Effects

2.1.2.1 Pathways Of Human Exposure

Inhalation exposure

Arsenic in air is usually a mixture of particulate arsenite and arsenate, with organic species of negligible importance except in areas of substantial application of methylated arsenic pesticides (WHO, 1997 [2]; ATSDR, 1998 [8]).

Current concentrations of arsenic in air range 0-1 ng/m³ in remote areas, 0.2-1.5 ng/m³ in rural areas, 0.5-3 ng/m³ in urban areas, and up to about 50 ng/m³ in the vicinity of industrial sites (cf. chapter 1.4.1).

Factors affecting the extent of absorption from the lungs include chemical form, particle size and solubility. Particles larger than 10 µm in aerodynamic diameter are predominantly deposited in the upper airways, particles between 5 and 10 µm are deposited in the part of the airways cleansed by mucociliary transport, and particles of diameters less than 2 µm penetrate significantly into the alveoli (WHO, 1997 [2]).

In the following table 2.1.2, an absorbed daily dose of inorganic arsenic is calculated. In addition, a ”low” and a ”high” average estimate are given. The latter values are not intended to represent the extremes of the possible range of exposure, instead, they should represent values to which a significant proportion of the population is probably exposed. Concentrations are chosen in order to reflect approximately the situation in rural (“low”), urban (“average”) and industrial areas (“high”), respectively.

For adults, a reference body weight of 60 kg and a reference respiratory volume of 20 m^3/d according to U.S. EPA recommendations (EPA, 1988 [9]) were assumed. According to the allometric relationship (EPA, 1988 [9]) of minute volume (MV in l/min) at rest to body weight (BW in kg)

$$\ln MV = -0.70048 + 0.65865 \ln BW$$

and using a factor of 1.44 to convert the respiratory volume from l/min to m^3/d, a respiratory volume of 10.6 m^3/d would be calculated for a 60-kg adult at rest. Assuming that the average person is resting for 8 hours/day and at light, non-occupational activity for 16 hours/day, the daily respiratory volume at rest has to be multiplied by a factor of 1.9 to give a value of 20 m^3/d.

For children, a reference body weight of 15 kg corresponding to an age of about 3 years was assumed. From the allometric relationship given above, a minute volume of 2.95 l/min can be calculated for a resting 15-kg child. By multiplying the value with 1.44 and 1.9, a respiratory volume of 8 m^3/d can be derived. In addition, it was assumed that indoor and outdoor air concentrations are identical.

The total absorption includes deposition rate and absorption rate of deposited amount. An average value of 50 % (WHO, 1997 [2]) was used.

Table 2.1.2: Calculation of the absorbed daily dose of inorganic arsenic. Source: Air

Exposure [1)]	Concentration in air (ng/m^3)	Percentage of inorganic arsenic (%)	Absorption (%)	Other assumptions	Absorbed dose (µg As/(kg•d))
Adults					
low	0.5	100	50	body weight: 60 kg respiratory volume: 20 m^3/d	0.0001
average	2	100	50		0.0003
high	20	100	50		0.0033
Children					
low	0.5	100	50	body weight: 15 kg respiratory volume: 8 m^3/d	0.0001
average	2	100	50		0.0005
high	20	100	50		0.0053

1) Exposures are classified in order to reflect approximately concentrations in rural, urban and industrial areas, respectively

Cigarette smoking

Tobacco smoke may contain arsenic, especially when the tobacco plants have been treated with lead arsenic insecticides. Although the use of arsenic pesticides is now prohibited in most countries, the natural content of arsenic in tobacco may still result in some exposure.

WHO estimated that the arsenic content of mainstream cigarette smoke is ranging from 40 to 120 ng per cigarette. Assuming 20 cigarettes smoked per day, the daily intake amounts to 0.8-2.4 µg (WHO, 1997 [2]). In humans exposed to cigarette smoke, deposition in the airways is estimated to be about 40 %, and the absorption is 75-85 % of deposited amount. Thus, overall absorption is 30-35 % of the inhaled amount (WHO, 1997 [2]). In a literature survey, the range given for arsenic in mainstream cigarette smoke is 0-1.4 µg As /cigarette which would translate to 0-28 µg As /day assuming that 20 cigarettes are smoked per day (Smith et al., 1997 [10]).

In the following Table 2.1.3, an absorbed daily dose of inorganic arsenic is calculated. In addition, a ”low” and a ”high” estimate are given. The latter values are not intended to represent the extremes of the possible range of exposure, instead, they should represent values to which a significant proportion of the population is probably exposed.

Table 2.1.3: Calculation of the absorbed daily dose of inorganic arsenic.
Source: Cigarette smoke

Exposure[1)]	Amount of arsenic in main-stream smoke per pack (µg)	Percentage of inorganic arsenic (%)	Absorption (%)	Other assumptions	Absorbed dose (µg As /(kg•d))
low	0	100	35	body weight: 60 kg	0
average	2.4	100	35		0.014
high	28	100	35		0.16

1) Exposure is estimated for consumption of 1 pack of cigarettes per day

Oral exposure (Water and Food)

Arsenicals in water are usually a mixture of arsenates and arsenites, with arsenates predominating. Methylated forms have been detected in surface water and groundwater, at levels ranging from 0.01 to 7.4 ppb, with most values below 0.3 ppb methylated arsenic of a total of 1-2 ppb arsenic (ATSDR, 1998 [8]).

In general, drinking water usually contains less than 10 µg As /l (WHO, 1987; 1997 [1,2]) or 1-2 µg As /l (WHO, 1996 [5]). Much higher values of up to 12 mg/l have been reported in regions with geogenic sources (WHO, 1996; 1997 [5,2]). In a survey of arsenic concentrations in drinking water in Germany in 1988/89, in 93.5 % of the samples concentrations were < 2 µg/l (with 74.4 % below detection limit) and 1.2 % were >10 µg/l (Dieter, 1994 [11]).

As the arsenic intake via food is greatly influenced by the amount of seafood in the diet, estimates of the amount of arsenic ingested via this pathway have to be differentiated by seafood consumption. Only a small part of the arsenic in fish is inorganic. Estimates given are 1.5 % for fish, 3 % for mussels, 20 % for shellfish, 0.1-41 % for total seafood (ATSDR, 1998 [8]).

All in all, the total arsenic intake (including organic arsenic) is estimated to be in the order of 1000 ng/(kg•d). The amount depends very much on whether fish consumption is included in the estimate and on the amount of fish consumption (this leads to, e.g., high values for Japan). A Canadian study, however, gives an estimate for the intake of inorganic arsenic of 117 ng/(kg•d) (WHO 1997 [2]).

Inorganic arsenic constituted 5.7-17 % of total arsenic ingested in a Japanese study (WHO, 1997 [2]). A slightly higher share of 25 % inorganic arsenic was estimated by WHO (1996 [5]) to be the percentage of total arsenic intake via food.

Both human and animal data indicate that more than 90 % of the ingested dose of dissolved inorganic trivalent or pentavalent arsenic is absorbed from the gastrointestinal tract. Organic arsenic compounds in seafood are also readily absorbed (75-85 %). Less soluble forms of arsenicals have much lower absorption (WHO, 1997 [2]). For example, insoluble arsenic triselenide did not lead to a measurable increase in urinary arsenic excretion indicating lack of absorption (ATSDR, 1998 [8]).

In the following tables 2.1.4 and 2.1.5, an absorbed daily dose of inorganic arsenic is estimated. In addition, a ”low” and a ”high” estimate are given. The latter values are not intended to represent the extremes of the possible range of exposure, instead, they should represent values to which a significant proportion of the population is probably exposed.

For adults, a reference body weight of 60 kg and a reference value of 2 l/day for water consumption are assumed according to U.S. EPA recommendations (EPA, 1988 [9]).

For children, a reference body weight of 15 kg is assumed. Therefore, instead of the reference drinking water rate of 1 l/day for a 10-kg child used by EPA‘s Office of Drinking Water (EPA, 1988 [9]) and by WHO, a daily water consumption of 1.5 l is used. This does not change the absorbed dose per kg and day.

Table 2.1.4: Calculation of the absorbed daily dose of inorganic arsenic.
Source: Drinking water

Exposure [1]	Concentration in water (µg/l)	Percentage of inorganic arsenic (%)	Absorption (%)	Other assumptions	Absorbed dose (µg As /(kg•d))
Adults					
low	0	100	100	body weight: 60 kg consumption of drinking water: 2 l/d	0
average	2	100	100		0.067
high	10	100	100		0.33
Children					
low	0	100	100	body weight: 15 kg consumption of drinking water: 1.5 l/d	0
average	2	100	100		0.2
high	10	100	100		1.0

[1] Very high geogenic exposures (up to 12,000 µg/l) are not considered; for the ”high” exposure estimate, the EC drinking water limit value of 10 µg/l is used

For the average total intake of adults of arsenic in food, a mean value of 1000 ng/(kg•d)) is assumed. For the “high” and “low” estimates, values of 2000 ng/(kg•d)) and 500 ng/(kg•d)), respectively, are used. The values are based on a mixed, fish-containing diet.

Only few studies compared arsenic intake of adults and children. In one study (WHO, 1996 [5]) the mean daily intake of children was about half that of adults, while in another study (Dabeka et al., 1993 [12]), the mean daily intake of children was twice that of adults. Therefore, for the arsenic intake of children, the same values as for adults are used.

Percentages of inorganic arsenic in proportion to the total arsenic content of average food are reported to be between 5.7 % and 25 % (WHO, 1996; 1997 [5,2]). Therefore, for the “low”, “average” and “high” estimates, values of 6 %, 15 % and 25 %, respectively, are used.

Table 2.1.5: Estimate of the absorbed daily dose of inorganic arsenic. Source: Food

Exposure	Amount ingested (µg As/(kg•d))	Percentage of inorganic arsenic (%)	Absorption (%)	Absorbed dose (µg As /(kg•d))
Adults and Children				
low	0.5	6	100	0.030
average	1.0	15	100	0.15
high	2.0	25	100	0.50

Soil and dust

In addition to the pathways mentioned above, the general population might be exposed to arsenic via soil and/or dust. WHO (1997 [2]) estimates that this pathway contributes an intake of 0.14-0.28 µg/d, corresponding to approximately 2.3-4.6 ng/(kg•d) if a body weight of 60 kg is assumed. However, this pathway of exposure is mainly relevant for children.

Only part of the arsenic in soil is soluble and can thus be absorbed. Using water, the extractability of arsenic from soil contaminated by hazardous waste was between 4.5 and 56 % (ATSDR, 1998 [8]).

Data on the bioavailability of arsenic show a wide range depending on several parameters, such as type of soil, soil particle size and concentration of organic carbon (Voß et al., 1996 [13]).

Bioavailability of arsenic in soil contaminated by smelter activities, following oral administration to rabbits was about 25 % (WHO, 1997 [2]). Here, species differences in the absorption rate from the gastrointestinal tract have to be taken into account. After oral administration of soluble arsenates and arsenites, faecal excretion of arsenic ranged 2-10 % in monkeys and mice, 10-40 % in hamsters to 45-52 % in rabbits, indicating a considerably lower absorption rate in rabbits.

Based on urinary excretion / blood levels of arsenic in cynomolgus monkeys, the bioavailability was assessed as 67.6 % / 91.3 % for soluble salt, 19.2 % / 9.8 % for household dust and 13.8 % / 10.9 % for soil (ATSDR, 1998 [8]).

Using a rat model, the bioavailability of arsenic pesticide-contaminated soil relative to As(III) and As(V) was found to range 1.02-9.87 % and 0.26-2.98 %, respectively (Ng et al., 1998 [14]).

In the following table 2.1.6, an average absorbed daily dose of inorganic arsenic is calculated. In addition, a ”low” and a ”high” estimate are given. The latter values are not intended to represent the extremes of the possible range of exposure, instead, they should represent values to which a significant proportion of the population is probably exposed.

For adults, a reference body weight of 60 kg according to U.S. EPA recommendations (EPA, 1988 [9]) is assumed. For children, a reference body weight of 15 kg is assumed.

For the average soil and dust intake of a 15-kg child, a value of 0.5 g/d is used. This value represents the 95-percentile for long-term soil intake of children up to 6 years old and includes pica activity (Ruck, 1990 [15]). For adults, the most often reported value for soil and dust intake is 0.1 g/d (Ruck, 1990 [15]).

For the absorption rate of arsenic from soil and dust after oral uptake, a value of 20 % is assumed, based on estimates derived from urinary excretion measurements in monkeys showing a bioavailability of arsenic from household dust and soil of 19.2 % and 13.8 %, respectively (ATSDR, 1998 [8]).

Table 2.1.6: Calculation of the absorbed daily dose of inorganic arsenic.
Source: Soil and dust

Exposure	Concentration in soil/dust (mg/kg)	Percentage of inorganic arsenic (%)	Absorption (%)	Other assumptions	Absorbed dose (µg As /(kg•d))
Adults					
low	1	100	20	body weight: 60 kg; average soil/dust intake: 0.1 g/d	0.00033
average	5	100	20		0.0017
high	20	100	20		0.0067
Children					
low	1	100	20	body weight: 15 kg; average soil/dust intake: 0.5 g/d	0.0067
average	5	100	20		0.033
high	20	100	20		0.13

Estimation of the total absorbed arsenic dose

In the following table 2.1.7, the ”low”, ”average” and ”high” estimates for individual exposure sources are combined from tables 2.1.2-6. The simple addition of ”low” and ”high” values, respectively, may result in rather extreme total values, since the variabilities for each source of arsenic are largely independent of each other, i.e., a high arsenic dose through smoking is not necessarily connected with a high dose of arsenic through the diet, or a low arsenic concentration in drinking water need not be connected with a low arsenic concentration in air.

An average absorbed daily dose of inorganic arsenic of 0.23 µg/(kg•d) for adults including the increased arsenic uptake by cigarette smoking (0.22 µg/(kg•d) for non-smokers), and 0.38 µg/(kg•d) for children is calculated. Under average circumstances, the oral uptake of arsenic via food and drinking water contributes the largest amount to the total dose. On average, arsenic uptake via ambient air contributes less than 1 % to the total absorbed arsenic dose.

Table 2.1.7: Calculation of the absorbed daily dose of inorganic arsenic, in µg As /(kg•d)

	Adults			Children		
Source	low (% of sum)	average (% of sum)	high (% of sum)	low (% of sum)	average (% of sum)	high (% of sum)
Air	0.0001 (<1)	0.0003 (<1)	0.0033 (<1)	0.0001 (<1)	0.0005 (<1)	0.0053 (<1)
Cigarette smoking	0 (0)	0.014 (6)	0.16 (16)	-	-	-
Drinking water	0 (0)	0.067 (29)	0.33 (33)	0 (0)	0.2 (52)	1.0 (61)
Food	0.03 (98)	0.15 (64)	0.5 (50)	0.03 (81)	0.15 (39)	0.5 (30)
Soil and Dust	0.0003 (1)	0.0017 (<1)	0.0067 (<1)	0.0067 (18)	0.033 (8)	0.13 (8)
Sum	0.030	0.233	1.0	0.037	0.38	1.63

Table 2.1.8: Average daily doses of absorbed inorganic arsenic

Source	Vahter 1994 (µg/d)	Calculated dose[1] (µg/(kg•d))	Valberg et al. 1997 (µg/d) (unusual uptake)	Calculated dose[1] (µg/(kg•d)) (unusual uptake)	WHO, 1997 (µg/d)
Air	0.05	0.00083	0.05 (24)	0.00083 (0.40)	rural areas 0.02-0.2; cities 0.4-0.6
Cigarette smoking	1-20	0.017-0.33	1.8-5.4	0.030-0.090	0.7-2.1; 6
Drinking water	<1-10	<0.017-0.17	4.5 (90)	0.075 (1.5)	no data
Food	5-20	0.083-0.33	11-14 (18)	0.18-0.23 (0.30)	60 (USA) 45 (Belgium) 7 (inorg., Canada)
Soil	no data	no data	0.14 (2.0)	0.0023 (0.033)	0.14-0.28
Sum	5-30	0.083-0.5	16-19 (138-156)	0.27-0.32 (2.3-2.6)	no data

1) The body weight-based dose is calculated using a body weight of 60 kg

The estimated absorbed daily doses of inorganic arsenic derived here are in good agreement with estimates of exposure to inorganic arsenic reported in the literature by Vahter (1994 [16]), Valberg et al. (1997 [17]) and WHO (1997 [2]) (presented in table 2.1.8) and with those by Hughes et al. (1994 [18]) (presented in table 2.1.9).

Hughes et al. (1994 [18]) have estimated the average daily intake of inorganic arsenic by five discrete age groups for both the general population in Canada not living near point sources and the population living near point sources, such as smelters, landfill sites, geological sources, and areas with a history of high arsenical pesticide application. Results are presented in table 2.1.9.

Table 2.1.9: Average daily doses of absorbed inorganic arsenic for the general population (and for a population living near point sources) (Hughes et al., 1994 [18])

Source	Estimated daily intake (µg As /(kg•d))				
	age 0-0.5 yr	age 0.5-4 yr	age 5-11 yr	age 12-19 yr	age 20-70 yr
Air	0.0003 (0.002-0.06)	0.0004 (0.003-0.08)	0.0004 (0.004-0.1)	0.0004 (0.003-0.08)	0.0003 (0.003-0.07)
Tobacco smoking	0 (0)	0 (0)	0 (0)	0.01-0.04 (0.01-0.04)	0.01-0.03 (0.01-0.03)
Drinking water	0.5 (0.5-54)	0.3 (0.3-31)	0.2 (0.2-17)	0.1 (0.1-11)	0.1 (0.1-11)
Food	0.2 (0.2)	0.3 (0.3)	0.2 (0.2)	0.1 (0.1)	0.08 (0.08)
Soil and dirt	0.03-0.07 (0.02-2.5)	0.02-0.05 (0.01-1.9)	0.006-0.02 (0.004-0.6)	0.002-0.005 (0.001-0.2)	0.001-0.004 (0.0009-0.1)
Sum	0.73-0.77 (0.72-57)	0.62-0.65 (0.6-33)	0.41-0.42 (0.41-18)	0.21-0.25 (0.21-11)	0.19-0.21 (0.19-11)

2.1.2.2 Toxicokinetics

Following absorption, arsenic is rapidly distributed throughout the body via the blood circulation. From autopsy data, it was concluded that muscles, bones, kidneys, liver and lungs contain the highest absolute amounts of arsenic, but skin and related structures, such as nails and hair, have the highest concentration.

Transplacental transfer of arsenic appears to occur in humans (WHO, 1997 [2]). This has been confirmed in a recent study in Northern Argentina on a population exposed to drinking water containing about 0.2 mg As/l. The concentration of arsenic in cord blood (median 9 µg/l) was almost as high as in maternal blood (median 11 µg/l) indicating that, at least in late gestation, arsenic is easily transferred to the foetus (Concha et al., 1998a [19]).

Maternal-fetal distribution of inorganic arsenic has also been demonstrated in rats, mice, rabbits, hamsters and monkeys (Golub et al., 1998 [20]).

Autopsy data from retired metal-smelter workers, obtained several years after cessation of occupational exposure, showed that arsenic levels in the lungs were 8 times higher than in a control group, suggesting the existence of arsenic compounds of very low solubility in the smelter environment (WHO, 1997 [2]).

Trivalent inorganic arsenic is oxidised in vivo in both animals and humans exposed to arsenite. Reduction of arsenate to arsenite can also occur, as has been demonstrated in mice and rabbits (WHO, 1997 [2]).

Both arsenite and arsenate, after reduction to arsenite, are methylated in the liver. The methylation yields monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) in humans and animals (WHO, 1997 [2]). Both methylated species are considered less toxic, bind less to tissues, and are eliminated more rapidly than the unmethylated forms. In humans, methylation is the most important way of detoxification. However, protein binding may be the initial protective mechanism (Aposhian, 1997 [21]). Sensitivity to (neuro)toxicity seems to be determined by the individual capacity to methylate, and thus to detoxify, arsenic (de Wolff, Edelbroek, 1994 [22]). Unlike humans, the marmoset monkey has been shown unable to methylate inorganic arsenic (WHO, 1997 [2]). In addition to marmoset monkeys, tamarin monkeys and guinea pigs do not methylate inorganic arsenic (ATSDR, 1998 [8]).

It is estimated that more than 75 % of the absorbed dose is excreted via urine (ATSDR, 1998 [8]). In workers exposed to arsenic trioxide dusts in smelters, the amount of arsenic excreted in the urine was about 40-60 % of the estimated inhaled dose (WHO, 1997 [2]).

There is a great variation in the urinary excretion of the different arsenic metabolites between species. The low urinary excretion of methylated arsenic metabolites in the rat is not an indication of low methylating capacity, but is due to a specific retention of DMA in erythrocytes. Only humans excrete significant amounts of MMA following exposure to inorganic arsenic. The rabbit seems to be the species most similar to humans with regard to the methylation of arsenic (WHO, 1997 [2]).

In human volunteers who ingested a single oral dose of 500 µg arsenic, either as arsenite, MMA or DMA, the excretion rate increased in the order inorganic arsenic < MMA < DMA. It has been suggested that when uptake exceeds a certain value, the methylation mechanism becomes saturated, and its efficiency declines as exposure increases. However, analysis of arsenic species in urine of occupationally exposed workers or volunteers did not support the methylation threshold hypothesis; at least an occupational exposure to up to 300 µg arsenic/m^3 does not saturate the methylation pathway. On average, 20-25 % of inorganic arsenic remains unmethylated regardless of exposure level (WHO, 1997 [2]) (table 2.1.10).

Table 2.1.10: Arsenic species excreted in humans

Exposure	Urinary arsenic (µg/l)	Inorganic arsenic (%)	Monomethyl-arsonate (%)	Dimethyl-arsinate (%)	Reference
Background	4.4-57.2	21	15	64	WHO, 1997 [2]
Occupational	10.2-245	19	15	65	WHO, 1997 [2]
General values for humans	no data	20-25	15-25	40-60	ATSDR, 1998 [8]

Since methylation is an enzymatic process, saturability of the methylation capacity can be assumed. However, even after ingestion of relatively high arsenic doses, the biomethylation process requires only a few percent of the total methyl intake via food (the methyl transferase requires S-adenosylmethionine as a methyl donating cosubstrate), so that the dose rate at which methylation capacity becomes saturated cannot be precisely defined with current data (ATSDR, 1998 [8]).

A study on a population in northern Argentina exposed to drinking water containing about 0.2 mg As /l revealed that children had a significantly higher percentage of inorganic arsenic in urine than women, about 50 % versus 32 %. This finding may indicate that children are more sensitive to toxic effects induced by inorganic arsenic than adults. However, the authors mention two studies in which the percentage of inorganic arsenic in the urine of children was much lower (about 13 %, i.e., it was about the same as in adults). Both children and women excreted very little MMA in urine which the authors interpreted as an indication of a polymorphism of an enzyme involved in arsenic methylation (Concha et al., 1998b [23]).

After oral intake of radiolabelled pentavalent arsenic, 66 % was excreted with a half-life of 2.1 days, 30 % with a half-life of 9.5 days and 3.7 % with a half-life of 38 days. In another human experiment, 48 % of a dose of 3 mg sodium arsenite was excreted within 5 days with a biological half-life of 30 hours. The organic species arsenobetaine present in seafood is apparently not metabolised in vivo and eliminated rapidly via the kidneys with a half-life of 18 hours (WHO, 1997 [2]).

The excretion of inorganic arsenic in human breast milk is comparatively low. In a study of a population exposed to arsenic via drinking water containing about 0.2 mg As /l, the average concentration of arsenic detected in human milk was 2.3 µg As /kg fresh weight, while concentrations of arsenic in maternal blood and maternal urine were much higher, averaging 10 µg/l and 320 µg/l, respectively (Concha et al., 1998c [24]). The median arsenic concentration in human milk sampled from mothers in the Faroe Islands, where the diet is rich in seafood, was 1.6 µg/kg (range 0.1-4.4 µg/kg) (ATSDR, 1998 [8]).

2.1.2.3 Health Effects Of Arsenic

Essentiality

There are several studies in animals that suggest that low levels of arsenic in the diet are beneficial and essential. Rats fed a low-arsenic diet (<0.05 ppm in food, corresponding to 2.5 µg As /(kg•d)) did not gain weight normally. Moreover, arsenic deprivation has been noted to decrease the growth of offspring from rats, goats and minipigs. Decreased reproductive success and increased postnatal mortality have also been noted in goats, minipigs and rats maintained on low-arsenic diets (ATSDR, 1998 [8]).

No cases of arsenic deficiency in humans have ever been reported and it is not proven if arsenic is essential or beneficial to humans. If so, the daily requirement for humans has been estimated at 10-50 µg/day (0.1-0.7 µg As /(kg•d); this level is usually provided in the normal diet (ATSDR, 1998 [8]).

Speciation

From the toxicological point of view, arsenic compounds may be classified into three major groups: inorganic arsenic compounds, organic arsenic compounds and arsine gas. The most common inorganic trivalent (As(III)) arsenic compounds are arsenic trioxide, sodium arsenite and arsenic trichloride. Pentavalent (As(V)) arsenic compounds are arsenic pentoxide, arsenic acid and arsenate, e.g., calcium arsenate. Common organic arsenic compounds are arsanilic acid, methylarsonic acid, dimethylarsonic acid (cacodylic acid) and arsenobetaine (WHO 1987, 1997 [1,2]).

The most common inorganic arsenical in air is arsenic trioxide, while in water, soil or food a variety of inorganic arsenates or arsenites occur (ATSDR, 1998 [8]). Although a number of studies have noted differences in the relative toxicity of these species, with trivalent arsenites tending to be somewhat more toxic than pentavalent arsenates (ATSDR, 1998 [8]), in the toxicological evaluation provided here, no distinction between trivalent and pentavalent will be made because

1. the differences in relative potency between As(III) and As(V) species are reasonably small (about 2-3 fold), often within the bounds of uncertainty regarding NOAEL and LOAEL levels (ATSDR, 199 [8]),
2. different arsenic species may be interconverted both in the environment and in the body (ATSDR, 1998 [8]),
3. in many cases of human exposure, the precise chemical speciation is not known.

Gallium arsenide is another inorganic arsenic compound of potential human health concern, due to its widespread use in the microelectronics industry. Gallium arsenide is poorly soluble in water, but it undergoes dissolution due to oxidation resulting in release of gallium trioxide and arsenite. However, since gallium arsenide is not a relevant arsenic species in ambient air, it will not be considered here. The same holds true for other less common inorganic arsenic compounds, such as arsenic trisulfide. Also arsine (AsH_3) and its methyl derivatives, although highly toxic, are not considered here since they occur only in certain occupational settings and not in ambient air.

The organic arsenicals found in seafood, such as arsenobetaine and arsenocholine, have been studied by several researchers and have been found to be compounds of low toxicological significance (ATSDR, 1998 [8]). Therefore, these compounds are not considered further here.

Although human health data on other organic arsenicals are sparse, it is generally considered that with respect to non-cancer effects, organic arsenicals are substantially less toxic than the inorganic forms. Data from animal studies suggest that adequate doses of methyl and phenyl arsenates can produce adverse health effects that resemble those of the inorganic arsenicals (ATSDR, 1998 [8]). Moreover, MMA and DMA can exert genotoxic effects. However, since these organic arsenicals are practically not present in ambient air, they are not considered further here.

Non-Cancer Effects

The clinical picture of chronic poisoning with arsenic varies widely. It is usually dominated by changes in the skin and mucous membranes and by neurological, vascular and haematological lesions. Involvement of the gastrointestinal tract, increased salivation, irregular dyspepsia, abdominal cramps and loss of weight may also occur (WHO, 1997 [2]).

Respiratory tract

Workers exposed to airborne arsenic dusts often experience irritation of the mucous membranes of the nose and throat. This may lead to laryngitis, bronchitis or rhinitis; very high exposures cause perforation of the nasal septum. Data existing on the exposure levels in these studies are insufficient to identify a no-effect level for respiratory tract irritation with confidence, but it appears that such effects are minor or absent at exposure levels of about 0.1-1 mg As/m^3 (Ide and Bullough, 1988 [25]; Perry et al., 1948 [26]; reviewed in ATSDR, 1998 [8]).

Nervous system

Arsenic and its inorganic compounds have long been known to be neurotoxic. Reports on neuropathy in beer-drinkers due to arsenic contamination were published about one century ago (Kelynack, 1900 [27], Reynolds, 1901 [28], Buchanan, 1901 [29]). Peripheral neuropathy in arsenic smelter workers was reported, too. Chronic exposure to arsenic dust at a concentration of about 50 µg/m^3 caused a significant decrease in peripheral nerve conduction velocity (Lagerkvist and Zetterlund, 1994 [30]). These findings support results of a study of Blom et al. (1985 [31]), who reported peripheral neuropathy in workers after inhalation of inorganic arsenicals at concentrations of 0.05 mg As/m^3.

Gastrointestinal tract

Nausea and anorexia occurred in one worker (but not in another) exposed to arsenic trioxide dust at a concentration of 0.11 mg As /m^3; no other studies with quantitative exposure data are available (Ide and Bullough, 1988 [25]).

Skin

The skin is a target organ in people (orally) exposed to inorganic arsenical compounds. Eczematoid symptoms develop with varying degrees of severity. Hyperkeratosis, warts and melanosis of the skin are the most commonly observed lesions in chronic exposure (WHO, 1997 [2]). Hyperkeratosis and hyperpigmentation are common in people exposed by the oral route, but have very rarely been reported after inhalation exposure (ATSDR, 1998 [8]).

Cardiovascular system

Increased mortality from cardiovascular diseases has not been found in all epidemiological investigations of smelter workers. Järup et al. (1989 [32]) failed to confirm an earlier finding (Axelson et al., 1978 [33]) of increased mortality from cardiovascular disease from the same cohort. A weak dose-response relationship has been found in other studies on two other cohorts (Enterline et al., 1995 [34]; Welch et al., 1982 [35]; Lee-Feldstein, 1983 [36]). Most studies were not controlled for smoking. Welch et al. (1982 [35]) found no significant difference in numbers of smokers according to arsenic exposure category.

Smelter workers exposed to inorganic arsenic dusts at concentrations of 50-500 µg As /m^3 (estimates based on air measurements at the plant) showed a higher incidence of Raynaud‘s disease and increased constriction of blood vessels in response to cold (Lagerkvist et al. 1986; 1988 [37,38]).

A study in non-smelter workers occupationally exposed to arsenic found a significantly higher systolic blood pressure in exposed workers compared to an unexposed control group (Jensen and Olsen, 1995 [39]; Jensen and Hansen, 1998 [40]). Although the study suggests that arsenic concentrations below 50 µg/m^3 might induce cardiovascular effects in exposed workers, the relevance of this study is rather limited due to the small number of workers, aggregation of workers with very different occupational exposure scenarios, possible additional arsenic exposure through skin contact and lack of analysis of the dose-response relationship.

Hypertension in persons with long-term exposure to arsenicals in drinking water at concentrations of 0.70-0.93 mg/l was reported in a study of Chen et al. (1995 [41]). An increase in blood pressure comparable in size to the one reported here (8 mm Hg), may considerably increase the incidence of coronary heart disease (Wilkins and Calabrese, 1985 [43]).

Gangrene of the extremities, known as Blackfoot disease, is due to peripheral vascular effects associated with oral exposure to arsenic (WHO, 1981 [44]).

Haematopoesis
Inorganic arsenic has an inhibitory effect on haematopoesis, giving rise to anaemia, most commonly of hypoplastic type. In severe cases of arsenical poisonings, agranulocytosis or thrombopenia may develop (WHO, 1981 [44]). Anaemia is often noted in humans exposed by the oral route, but has not been observed after inhalation exposure (ATSDR, 1998 [8]).

Reproduction and development

At relatively high exposure levels, arsenic is teratogenic in a number of animal species, including hamster, rat and mouse. Such effects have generally been observed after parenteral administration of either arsenite or arsenate. Oral exposures have not produced any notable effects on reproduction or development (WHO, 1997 [2]).

Two recent thorough reviews of the developmental toxicity of inorganic arsenic (DeSesso et al., 1998 [45]; Golub et al., 1998 [20]) came to the conclusion that inorganic arsenic induces intrauterine death and growth retardation as well as neural tube defects and other malformations in rodents only when administered early in gestation and under the conditions of extreme dosages attainable exclusively by means of intravenous or intraperitoneal injections or by gavage. In many studies, maternal toxicity occurred at the same doses as developmental toxicity. High-dose exposures by oral, inhalation or dermal routes have not produced dose-related increases in neural tube or other defects. In studies following GLP (Good Laboratory Practice) rules, repeated oral doses to rats, mice and rabbits have also failed to cause a dose-related increase in malformations. No effects on fertility of male or female animals were reported in available studies. Epidemiologic studies have not demonstrated a credible association between environmental exposure to inorganic arsenic and neural tube defects or other adverse pregnancy outcomes (DeSesso et al., 1998 [45]).

Reports of reduced sexual activity in persons with chronic arsenic exposure are frequent (WHO, 1981 [44]). An increased rate of spontaneous abortions and lower mean birth weights has been reported among Swedish smelter workers and among subjects living in the vicinity of the smelter. The rate of congenital malformations in the offspring of women working at the smelter was also higher. It was not possible to link these effects with exposure to any specific compound in the smelter environment (WHO, 1981 [44]).

A hospital-based case-control study (Ihrig et al., 1998 [46]) found an increased odds ratio for stillbirths in Hispanics, but not in African-Americans and White Non-Hispanics exposed to the same air concentration. The effect showed a dose-dependency. The authors speculate that the difference might be due to a genetic polymorphism. This study suggests that an increased rate of stillbirths may be a relevant endpoint after exposure to arsenic in ambient air. This conclusion is supported by similar observations from the Swedish smelter study (see above, WHO, 1981 [44]). However, the authors reported that the high exposure group was exposed to arsenic concentrations above 100 ng/m^3 without giving a more precise estimate. Moreover, possible other sources contributing to the higher total arsenic exposure, e.g., via higher arsenic concentrations in soil, food and water were not discussed. Therefore, no quantitative risk assessment can be based on this study.

Genotoxic Effects

An increased frequency of chromosomal aberrations has been found in peripheral blood lymphocytes of wine-growers exposed to arsenic, in psoriasis patients treated with arsenic, and in arsenic-exposed workers at a copper smelter. Sodium arsenate inhibits DNA repair in human skin biopsy cells and in lymphocytes (WHO, 1981 [44]).

Recent studies (see table 2.1.11) support the view that inorganic arsenicals are either inactive or very weak mutagens, but are able to produce chromosomal effects (aberrations, sister chromatid exchange) in most systems.

A comprehensive review of the dose-response relationships observed in arsenic genotoxicity assays has been published by Rudel et al. (1996 [47]). With the exception of sister chromatid exchanges, sublinear dose-response relationships for arsenic(V)-induced chromosomal aberrations were observed repeatedly in different mammalian and human cell systems. For arsenic(III) effects, sublinearity is questionable. Arsenic also enhanced the clastogenicity and mutagenicity of other DNA-damaging agents with a sublinear dose response. Consistently with the dose response of arsenic-induced genetic alterations, arsenic also inhibited DNA ligases I and II - enzymes playing a role in DNA repair - with a sublinear dose response.

In an assay able to detect both intragenic and multilocus mutations, arsenite was a strong dose-dependent mutagen that induces mostly large deletion mutations. The authors conclude that the carcinogenicity of arsenite can be explained at least in part by arsenite being a mutagen that depends on reactive oxygen species for its activity (Hei et al., 1998 [48]). However, these reactions were seen at concentrations clearly reducing the survival fraction in the cell culture tested.

Although the genotoxicity of organic arsenicals has not been studied as thoroughly as that of inorganic arsenicals, several tests indicate that DMA may be able to cause mutations and DNA strand breaks (see table 2.1.12).

Table 2.1.11: Genotoxicity of inorganic arsenicals in vitro without metabolic activation

Valence	Test system	End point	Result	Reference
As(III)	E. coli PQ37	gene mutation	negative	Lantzsch and Gebel, 1997 [49]
As(III)	Chinese hamster ovary cells	micronuclei	positive	Liu and Huang, 1997 [50]
As(III)	Human lymphocytes	DNA-protein cross-links	negative	Costa et al., 1997 [51]
As(III)	Human fibroblasts	DNA repair and mutant frequencies	positive	Wiencke et al., 1997 [52]
As(III) / As(V)	Human T-cell lymphoma-derived cell line Molt-3	PARP activity inhibition	positive	Yager and Wiencke, 1997 [53]
As(III)	Human skin fibroblasts	chromosomal aberrations	positive	Yih et al., 1997 [54]
As(III) / As(V)	Mouse lymphoma cells L5178Y/TK$^+$/$^-$3.7.2C	chromosomal mutations	positive	Moore et al., 1997 [55]
As(III)	Human lymphocytes	hyperploidy and chromosomal breakage	(positive)	Rupa et al., 1997 [56]
As(III)	Human lymphocytes	sister chromatid exchange	positive	Rasmussen and Menzel, 1997 [57]
As(V)	Human lymphocytes	sister chromatid exchange	negative	Rasmussen and Menzel, 1997 [57]
As(III)	Human lymphocytes	hyperdiploid nuclei	positive	Ramirez et al., 1997 [58]
As(III)	Chinese hamster ovary cells CHO-K1	DNA strand breaks	positive	Lynn et al., 1997 [59]
As(III)	Human fibroblasts	DNA repair inhibition	positive	Hartwig et al., 1997 [60]
As(III)	Syrian hamster embryo (SHE) cells	micronuclei induction	negative	Gibson et al., 1997 [61]
As(III)	Human lymphocytes	Sister chromatid exchange	positive	Gebel et al., 1997 [62]
As(V)	Human lymphocytes	Sister chromatid exchange	negative	Gebel et al., 1997 [62]
As(III)	Human pulmonary epithelial (L-132) cells	DNA single-strand breaks	negative	Yamanaka et al., 1997 [63]

After in vivo application of DMA to mice, aneuploidy and mitotic arrest were observed in bone marrow cells (Kashiwada et al., 1998 [64]).

When arsenite and DMA were assayed for induction of DNA damage in human alveolar epithelial type II (L-132) cells, DNA single-strand breaks were only observed with DMA at concentrations of 5-100 µM, but not with arsenite at concentrations up to 100 µM (Yamanaka et al., 1997 [63]).

Using the mouse lymphoma L5178Y/TK^{+}/$^{-}$ assay, Moore et al. (1997 [55]) found that the minimal concentrations required for chromosomal mutations were 1-2 µg/ml for sodium arsenite, 10-14 µg/ml for sodium arsenate, 2500-5000 µg/ml for MMA and 10000 µg/ml for DMA.

Table 2.1.12: Genotoxicity of organic arsenicals in vitro without metabolic activation

Substance	Test system	End point	Result	Reference
DMA	Human pulmonary epithelial (L-132) cells	DNA single-strand breaks	positive	Yamanaka et al., 1997 [63]
DMA	Mouse lymphoma cells (L5178Y/TK^{+}/$^{-}$ 3.7.2C)	chromosomal mutations	positive	Moore et al., 1997 [55]
MMA	Mouse lymphoma cells (L5178Y/TK^{+}/$^{-}$ 3.7.2C)	chromosomal mutations	positive	Moore et al., 1997 [55]
DMA	Chinese hamster V79 cells	chromosomal aberrations	positive	Ueda et al., 1997 [65]
DMA	Chinese hamster V79 cells	Tetraploids and mitotic arrest	positive	Eguchi et al., 1997 [66]
MMA	Chinese hamster V79 cells	Tetraploids and mitotic arrest	positive	Eguchi et al., 1997 [66]

Cancer Effects

There is a noticeable absence of positive two-year carcinogenicity studies in animals for either the inhalation or oral route of exposure. However, in a recent study, C57BL/6J mice of very low incidence of spontaneous tumors were exposed to arsenic in drinking water (2 µg/d, corresponding to 67 µg/kg body weight, similar to people drinking 8 l/d of water containing 500 µg/l As in, e.g., Bangladesh). The highest tumor incidences were found in the lungs (17.5 %) and in the intestinal tract (14.4 %) (IPCS, 1999 [67]).

On the other hand, there is sufficient evidence that inorganic arsenic compounds are skin and lung carcinogens in humans. Several studies have shown that exposure to inorganic compounds can increase the risk of lung cancer in smelter workers, persons in the production of arsenic containing pesticides and metal ore miners. The data often indicate a positive dose-response relationship. Both trivalent and pentavalent arsenic compounds have occurred in these exposure situations. At present the possibility cannot be ruled out that any form of inorganic arsenic may be carcinogenic. Study results on the interaction between arsenic and smoking showed this interaction to be intermediate between additive and multiplicative and to appear less pronounced among heavy smokers (WHO 1997 [2]).

Exposure to airborne arsenic increases not only the risk of cancer in the lungs, but is also associated with an increased risk of cancer in other organs. Enterline et al. (1995 [34]) found an overall increase in incidence of cancer of the large intestine in copper smelter workers which did not appear to be dose-related. There was a dose-related increase in bone cancer but there were very few cases and these cancers could have been metastases. Kidney cancer showed a dose-related increase but was not significantly increased overall. Lagerkvist and Zetterlund (1994 [30]) found an increase in the risk of colon cancer among workers in Swedish copper smelters. Wingren and Axelson (1993 [68]) examined cancer risks in relation to occupational exposure to complex mixtures of trace elements in the art glass industry in south-east Sweden. For exposure to arsenic, results showed a dose-related association among glass workers between stomach cancer and colon cancer, although results may have been confounded by other metals.

Significantly elevated standard mortality ratios for cancer of the bladder, lung, liver, kidney, skin and colon were found in the population living in an area of Taiwan where arsenic contamination of water supply was endemic (Bates et al., 1992 [69]; Tseng, 1977 [70], WHO 1987 [1]).

In general, however, lung cancer is considered to be the critical effect following exposure to arsenic via inhalation.

Pinto et al. (1977 [71]) reported a relative risk of about 3 for the workers exposed at the Tacoma smelter (Washington) at an estimated average air concentration of 50 $\mu g/m^3$ for an average exposure duration of more than 25 years. The lifetime risk of lung cancer was calculated to be 7.5×10^{-3} per µg As /m^3.

Enterline and Marsh (1982 [72]) and Enterline et al. (1987 [73]) presented updated reports on the Tacoma cohort. Based on the first paper, the resulting unit risk of 7.2×10^{-3} per µg As /m^3 was very close to the earlier estimate. In 1987, however, the authors used revised exposure estimates based on new relations between arsenic in the air and in urine samples. These new estimates considerably increased the upper end of exposure estimates and lead to a clearly lower unit risk (1.28×10^{-3} per µg As /m^3) if compared to the previous estimate. Another update based on 10 more years of follow-up yielded higher lung cancer mortality rates (Enterline et al., 1995 [34]). Mortality rates in the subgroup with less than 20 years after first exposure to arsenic and in workers with more than 20 years were very similar, suggesting a rather short latency period. As a reason for this short latency period, the authors discuss that this might be due to exposure via inhalation or to a particular susceptibility of the lung. However, confounding, i.e., increased mortality after relatively short latency periods (and low cumulative exposure) not causally linked with exposure to arsenic but to some other kind of exposure, might also be a reasonable explanation.

Lee-Feldstein (1983 [36]) used the data on the workers of the Anaconda smelter (Montana). The expected number of cancer deaths was calculated on an age-adjusted basis. Exposure to airborne arsenic levels was estimated to average 11.27, 0.58 and 0.27 mg/m^3 in the heavy, medium and light exposure areas, respectively. Based on data that respirators were used with a varying degree of constancy in the areas of highest exposure, and assuming that the use of respirators would roughly have reduced the exposure by a factor of 10, the high-exposure concentration was reduced to 1.127 mg/m^3. The average duration of exposure was estimated to be 15 years for all three groups. From the lower, medium and higher estimation of time-weighted average exposures, the average lifetime daily exposures were derived by multiplication with 0.047 (considering working hours, working days, working years: 8/24x240/365x15/70) as 12.6, 27.2 and 52.9 µg/m^3, respectively. The estimated relative risks were 2.3, 4.5 and 5.1 for the light, medium and heavy exposure groups, respectively. The unit risk estimates were 3.9 x 10^{-3}, 5.1 x 10^{-3} and 3.1 x 10^{-3}, respectively, with a geometric mean of 4 x 10^{-3}. An additional publication on this cohort with updated exposure estimates has been provided in 1986 (Lee-Feldstein, 1986 [74]).

A cohort of 3,916 male workers employed in the Rönnskär smelter in Sweden for at least 3 months from 1928 through 1967 was followed by Järup et al. (1989 [32]) through 1981. Arsenic levels in the air of all workplaces within the smelter were estimated for three different time periods. Lung cancer mortality was found to be related to cumulative arsenic exposure. However, this relation was mainly seen to the estimated average intensity of exposure to arsenic but not to the duration of exposure. In the lower dose categories (< 15 mg/m^3 x years), there was no apparent dose-response relationship, and there was a significantly increased relative risk of dying from lung cancer already in the low intensity/short exposure time category (Järup et al., 1989 [32]).

Hertz-Picciotto and Smith (1993 [75]) reviewed studies on the dose-response curve for arsenic exposure and lung cancer. They concluded that all of the studies with quantitative data are consistent with a supralinear dose-response relationship, and that the much steeper slopes at low as opposed to high doses in these studies suggest that the use of linear models applied to occupational epidemiologic data may, in some situations, result in an underestimation of the true risks at lower exposures. On the other hand, the authors discuss confounding from smoking and measurement errors especially at high concentrations as possible reasons for a supralinear shape of the dose-response curve. However, the relevance of these considerations with respect to the shape of the dose-response curve is difficult to evaluate. Keeping in mind that the flattening of the dose-response curve mainly appears at cumulative exposures in the range of at least 5 mg/m^3 x years or even far higher and that exposures of the general population are lower by roughly three orders of magnitude, this possibly supralinear curve may be the upper part of a sigmoidal curve with sublinearity in the relevant range.

Viren and Silvers (1994 [76]) discussed the updated 1987 exposure estimates for the Tacoma smelter workers and the Swedish results. With respect to the Rönnskär cohort, the authors point to a statistically significant background risk not accounted for by arsenic exposure related to a greater frequency of smokers in the cohort than in the local reference population (also mentioned by Järup et al., 1989 [32]). The authors concluded that the old unit risk estimates should be revised downward.

In a first step in 1994, WHO considered the data on workers exposed at the Rönnskär smelter. For three groups of workers exposed to average airborne arsenic levels of 0.05, 0.15 and 0.30 mg/m^3, relative risks of 2.01, 3.53 and 4.8, respectively, were determined, and unit risks of 3.77 x 10^{-3}, 3.1 x 10^{-3} and 2.4 x 10^{-3} were calculated. Together with risk estimates based on the Tacoma and Anaconda cohorts, WHO estimated a lifetime unit risk of 3 x 10^{-3} (WHO, 1994a [77]).

During the further course of the update and revision process of the WHO Air Quality Guidelines for Europe, WHO largely adopted the results of Viren and Silvers (1994 [76]) and their pooled estimate based on updated Tacoma estimates (1.28 x 10^{-3}), Montana estimates (2.56 x 10^{-3}) and Rönnskär estimates (0.89 x 10^{-3}) and thus derived a lifetime unit risk of 1.5 x 10^{-3} (WHO, 1997 [2]).

Some investigations of populations living near copper smelters and other point sources of arsenic emission to the air have revealed moderate increases in lung cancer mortality, while other studies have failed to detect an effect in such situations.

In a study of lung cancer mortality of the general population 1950-69, average mortality rates were significantly increased in US counties with copper, lead, or zinc smelting and refining industries (+17 % for males, +15 % for females), but not in counties where other non-ferrous ores are processed. The authors (Blot and Fraumeni, 1975 [78]) conclude that their findings suggest the influence of community air pollution from industrial emissions containing inorganic arsenic. However, community-wide levels of airborne arsenic concentrations during 1950-69 or earlier were not available. A study of cancer mortality in the population residing near a chemical plant which produced insecticides, herbicides, and other arsenic products showed an increase in lung cancer. However, there are no quantitative estimates of inhalation exposure to arsenic, the pattern of lung cancer excess is not in agreement with the wind directions in that area, and the increase in lung cancer was restricted to men (Matanoski et al., 1981 [79]).

In the vicinity of the Rönnskär smelter, a cohort study and a case-referent study were carried out. The concentrations of arsenic and lead were mostly below 0.5 µg/m^3, but during certain weeks the levels exceeded 1 µg/m^3. In the cohort study, a significant increase in lung cancer mortality was seen in men living near the smelter in comparison to a selected control population, but not in comparison to the national lung cancer rates. After exclusion of occupationally exposed men, this increase was no longer significant. In women, no increase was seen (Pershagen et al., 1977 [80]). The case-referent study showed an increased risk for lung cancer in men (smelter employees and miners excluded) associated with residence in an area close to the smelter (Pershagen, 1985 [81]). This increase was confirmed for the subgroup with year of death during the period 1961-1979 (RR = 1.7, 95 % C.I. 1.0-2.9), but among those who died later (1980-1990), the RR was reduced to 1.1 (95 % C.I. 0.6-2.2) and no longer of statistical significance (Pershagen and Nyberg, 1996 [82]).

In general, these non-occupational studies lack of reliable exposure data. Therefore, they usually are neither adequate to confirm nor to disprove relationships found between (occupational) exposure to airborne arsenic and health effects, especially lung cancer.

This holds true, too, for a study by Buchet and Lison (1998 [83]) who investigated the causes of mortality (including lung cancer) in groups of the Belgian population living around zinc smelters. The authors conclude that a low to moderate level of environmental exposure to inorganic arsenic (20-50 µg As/l of drinking water; 0.3 µg As/m^3 of air) does not increase lung cancer mortality. However, the relevance of this study for the derivation of ambient air quality limit values is limited because the characterisation of the arsenic exposure via ambient air is unclear. The reported mean concentration of 0.3 µg As /m^3 for a distance between 2 and 10 km away from the emitting smelters is difficult to trace. Therefore, data on exposure via inhalation used in this study must be considered insufficient.

The classifications of arsenic and arsenic compounds by several organizations are given in table 2.1.13.

Table 2.1.13: Classification* of arsenic and arsenic compounds with respect to carcinogenicity

Arsenic species	Organization			
	IARC	EC	US EPA	NTP-BSC
Arsenic and arsenic compounds	1		A	
Arsenic trioxide		1		
Arsenic pentoxide		1		
Arsenates		1		
Arsenites		1		

* Carcinogen Classifications:

IARC:

Group 1 - The agent (mixture) is carcinogenic to humans.
Group 2A - The agent (mixture) is probably carcinogenic to humans.
[Defined as limited evidence in humans and sufficient evidence in animals.]
Group 2B - The agent (mixture) is possibly carcinogenic to humans.
[Defined as limited evidence in humans and insufficient evidence in animals.]
Group 3 - The agent (mixture, exposure circumstance) is not classifiable as to its carcinogenicity to humans.
Group 4 - The agent (mixture) is probably not carcinogenic to humans.
[Defined as when evidence exists suggesting a lack of carcinogenicity in humans and animals.]

EC:

1 - Substances known to be carcinogenic to man
2 - Substances which should be regarded as if they are carcinogenic to man
3 - Substances which cause concern for man owing to possible carcinogenic effects, but in respect of which the available information is not adequate for making a satisfactory assessment

U.S. EPA:

A - Confirmed Human carcinogen
B1 - Probable Human Carcinogen with Limited Human Evidence
B2 - Probable Human Carcinogen with Sufficient Evidence in Animals and Inadequate or No Evidence in Humans
C - Possible Human Carcinogen

NTP-BSC (National Toxicology Program Board of Scientific Counselors):

Known to be human carcinogen
Reasonably anticipated to be a human carcinogen

2.1.2.4 Human Biomonitoring

After exposure to inorganic arsenic, the only significant arsenic species excreted in urine are inorganic arsenic, MMA and DMA. The determination of the three species is the method of choice for the biological monitoring of workers exposed to inorganic arsenicals as this measurement is not influenced by the presence of organoarsenic compounds of dietary origin, especially from seafood. Significant (log scales) correlation was found between airborne time-weighted average exposure concentrations of arsenic (ranging from 6 to 502 µg As /m^3) and the inorganic arsenic metabolites in urine collected immediately after shift, or just before the next shift. For a concentration of 50 µg As /m^3, the mean concentration of the sum of arsenic and the arsenic metabolites in a postshift urine sample amounted to about 55 µg As /g creatinine (WHO, 1997 [2]).

Arsine generation followed by atomic absorption spectrometry is the method of choice for biological monitoring of exposure to inorganic arsenic because it allows the simultaneous determination of inorganic arsenic, MMA and DMA eliminating the possible influence of arsenobetaine contained in food. Recent data suggest, however, that a possible direct release of DMA from the organoarsenicals during digestion may occur. Therefore, it still seems justified to instruct the workers to refrain from eating seafood during at least 48 hours before urine is collected for assessing exposure to inorganic arsenic (WHO, 1997 [2]).

In Europe, the total As concentration in urine of non-exposed individuals is about 10-20 µg/l (Ritsema et al., 1998 [84]). Another study reported 5.1-11.3 nmol total As /mmol creatinine, i.e., 3.4-7.5 µg/g creatinine (Jensen and Olsen, 1995 [39]).

Results of the German Environmental Survey (Schulz, 1998 [85]; Seiwert et al., 1999 [86]) concerning urine concentrations of arsenic in the German population between 1990-1992 are presented in table 2.1.14.

Table 2.1.14: Arsenic concentrations in urine in the German population in 1990-1992 (Schulz, 1998 [85]; Seiwert et al., 1999 [86])

	Geometric mean	Arithmetic mean	10th Percentile	50th Percentile	90th Percentile
Adults (age 25-69, n = 4001)					
µg As /l urine	6.29	10.52	1.8	7.0	19.8
µg As /g creatinine	4.60	7.64	1.4	4.9	15.3
Children (age 6-14, n = 730)					
µg As /l urine	6.01	9.50	1.6	7.0	19.2
µg As /g creatinine	4.28	7.08	1.1	4.9	14.1

2.2 Cadmium

2.2.1 Sources And Occurrence In The Environment

2.2.1.1 Air

Volcanic activity is a major natural source of cadmium; in the plume of Mount Etna, Sicily, concentrations of about 90 ng/m³ have been found. Anthropogenic emissions are mainly due to non-ferrous metal production (copper, zink, cadmium), iron and steel production, incineration of refuse (cadmium pigments and stabilizers in plastics, nickel-cadmium batteries), and combustion of coal and oil (IPCS/WHO, 1992 [87]). For more details, see Chapter 1.3.

2.2.1.2 Indoor Dust

In a study of German households, the amount of cadmium in dust deposited on indoor surfaces and the concentration of cadmium in dust samples taken from vacuum cleaner bags were measured (Krause et al., 1991 [4]); the results are given in table 2.2.1.

Table 2.2.1: Cadmium in household dust (Krause et al., 1991 [4])

	Cadmium dust deposition	Cadmium concentration in dust
n	2184	2631
10th percentile	7 ng / (m^2•d)	0.34 mg / kg
50th percentile	16 ng / (m^2•d)	1.72 mg / kg
95th percentile	50 ng / (m^2•d)	6.68 mg / kg
Arithmetic mean	21 ng / (m^2•d)	2.51 mg / kg
Geometric mean	16 ng / (m^2•d)	1.51 mg / kg

Most of the cadmium in the air is bound to small-size particulate matter (≤ 1 µm). Cadmium is emitted to the atmosphere as elemental cadmium and/or cadmium oxide and - from some sources - as sulfide or chloride. Part of the emissions precipitate in the direct vicinity of the sources, but particle-bound cadmium is also subject to medium or long-range transport.

2.2.1.3 Water

Measurements of dissolved cadmium in surface waters of the open oceans yielded values below 5 ng/l. Cadmium concentrations in non-polluted surface water range 0.01 - 0.04 µg/l depending on geochemical conditions (IPCS/WHO, 1992 [87]).

2.2.1.4 Soil

Cadmium is widely distributed in the earth crust. It is a relatively rare element (0.1-0.2 mg/kg). Higher concentrations are found in association with zink, lead and copper ores. Sedimentary rocks and marine phosphates contain about 15 mg/kg. Depending on the origin, the cadmium content of phosphate fertilizers varies between 2 and about 200 mg/kg. In soil of agricultural or horticultural use, cadmium concentrations range 0.2-1 mg/kg in rural and 0.5-1.5 mg/kg in urban areas (IPCS/WHO, 1992 [87]).

2.2.2 Human Exposure, Uptake And Effects

2.2.2.1 Pathways Of Human Exposure

Inhalation exposure

In remote areas, annual mean cadmium concentrations in air are usually around 0.1 ng/m³, in rural areas 0.1-0.4 ng/m³, in urban areas 0.2-2.5 ng/m³, and in industrial areas 2-20 ng/m³ with a clear decreasing trend during the last two decades (cf. Chapter 1.4).

In the following table 2.2.2, an absorbed daily dose of cadmium from inhalation exposure is calculated. In addition, a “low” and a “high” estimate are given. The latter values are not intended to represent the extremes of the possible range of exposure, instead, they should represent values to which a significant proportion of the population is probably exposed. Concentrations are chosen in order to reflect approximately the situation in rural (“low”), urban (“average”) and industrial areas (“high”), respectively.

Table 2.2.2: Calculation of the absorbed daily dose of cadmium. Source: Air

Exposure [1)]	Concentration in air (ng/m^3)	Absorption (%)	Other assumptions	Absorbed dose (ng Cd /(kg•d))
Adults				
low	0.5	50	body weight: 60 kg respiratory volume: 20 m^3/d	0.083
average	1.5	50		0.25
high	15	50		2.5
Children				
low	0.5	50	body weight: 15 kg respiratory volume: 8 m^3/d	0.133
average	1.5	50		0.4
high	15	50		4.0

1) Exposures are classified in order to reflect approximately the concentrations in rural, urban and industrial areas, respectively

For adults, a reference body weight of 60 kg and a reference respiratory volume of 20 m^3/d according to U.S. EPA recommendations are assumed (EPA, 1988 [9]). For children, a reference body weight of 15 kg corresponding to an age of about 3 years and a respiratory volume of 8 m^3/d are assumed (for more details, see Chapter 2.1.2.1 Arsenic). In addition, it is assumed that indoor and outdoor air concentrations are identical.

Deposition in the lungs varies between 10 and 50 %, depending on particle size. Pulmonary absorption varies with the chemical nature of the particles. An upper estimate of 100 % is a reasonable worst case assumption. The total absorption includes deposition rate and absorption rate of deposited amount. An average value of 50 % is used, according to WHO (1997 [88]).

Cigarette smoking

Tobacco plants can accumulate cadmium. This results in relatively high cadmium concentrations in the leaves and consequently in cigarettes. Therefore, cigarette smoke is a very important cadmium source. If one cigarette contains 1-2 µg cadmium with 10 % being inhaled and 50 % of the inhaled cadmium absorbed, smoking 20 cigarettes per day results in an increase of the absorbed amount of cadmium by 1-2 µg/d (Ewers and Wilhelm, 1995 [89]).

In the following table 2.2.3, an absorbed daily dose of cadmium is calculated. In addition, a "low" and a "high" estimate are given. The latter values are not intended to represent the extremes of the possible range of exposure, instead, they should represent values to which a significant proportion of the population is probably exposed.

Table 2.2.3: Calculation of the absorbed daily dose of cadmium. Source: Cigarette smoke

Exposure	µg Cadmium/ cigarette	Absorption (%)	Other assumptions	Absorbed dose (ng Cd /(kg•d))
Adults				
low	0.5	5	body weight: 60 kg 20 cigarettes/d	8.3
average	1.5	5		25
high	2.5	5		41.7

Oral exposure (Water and Food)

In general, drinking water contains cadmium in concentrations between 0.01 and 1 µg/l. In Germany, cadmium concentrations in water provided by water works usually are less than 0.1 µg/l. Due to some uptake from the water pipes (galvanized steel pipes), the concentration increases to about 0.1 µg/l at the water-tap. In the German Environmental Survey, more than 98 % of the samples provided by the water works had concentrations below 1 µg/l. However, at the water-tap, maximum values exceeded 10 µg/l (Becker et al., 1997 [90]).

The EC limit value for cadmium in drinking water (Directive EC 98/83) is 5 µg/l.

Meat, fish, and fruit generally contain cadmium in concentrations around 5-10 µg/kg fresh weight. Vegetables usually contain cadmium in higher concentrations. A reasonable estimate is 25 µg/kg fresh weight in cereals and root vegetables. Especially celeriac, spinach and green kale show a high uptake of cadmium from soil. In regions with high cadmium levels in soil, persons preferably consuming locally grown vegetables may considerably increase their cadmium exposure. Some kinds of wild fungi also contain cadmium in high concentrations (IPCS/WHO, 1992 [87]).

Among animal products, kidneys of cattle and pigs contain the highest amounts of cadmium (on average 0.1-0.5 mg/kg fresh weight, maxima up to 5 mg/kg). In liver, cadmium contents usually are found below 0.1 mg/kg fresh weight. Milk and dairy products, meat and eggs contain cadmium in concentrations below 0.05 mg/kg fresh weight. The cadmium burden in animal products mainly originates from the uptake of contaminated grass or other food and, in part, from ingestion of contaminated soil (IPCS/WHO, 1992 [87]).

The average daily intake of cadmium via food in European countries and North America is 15-25 µg, but there may be large variations depending on age and dietary habits (WHO, 1997 [88]). Duplicate food samples in Germany suggest a lower intake of about 10 µg/d and maximal values around 100 µg/d (Schulz, 1998 [85]).

Intestinal absorption of cadmium from drinking water and food is about 5 %. In case of iron, calcium, or protein deficiency, absorption may increase (Ewers and Wilhelm, 1995 [89]).

In the following tables 2.2.4 and 2.2.5, an absorbed daily dose of cadmium is calculated. In addition, a “low” and a “high” estimate are given. The latter values are not intended to represent the extremes of the possible range of exposure, instead, they should represent values to which a significant proportion of the population is probably exposed.

For adults, a reference body weight of 60 kg and a reference value of 2 l/day for water consumption according to U.S. EPA recommendations (EPA, 1988 [9]) are assumed.

For children, a reference body weight of 15 kg is assumed. Therefore, instead of the reference drinking water rate of 1 l/day for a 10-kg child used by EPA‘s Office of Drinking Water (EPA, 1988 [9]), a daily water consumption of 1.5 l is used. This does not change the absorbed dose per kg and day. The amount of food is assumed to be 50 % of that of an adult.

Table 2.2.4: Calculation of the absorbed daily dose of cadmium. Source: Drinking water

Exposure [1)]	Concentration in water (µg/l)	Absorption (%)	Other assumptions	Absorbed dose (ng Cd /(kg•d))
Adults				
low	0.02	5	body weight: 60 kg	0.033
average	0.1	5	consumption of drinking water:	0.167
high	5	5	2 l/d	8.33
Children				
low	0.02	5	body weight: 15 kg	0.1
average	0.1	5	consumption of drinking water:	0.5
high	5	5	1.5 l/d	25

1) For the “high” exposure estimate, the EC drinking water limit value of 5 µg/l is used

Table 2.2.5: Calculation of the absorbed daily dose of cadmium. Source: Food

Exposure	Amount ingested (µg Cd / d)	Absorption (%)	Other assumptions	Absorbed dose (ng Cd / (kg•d))
Adults				
low	5	5	body weight:	4.17
average	10	5	60 kg	8.33
high	50	5		41.6
Children				
low	2.5	5	body weight:	8.33
average	5	5	15 kg	16.7
high	25	5		83.2

Soil and Dust

Especially in small children, uptake of house dust or soil/sand of playing grounds may also be a source of cadmium exposure.

In the following table 2.2.6, an average absorbed daily dose of cadmium is calculated. In addition, a “low” and a “high” estimate are given. The latter values are not intended to represent the extremes of the possible range of exposure, instead, they should represent values to which a significant proportion of the population is probably exposed.

For adults, a reference body weight of 60 kg according to U.S. EPA recommendations (EPA, 1988 [9]) is assumed. For children, a reference body weight of 15 kg is assumed.

Table 2.2.6: Calculation of the absorbed daily dose of cadmium. Source: Soil and dust

Exposure	Concentration in soil/dust (µg Cd/g)	Absorption (%)	Other assumptions	Absorbed dose (ng Cd /(kg•d))
Adults				
low	0.3	5	body weight: 60 kg average soil/dust intake: 0.1 g/d	0.025
average	2	5		0.167
high	10	5		0.83
Children				
low	0.3	5	body weight: 15 kg average soil/dust intake: 0.5 g/d	0.5
average	2	5		3.33
high	10	5		16.7

For the average soil and dust intake of a 15-kg child, a value of 0.5 g/d is used. This value represents the 95th percentile for long-term soil intake of children up to 6 years old and includes pica activity (Ruck, 1990 [15]). For adults, the most often reported value for soil and dust intake is 0.1 g/d (Ruck, 1990 [15]).

For the absorption rate of cadmium from soil and dust after oral uptake, a value of 5 % is assumed, corresponding to the intestinal absorption of cadmium from food and drinking water.

Estimation of the total absorbed cadmium dose

In the following table 2.2.7, the “low”, “average” and “high” estimates for individual exposure sources are combined from tables 2.2.2-6. The simple addition of “low” and “high” values, respectively, may result in rather extreme total values, since the variabilities for each source of cadmium are largely independent of each other, i.e., a high cadmium dose through smoking is not necessarily connected with a high dose of cadmium through the diet or a low cadmium concentration in drinking water need not be connected with a low cadmium concentration in air.

Table 2.2.7: Estimation of the absorbed daily dose of cadmium, in ng Cd / (kg•d)

	Adults			Children		
Source	low (% of sum)	average (% of sum)	high (% of sum)	low (% of sum)	average (% of sum)	high (% of sum)
Air	0.083 (<1)	0.25 (<1)	2.5 (3)	0.133 (1)	0.4 (2)	4.0 (3)
Cigarette smoking	8.3 (66)	25 (74)	41.7 (44)	-	-	-
Drinking water	0.033 (<1)	0.167 (<1)	8.33 (9)	0.1 (1)	0.5 (2)	25.0 (19)
Food	4.17 (33)	8.33 (24)	41,7 (44)	8.33 (92)	16.7 (80)	83.3 (65)
Soil and Dust	0.025 (<1)	0.167 (<1)	0.83 (<1)	0.5 (6)	3.33 (16)	16.7 (13)
Sum	13	34	95	9	21	129

An average absorbed daily dose of cadmium of 34 ng / (kg•d) for adults including the increased cadmium uptake by cigarette smoking (9 ng / (kg•d) for non-smokers), and 21 ng / (kg•d) for children is calculated. Under average circumstances, the oral uptake of cadmium via food and drinking water contributes the largest amount to the total dose. On average, cadmium uptake via ambient air contributes less than 3 % to the total absorbed cadmium dose. In smokers, however, inhalation of cigarette smoke results in an important contribution which can represent the dominant factor for the absorbed cadmium dose.

2.2.2.2 Kinetics And Metabolism

Lung deposition of cadmium compounds depends on particle size with higher deposition of smaller particles. Cadmium oxide is poorly soluble in water, but cadmium chloride as well as cadmium oxide are solubilized in the lung. Part of the cadmium containing particles are removed by mucociliary clearance and swallowed.

Absorption from the lungs is estimated to amount to 90 % in the case of cadmium oxide, whereas absorption of cadmium sulfide is much lower and is estimated to be about 10 % (Oberdörster, 1990 [91]).

Gastrointestinal absorption of cadmium is very low in mice, rats, and monkeys (0.5-3 %). In humans, the estimated range of absorption is 3-8 %. Therefore, 5 % seems to be a reasonable estimate for gastrointestinal absorption (Ewers and Wilhelm, 1995 [89]). However, an increased gastrointestinal uptake of ingested cadmium due to low iron stores - more often seen in women than in men - has been described (Järup et al., 1988 [92]).

Absorbed cadmium is transported to the liver where it is bound to metallothionein. Bound to metallothionein, it is transported to the kidney where it is filtered and reabsorbed. In the kidney, cadmium is set free, inducing local synthesis of metallothionein. If renal synthesis of metallothionein cannot provide amounts of metallothionein sufficient to bind all cadmium, remaining free cadmium can induce renal damage (IPCS/WHO, 1992 [87]; Ewers and Wilhelm, 1995 [89]; WHO 1997 [88]).

Cadmium excretion in urine of cadmium-exposed workers increases proportionally to the body burden of cadmium (Roels et al., 1981 [93]). In case of renal damage, however, urinary excretion is further increased, but without renal damage, cadmium in urine is the best indicator of renal cadmium burden and cumulative exposure to cadmium. On the other hand, blood cadmium is a better indicator of current exposure (Lauwerys et al., 1979 [94]).

Estimates of biological half-life of cadmium in humans range from 5-10 years in the liver to 10-30 or even up to 100 years in the kidney. Such a long half-life means that a steady state will - if ever - be reached late in human´s life. For toxicokinetic models, 20 years are a reasonable estimate (Oberdörster, 1990 [91]; EPA, 1999a [95]). However, only limited data exist for testing these models.

2.2.2.3 Health Effects Of Cadmium

Essentiality

There are no reasons to suppose cadmium to be an essential trace element in humans. On the contrary, cadmium seems to mimic essential elements like calcium. This results in a competitive replacement at some receptors and a lack of the physiologically necessary substances. This malnutrition leads to adverse effects on, e.g,. bone stability. Adverse effects of cadmium seem to be associated with the metal ion and not with other components of salts or complexes (EPA, 1999a [95]).

Non-cancer Effects

Acute intoxications are rare events which occur only at concentrations far higher than those found outside occupational environments. Exposure to 5 mg/m³ during 8 hours can be lethal. Exposure to freshly generated cadmium fume (200-500 µg/m³) may cause symptoms similar to those of metal fume fever usually followed by a complete recovery within a few days. Oral intoxication leads to nausea, vomiting, and headache. Acute intoxications caused by cadmium-polluted food have not been reported (IPCS/WHO, 1992 [87]).

Renal effects

The kidney is the critical organ with respect to long-term occupational or environmental exposure to cadmium. Cadmium-induced nephropathy is characterized by an increased excretion of low molecular weight proteins, amino acids and other low molecular components in urine due to reduced re-absorption in the proximal renal tubules. In addition, higher molecular weight proteins may be found in urine, too, probably due to an increase in permeability of the glomerular capillaries which results in a filtration of proteins normally retained.

The sensitivity to adverse influences is different in specific sites of the nephron. Thus, there is a graduate reaction of the kidney to different cadmium concentrations. In addition, individual sensitivity varies, too. Therefore, the individual critical levels of cadmium concentration in the kidney cortex leading to increased excretion of specific markers for renal damage are expected to show considerable variation in the general population.

With respect to health relevance, however, there is no sharp line between adverse effects, effects of unknown relevance, and changes supposed to be without health relevance. This holds true for the qualitative classification of these renal effects as well as for their frequency in the population studied because all these changes in renal excretion are not cadmium-specific, but may be caused by factors other than cadmium exposure as well.

Renal effects are usually described in relation to cadmium excretion in urine which is taken as an indicator of renal cadmium burden (Roels et al., 1981 [93]). Therefore, in a first step, levels of cadmium in urine are estimated which are associated with renal effects. In a second step, the contribution to renal cadmium burden of gastrointestinal uptake and absorption as well as inhalation can be considered.

Knowledge on cadmium induced nephropathy is based on occupational studies and on studies in the general population residing in cadmium polluted areas, e.g,. in Japan, Belgium, and Germany.

Lauwerys et al. (1974, [96]) compared 3 groups of cadmium-exposed workers with matched control groups. Exposure estimates were available not only related to total cadmium concentration but also related to the respirable fraction (given as PM_5). In a group of 31 women in an electronic workshop (mean exposure time 4.1 years, total and respirable airborne cadmium dust concentration 31 µg/m³ and 1.4 µg/m³, respectively), Cd concentration in urine was increased (5 µg/g creatinine vs. 2 µg/g creatinine in the control group). No renal or pulmonary changes were seen. A group of workers in a nickel cadmium storage battery factory was exposed to cadmium concentrations of 88 µg/m³ (based on PM_5) and 134 µg/m³ (based on TSP). In a group of 22 men (smokers) exposed in a cadmium producing plant for 28 years on average to total and respirable airborne cadmium dust concentrations of 66 µg/m³ and 21 µg/m³, respectively, Cd in urine amounted to 31 µg/g creatinine. Abnormal urinary protein electrophoresis was found in 15 of these 22 men, and lung function values (FVC, FEV_1, PEFR) were found to be significantly lower than in the smoking control group. The authors conclude that this study demonstrates that the kidney is more sensitive to Cd than the lung. For respirable cadmium, this study indicates a LOAEL of 21 µg/m³ with 68 % of the workers showing increased proteinuria. However, cumulative exposure may have been less than 585 µg/m³•years (= 28 years at 21 µg/m³) if respiratory protective devices have been used.

Kjellström et al. (1977 [97]) found excretion of $ß_2$-microglobulin being increased in workers after 6-12 years of occupation in a Swedish battery factory. The geometric mean of workplace cadmium concentrations was 53 µg/m³ based on personal sampling, whereas stationary sampling suggested 28 µg/m³. Personal protection masks were not used uniformly or continuously. For this subgroup of workers, the estimated cumulative exposure to cadmium amounts to 168-636 µg/m³•years provided that the measurements mentioned above can be extrapolated to the period under study and that 28 µg/m³ corresponds to a lower estimate of exposure concentration. However, if protection masks have be worn, the lower end of the cumulative exposure might have been less than 168 µg/m^3•years.

In an extension of the Kjellström study, $ß_2$-microglobulin was found increased (9.2 %) in the subgroup of workers with an estimated cumulative exposure to cadmium ranging 359-1710 µg/m^3•years. In the subgroup with the lowest cumulative exposure (<359 µg/m^3•years), increased $ß_2$-microglobulin was only seen in 1.1 % of the workers. A cut-off level of 500 µg/m^3•years correctly classified 90 % of the workers with tubular proteinuria (Järup et al., 1988 [92]).

Ellis et al. (1985 [98]) studied cadmium in liver and kidney and renal function in relation to cumulative cadmium inhalation exposure in 82 workers of a cadmium smelter. Liver cadmium values started to exceed the normal range when the cumulative exposure reached 80-100 µg/m^3•years. Using the logistic regression model derived from this study, a cumulative exposure of 100 µg/m^3•years would indicate approximately a 7 % probability of having renal dysfunction. At an exposure level of 400 µg/ m^3•years, the probability would increase to nearly 29 %.

WHO (1997 [88]) refers to a lowest estimate of the critical cumulative exposure to airborne cadmium of 100 µg/m^3•years as quoted by Thun et al. (1991 [99]). The data of Kjellström (Kjellström et al., 1977 [97]) and Ellis (Ellis et al., 1985 [98]) support this estimate. As indicated by the concentration data provided by Lauwerys et al. (1974 [96]), under workplace conditions the concentration of respirable cadmium may be significantly lower than the concentrations based on total cadmium measurements. This means that the “effective” cumulative dose might have been clearly lower than estimated, i.e., effects may be associated with lower cumulative doses.

Studies of workers exposed to cadmium at their workplaces suggest three levels of cadmium in urine above which the probability of alterations in parameters of kidney function is found to increase. The lowest of these levels is about 2 µg/g creatinine for biochemical alterations, at about 4-5 µg/g creatinine there are an onset of high molecular weight proteinuria and some signs of cytotoxicity, and around 10 µg/g creatinine tubular proteinuria may begin to develop (Lauwerys et al., 1993 [100]).

The largest epidemiological study on cadmium effects on humans is the Cadmibel Study carried out in Belgium 1985-1989 in areas contaminated by past emissions of cadmium from zink smelters. In the general population, the above-mentioned alterations in renal excretion can be seen at levels lower than those associated with renal effects in workers possibly due to the “healthy workers” effect or to larger sample sizes in epidemiological studies. Subclinical renal effects are likely to occur in the general population with a probability of 10 % (corresponding to a relative risk of 2) when urinary cadmium excretion exceeds 2-4 µg/24 h. An estimated 10 % of the Belgian population had a cadmium excretion higher than 2 µg/24 h (Buchet et al., 1990 [101], Lauwerys et al., 1993 [100]).

In Japan, renal effects (low molecular weight proteinuria) have been reported at CdU levels in the same range as those found in the Cadmibel Study (WHO, 1997 [88]; see, e.g., Nishijo et al., 1994 [102]; Ishizaki et al., 1989 [103]) and in a cadmium-nonpolluted area in Japan (Yamanaka et al., 1998 [104]).

Data from Belgium (Staessen, 1994 [105]) and Sweden, however, indicate that subtle effects (enzymuria) may occur in the general population at even lower urine Cd concentrations. A statistically significant correlation between urinary cadmium (0.1-3.2 µg/g creatinine) and the excretion of total NAG in urine with no evidence of a threshold was described (Järup et al., 1995 [106]).

The probability of increased excretion of markers of renal dysfunction like $ß_2$-microglobulin, N-acetyl-ß-glucosaminidase or retinol-binding protein seems to increase with higher urinary cadmium excretion without a threshold (Lauwerys et al., 1993 [100]).

Age has an influence on renal excretion of $ß_2$-microglobulin, too. In a study of Swedish battery workers, Järup et al. (1994 [107]) found a 10 % prevalence of tubular proteinuria at urinary cadmium levels of 1.5 µg/g creatinine in the older age group (cut-off point at 60 years of age), whereas this 10 % response level was found at 5.0 µg/g creatinine in the younger age group. The higher prevalence in older people might be explained by age-related renal changes resulting in an increased susceptibility to cadmium in the elderly.

In the early 1980s, the critical cadmium concentration in kidney cortex was estimated to be about 200 ppm. In later calculations, this estimate was considerably reduced. Buchet et al. (1990 [101]) calculated that a cadmium excretion in urine of 2 µg/24 h corresponds to 50 ppm cadmium in the renal cortex. This estimate is similar to results of a model by Oberdörster (1990 [91]) modified by U.S. EPA (1999a [95]) which predicts a renal cortex concentration of 41 ppm corresponding to a daily cadmium excretion of 2.7 µg Cd in urine.

The reversibility of cadmium-induced tubular proteinuria is still under discussion. During a ten-year period of follow-up, all the discovered cases of $ß_2$-microglobulinuria in workers were irreversible (Järup et al., 1988 [92]). The prognosis of changes at low levels is unclear (Lauwerys et al., 1993 [100]). In a 5-year follow up of Cd workers originally exposed to high levels of cadmium and subsequently removed from this high exposure, it was found that in those cases where - at the moment of removal from exposure - the increase in microproteins in the urine was limited, the micro-proteinuria was reversible. At higher levels of accumulated exposure, leading to a more severe degree of micro-proteinuria, the effects were, however, irreversible and predictive of an exacerbation of the age-related renal effects (Roels et al., 1997 [108]). A recent follow-up of the Cadmibel study showed a decrease in cadmium in blood and in urine as well as a decrease in the prevalence of higher than normal renal values (Hotz et al., 1999 [109]). The authors draw the conclusion that the results of their study indicate that the renal effects due to a cadmium body burden as found in this environmentally exposed population (in Belgium) are weak, stable, or even reversible after the introduction of measures to reduce exposure; and that tubular effects are not necessarily associated with a subsequent deterioration in glomerular function. In their view, these subclinical effects most likely represent non-adverse manifestations.

All in all, first renal effects may be expected at cadmium concentrations in urine lower than 10 µg/g creatinine, a level which was thought to be a safe level in the 1970s. Mainly based on the Cadmibel study, there is evidence of cadmium-induced renal damage already at cadmium concentrations in urine exceeding 2-3 µg/g creatinine (Buchet et al., 1990 [101]). According to Järup et al. (1998 [110]), early signs of renal effects are detected in large groups already at U-Cd levels in the range of 0.5-2 µg/g creatinine. However, with respect to health and long-term prognosis, for many of the “new” renal excretion parameters like, e.g., NAG and other low molecular weight proteins, the relevance of excretions higher than the respective reference values in the general population is still under discussion. The adversity of changes like increased $ß_2$-microglobulinuria as such may be questioned. However, in Japan, mortality was increased not only in persons with proteinuria, but also in those with increased $ß_2$-microglobulinuria (Nishijo et al., 1994 [102]). Therefore, these markers of renal dysfunction may be indicators of more severe changes.

Cardiovascular effects

Results from animal studies suggest cadmium to induce hypertension. There is no clear support from epidemiological studies of workers and of the general population for comparable changes to occur in humans (IPCS/WHO, 1992 [87]).

Effects on bones and calcium metabolism

The so-called “Itai-Itai disease” is a chronic osteomalacia, i.e., the stability of the bones is reduced, resulting in severe bone pain, fractures and malformations. The results of epidemiological and clinical investigations indicate an association with cadmium exposure, although the "Co-operative Research Committee on Itai-itai Disease" (1967) stated that “malnutrition (low protein, low calcium diets) and multiple pregnancies may also be involved” (IPCS/WHO, 1992 [87]). In a study of CadmiBel participants, a doubled urinary cadmium concentration was associated with a relative risk of bone fractures in women of 1.7 (95 % C.I. 1.16-2.57) and of height loss in men (RR = 1.6, C.I. 0.94-2.72) (Staessen et al., 1999 [111]).

Effects on the respiratory system

Workers exposed to high cadmium workplace concentrations (> 20 µg/m³ for > 20 years) suffered chronic respiratory effects (bronchitis, chronic obstructive pulmonary diseases (COPD), emphysema) (WHO, 1997 [88]). In the general population, non-cancer cadmium effects on the respiratory system are without known health relevance. In general, however, routine lung function measurements are not accepted as indicators sensitive enough to show small and early pulmonary effects.

Reproduction and development

Cadmium concentrations in the human placenta are about 10 times higher than in maternal blood, whereas cadmium concentrations in fetal blood are only half of those found in maternal blood. Therefore, with respect to cadmium, the placenta seems to provide some - but incomplete - protection of the fetus (Ewers and Wilhelm, 1995 [89]).

U.S. EPA describes reproductive and developmental studies and summarizes that when usual indicators for developmental toxicity of cadmium such as birth weight, various malformations and variations are examined in parallel with evaluation of neurodevelopmental effects, the latter are more sensitive. Both inhalation and oral studies show that cadmium may also be a developmental toxin, with effects such as decreased fetal weight occurring at higher doses than neurodevelopmental effects, and teratogenic effects occurring at levels concomitant with severe maternal toxicity (EPA, 1999a [95]).

Genotoxicity

Cadmium has been tested in genotoxicity assays with mixed results. At least in some tests, positive results including mutations and chromosomal aberrations have been observed in vitro, in mammalian and bacterial cells, and in vivo, in mice (reviewed in IARC, 1993 [112]).

An increase in chromosome aberrations was observed in peripheral blood lymphocytes from factory workers who were also exposed to zinc, copper, and silver alloys. Other studies of workers exposed to cadmium and in persons with high environmental exposure to cadmium reported small, and occasionally statistically significant, increases in chromosomal aberrations and sister chromatid exchanges or no effect. Most of these studies, however, did not control for exposure to other mutagenic agents (IARC, 1993 [112]).

Mutagenicity of cadmium compounds in bacteria was strongly influenced by the choice of buffers and culture medium (Pagano and Zeiger, 1992 [113]).

The genotoxic potential of cadmium chloride was evaluated in four different rodent cell lines. Increases in DNA damage were observed only at cadmium doses completely arresting cell growth. These cellular tests indicate that cadmium is not directly genotoxic (Misra et al., 1998 [114]).

EPA summarizes mutagenicity and genotoxicity results as equivocal mutagenicity and chromosomal aberration induction in in vivo and in vitro test systems, coupled with several plausible mechanisms by which mutagenicity might occur other than by direct DNA alkylation (EPA, 1999a [95]).

Carcinogenicity

Animal studies

In inhalation studies with cadmium chloride, cadmium sulfide/sulfate, cadmium sulfate or cadmium oxide fume and dust in rats and mice, malignant lung tumours were observed. With the same compounds, no increase in lung tumours was observed in hamsters. Malignant pulmonary tumours were also found in rats following intratracheal installation of cadmium chloride or cadmium sulfide. Administration of excess zinc by inhalation, parenteral or oral route has been shown to reduce the carcinogenic potential of cadmium compounds after exposure by inhalation. Also following other routes of administration (oral, intramuscular injection) cadmium compounds were carcinogenic in rats (IARC, 1993 [112].

Based on studies in male Wistar rats exposed to cadmium chloride (Takenaka et al., 1983 [115]), a unit risk of around 4×10^{-2} $(\mu g/m^3)^{-1}$ was calculated, which can be used for comparison with occupational data. However, since occupational data are available and since there are uncertainties in the dosimetric extrapolation from animals to humans, occupational studies provide a better basis for risk assessment (EPA, 1999a [95]).

Occupational studies

Studies in workers in several types of factories have been carried out, e.g., in several nickel-cadmium battery plants and copper-cadmium alloy plants, in a cadmium recovery plant in the

U.S. and in cadmium processing plants in the UK. Mainly based on a reported excess in lung cancer mortality in the latter studies, IARC has classified cadmium/cadmium compounds as Class 1 human carcinogen in 1993, having concluded that there was sufficient evidence for cadmium being carcinogenic to humans and animals. U.S. EPA has classified cadmium and cadmium compounds as probable human carcinogen by inhalation exposure (Classification: B1; limited evidence from epidemiologic studies by the inhalation route and sufficient evidence of carcinogenesis in animals by the inhalation route).

In the U.S., the National Toxicology Program Board of Scientific Councelors Report on Carcinogens Subcommittee recommended to upgrade cadmium and cadmium compounds to “known to be human carcinogens” [116]. This upgrade is still pending, but there is indication that in the 9th Edition of the “Report on Carcinogens” scheduled for publication in 2000, cadmium and cadmium compounds will be included.

Retrospective mortality studies of workers were carried out in a plant that operated in the U.S. as a lead smelter from 1896 to 1919, then as an arsenic smelter from 1920 to 1925, and finally as a cadmium recovery plant from 1926 onwards (NIOSH study) (Thun et al., 1985 [117], Stayner et al., 1992 [118], Sorahan and Lancashire, 1997 [119]).

Based on the NIOSH study as assessed by Thun et al. (1985 [117]), U.S. EPA derived a unit risk estimate of 1.8×10^{-3} $(\mu g/m^3)^{-1}$. In this risk estimate, the calculated SMR (Standard Mortality Ratio) was based on the U.S. population as a reference.

Results published in 1992 refer to a study population of white male workers who were employed for at least 6 months between 1940 and 1969, and who were first employed at the facility on or after January 1, 1926. An excess in mortality from lung cancer was observed for the entire cohort (SMR = 149, 95 % confidence interval (CI) 95-222). Lung cancer mortality was greatest among non-Hispanic workers (SMR = 211, CI 131-323), among workers in the highest cadmium exposure group (SMR = 272, CI 123-513), and among workers with 20 or more years since their first exposure (SMR = 161, CI 100-248). SMRs were calculated based on comparisons within the cohort, i.e., avoiding a possible “healthy worker effect” and reducing the potential influence of confounding by cigarette smoking (Stayner et al., 1992 [118]).

U.S. EPA now proposes to base lung cancer risk estimates on the NIOSH cadmium cohort (as described by Stayner et al., 1992 [118]). The maximum likelihood estimate (MLE) lung cancer risk at 200 $\mu g/m^3$ of 112.1/1000 (upper bound 177.9/1000) was derived by OSHA (Occupational Safety and Health Administration). The corresponding risk at 100 $\mu g/m^3$ was 58.3/1000 (upper bound 95/1000). Using a Poisson Regression Model, the 95 % upper confidence limit at 1 $\mu g/m^3$ was 1.0/1000. These estimates are derived under occupational exposure scenarios. Risk under continuous exposure conditions was extrapolated by using a correction factor of 4.36 for 5 days a week, 45 of 70 years of life, and 10 versus 20 m^3 breathing volume per day. This leads to a unit risk of 4.2×10^{-3} which is in good agreement with a unit risk of 4.4×10^{-3} based on the Poisson Regression Model. The MLE of the risk of continuous exposure at 1 $\mu g/m^3$ was 2.45×10^{-3} (EPA, 1999a [95]).

A reanalysis of this cohort using cumulative exposure estimates based on more detailed job histories (Sorahan and Lancashire, 1997 [119]) confirmed an association between cumulative exposure to cadmium and lung cancer mortality. However, a significant trend for a risk of lung cancer was found only for exposures to cadmium received in the presence of arsenic trioxide. The authors propose three hypotheses to be consistent with their findings:

(a) cadmium oxide in the presence of arsenic trioxide is a human lung carcinogen,
(b) cadmium oxide and arsenic trioxide are human lung carcinogens and cadmium sulfate and cadmium sulfide are not (or they are less potent carcinogens), or
(c) arsenic trioxide is a human lung carcinogen and cadmium oxide, cadmium sulfate, and cadmium sulfide are not.

The problem to which agent the increased risk of lung cancer can be attributed was also seen in a UK study at a zinc-lead-cadmium smelter. The authors concluded that their analysis shows that lung cancer mortality is positively related to duration of employment and to cumulative exposure to arsenic and lead but not to cumulative exposure to cadmium (Ades and Kazantzis, 1988 [120]).

Recently, a meta-analysis of studies in cadmium-exposed workers (including the 1992 Stayner study [118]) has been published (Bochmann et al., 1998 [121]). The authors came to the conclusion that an increased cancer risk due to occupational cadmium exposure by inhalation could not be confirmed. Their arguments were

(a) that a consistent increase of SMR with duration of exposure could not be demonstrated,
(b) that this inconsistency holds true after separate consideration of low, medium, or high exposure categories, and
(c) that confounding by smoking and exposure to other possible carcinogens like arsenic and nickel may have occurred.

Initial results of the NIOSH study indicating an increase in carcinomas of the prostate could not be confirmed in further follow-up studies of the same study group (Sorahan and Waterhouse, 1985 [122], Thun et al., 1985 [117]).

General population
There are only few studies on lung cancer or prostatic cancer in the general population, e.g., in Japan with population exposure by cadmium-polluted rice (Shigematsu et al., 1982 [123], cited from IPCS/WHO 1992 [87]). They do not provide a consistent picture (IPCS/WHO 1992 [87], EPA 1999a [95]) and thus can neither confirm nor refute cadmium cancerogenicity in the general population without occupational exposure to cadmium.

The classifications of cadmium and cadmium compounds by several organizations are given in table 2.2.8. Health and Environment Canada classifies cadmium to be a probable human carcinogen, too [123a].

Table 2.2.8: Classification of cadmium and cadmium compounds with respect to carcinogenicity. For the exact meaning of the classifications, see footnote in table 2.1.13 of chapter 2.1.2.3.

Cadmium species	Organization			
	IARC	EC	US EPA	NTP-BSC
Cadmium and cadmium compounds	1		B1	Known to be human carcinogens *(still pending)*
Cadmium chloride		2		
Cadmium oxide		2		
Cadmium sulfate		2		
Cadmium sulfide		3		

2.2.2.4 Human Biomonitoring

In human biomonitoring, cadmium in blood (CdB) and cadmium in urine (CdU) are useful indicators to characterize exposure to cadmium at different time scales.

CdB reflects short-term cadmium exposure during a period of days up to a few weeks before sampling. To a minor extent, CdB is influenced by cadmium body burden which increases by age. However, this increase is small in never- or former smokers but much more important in long-term smokers. Smokers show cadmium concentrations in blood about four to five times those of non-smokers. Therefore, information on smoking habits is essential when assessing CdB levels.

In non-smokers, women show slightly higher CdB values than men, probably due to an increased intestinal cadmium resorption under conditions of iron deficiency.

CdU reflects cadmium body burden, especially renal cadmium concentration, and can thus serve as an indicator of cumulative long-term exposure. There is a clear age-dependent increase in CdU, which is more pronounced in smokers than in nonsmokers. Renal tubular damage caused by cadmium leads to cadmium release from renal depots resulting in increased cadmium excretion via urine. Diagnosis of proximal tubular damage is based on increased excretion of low molecular weight proteins and other substances. However, similar changes in protein excretion may be due to causes other than cadmium exposure, too.

Cadmium in hair reflects cadmium exposure during the period of the respective hair sample´s growth. However, endogeneous cadmium and exogeneous cadmium contamination cannot be distinguished, and the correlation between cadmium in hair and in blood or urine is poor. Therefore, cadmium in hair is not a reliable indicator of corporal cadmium exposure or cadmium body burden of an individual.

Cadmium content of tissue samples would be a valuable information, especially in renal or liver samples. For obvious reasons, sample availability is very poor.

Table 2.2.9: Cadmium concentrations in **urine (in µg Cd /l urine)** in the German population in 1990-1992

	Geometric mean	Arithmetic mean	10th Percentile	50th Percentile	90th Percentile
Adults (age 25-69)					
all (n=4002)	0.29	0.43	0.09	0.30	0.92
never-smokers (n=1689)	0.23	0.33	0.08	0.24	0.65
ex-smokers (n=1052)	0.27	0.39	0.09	0.29	0.76
smokers (n=1260)	0.41	0.60	0.13	0.44	1.29
Children (age 6-14)					
(n = 732)	0.09	0.12	<0.05	0.10	0.21

Results of the German Environmental Survey concerning urine and blood concentrations of cadmium (Seiwert et al., 1999 [86]; Schulz 1998 [85]; Krause et al., 1996 [124]) in the German population between 1990-1992 are presented in tables 2.2.9-11. In a smaller study in Italy, blood cadmium concentrations were found in a comparable range in smokers and somewhat higher in non-smokers (dell´Omo et al., 1999 [125]).

Table 2.2.10: Cadmium concentrations in **urine (in µg Cd /g creatinine)** in the German population in 1990-1992

	Geometric mean	Arithmetic mean	10th Percentile	50th Percentile	90th Percentile
Adults (age 25-69)					
all (n=4002)	0.21	0.32	0.06	0.22	0.66
never-smokers (n=1689)	0.18	0.27	0.05	0.18	0.53
ex-smokers (n=1052)	0.20	0.29	0.07	0.22	0.58
smokers (n=1260)	0.28	0.41	0.09	0.29	0.89
Children (age 6-14)					
(n = 731)	0.06	0.09	0.02	0.06	0.15

Table 2.2.11: Cadmium concentrations in **blood (in µg Cd /l)** in the German population in 1990-1992

	Geometric mean	Arithmetic mean	10th Percentile	50th Percentile	90th Percentile
Adults (age 25-69)					
all (n=3965)	0.36	0.69	0.1	0.3	1.9
never-smokers (n=1670)	0.21	0.29	0.1	0.2	0.5
ex-smokers (n=1036)	0.25	0.36	0.1	0.3	0.7
smokers (n=1258)	1,04	1.51	0.3	1.3	3.0
Children (age 6-14)					
(n = 713)	0.14	0.17	0.1	0.1	0.3

Based on data of the German Environmental Surveys (Krause et al., 1996 [124]), reference values (based on 95th percentiles) are given in table 2.2.12.

Table 2.2.12: Reference values for cadmium (based on results of the German Environmental Survey 1990-92)

Group	Cadmium in blood	Cadmium in urine
Children (6-12 y)	0.5 µg/l whole blood	0.5 µg/g creatinine
Adults (nonsmokers, 25-69 y)	1.0 µg/l whole blood	1.0 µg/g creatinine

In addition to reference values, which can only give descriptive information without toxicological meaning, so-called “human biomonitoring values” have been derived which are based on health risk assessment (Kommission Human-Biomonitoring, 1998 [126]; Krause et al., 1999 [127]). They provide a two-stage classification with the “human biomonitoring value I (HBM I)” indicating a level below which no increased health risk is seen according to the present view and knowledge of the Human Biomonitoring Commission of the Federal Environmental Agency. The HBM II indicates a level where the possibility of relevant health effects is no longer negligible. For cadmium, the cumulative long-term exposure raises concern. Therefore, HBMs are defined for cadmium in urine (table 2.2.13) as an indicator of cadmium content of renal tissue. In children and juveniles, critical concentrations in renal tissue shall be prevented with respect to their later life. In adults, however, subtle cadmium-induced nephrotoxic effects may occur above the HBM I.

Table 2.2.13: Human Biomonitoring Values for cadmium

Group	Cadmium in urine, HBM I	Cadmium in urine, HBM II
Children and juveniles	1 µg/g creatinine	3 µg/g creatinine
Adults	2 µg/g creatinine	5 µg/g creatinine

2.3 Nickel

2.3.1 Sources And Occurrence In The Environment

2.3.1.1 Air

Nickel is a ubiquitous trace metal and occurs in soil, water, air, and in the biosphere. The most common forms of nickel in ambient air are nickel sulfate, complex nickel oxide, and complex nickel-ferric oxide. Nickel is mainly (66 %) used in stainless steel production.

Nickel emissions to the atmosphere may occur from natural sources such as windblown dust, volcanoes, and vegetation. The main anthropogenic sources of nickel emissions into the ambient air are the combustion of oil for heat or power generation, nickel mining and primary production, the incineration of waste and sewage sludge, steel manufacture, electroplating, and coal combustion (IPCS/WHO, 1991 [128], Lewis and Caldwell, 1999 [129]). For more details, see Chapter 1.3.

2.3.1.2 Indoor Dust

In a study of German households, the amount of nickel in dust settled on indoor surfaces and the concentrations of nickel in dust samples taken from vacuum cleaner bags were measured (Krause et al., 1991 [4]); the results are given in table 2.3.1.

Table 2.3.1: Nickel concentration in household dust (Krause et al., 1991 [4])

n	2615
10th percentile	7 mg/kg
50th percentile	23 mg/kg
95th percentile	66 mg/kg
Arithmetic mean	29 mg/kg
Geometric mean	20 mg/kg

2.3.1.3 Water

The natural background levels of nickel in water range from 0.2 to 0.7 µg/l in open-ocean water and from 2 to 10 µg/l in fresh water. (IPCS/WHO, 1991 [128], WHO, 1997 [130]).

In surface or ground waters not polluted by human activities, the nickel content often reflects the weathering process of the parent soil or rock. Part of the nickel is transported via rivers and streams to the ocean. Riverine suspended particulate input is estimated to be 135 x 10^7 kg/a, industrial and municipal waste and atmospheric fallout contribute 0.4 x 10^7 kg/a and 2.5 x 10^7 kg/a, respectively (Nriagu, 1980 [131], from IPCS/WHO, 1991 [128]).

2.3.1.4 Soil

The average nickel content in the earth´s crust is about 0.008 %; agricultural soils contain between 3 and 1000 mg/kg (IPCS/WHO, 1991 [128]).

Atmospheric input of nickel into the soil and inputs by waste disposal and through the application of fertilizers are estimated to be 5.5 x 10^4 kg/a and 1.4 x 10^4 kg/a, respectively (IPCS/WHO, 1991 [128]).

2.3.2 Human Exposure, Uptake And Effects

2.3.2.1 Pathways Of Human Exposure

Inhalation exposure

In remote areas, annual mean nickel concentrations in air are around 1 ng/m³ or less and in rural areas 0.4-2 ng/m³. In urban areas, 1.4-13 ng/m³ seems to be a realistic range. In industrial areas in most EC countries, nickel concentrations range from 10 to 50 ng/m³. However, in heavily industrialized areas, concentrations up to 100 ng/m³ are possible (cf. Chapter 1.4).

In the following table 2.3.2, an absorbed daily dose of nickel from inhalation exposure is calculated. In addition, a “low” and a “high” estimate are given. The latter values are not intended to represent the extremes of the possible range of exposure, instead, they should represent values to which a significant proportion of the population is probably exposed. Concentrations are chosen in order to reflect approximately the situation in rural (“low”), urban (“average”) and industrial areas (“high”), respectively.

For adults, a reference body weight of 60 kg and a reference respiratory volume of 20 m^3/d according to U.S. EPA recommendations are assumed. For children, a reference body weight of 15 kg corresponding to an age of about 3 years and a respiratory volume of 8 m^3/d are assumed (for more details, see Chapter 2.1.2.1 Arsenic). In addition, it is assumed that indoor and outdoor air concentrations are identical.

Table 2.3.2: Calculation of the absorbed daily dose of nickel. Source: Air

Exposure [1]	Concentration in air (ng/m^3)	Absorption (%)	Other assumptions	Absorbed dose (ng Ni /(kg•d))
Adults				
low	1	50	body weight: 60 kg	0.17
average	5	50	respiratory volume:	0.83
high	15	50	20 m^3/d	2.5
Children				
low	1	50	body weight: 15 kg	0.27
average	5	50	respiratory volume:	1.33
high	15	50	8 m^3/d	4.0

1) Exposures are classified in order to reflect approximately concentrations in rural, urban and industrial areas, respectively

Deposition in the lungs varies between 10 and 50 %, depending on particle size. Pulmonal absorption varies with the chemical nature of the particles. An upper estimate of 100 % is a reasonable worst case assumption. The total absorption includes deposition rate and absorption rate of deposited amount. An average value of 50 % is used, according to the assumptions in the case of cadmium (Chapter 2.2.2.1).

Cigarette smoking

Cigarette smoke can contribute to nickel exposure. About 0.04-0.58 µg nickel is estimated to be released with the mainstream smoke of one cigarette. The possibility that in the mainstream smoke nickel occurs in part as nickel carbonyl has been suspected but not been substantiated (IPCS/WHO, 1991 [128], WHO, 1997 [130]).

In the following table 2.3.3, an absorbed daily dose of nickel is calculated. In addition, a ”low” and a ”high” estimate are given. The latter values are not intended to represent the extremes of the possible range of exposure, instead, they should represent values to which a significant proportion of the population is probably exposed.

Table 2.3.3: Calculation of the absorbed daily dose of nickel. Source: Cigarette smoke

Exposure	µg Nickel in mainstream smoke/cigarette	Absorption (%)	Other assumptions	Absorbed dose (ng Ni / (kg•d))
Adults				
low	0.05	50	body weight: 60 kg	8.3
average	0.2	50		33
high	0.6	50	20 cigarettes/d	100

Oral exposure (Water and Food)

In general, drinking water contains nickel in concentrations of 5-10 µg/l. In Germany, nickel concentrations in water provided by water works usually are lower than 10 µg/l. In the German Environmental Survey, median nickel concentrations in samples provided by the water works were below 1 µg/l (Becker et al., 1997 [90]).

The provisional EC limit value for nickel in drinking water (Directive EC 98/83) is 20 µg/l.

Most food products contain less than 0.5 mg Ni/kg fresh weight. Cocoa products and nuts may, however, contain as much as 10 and 3 mg/kg, respectively. Fish and molluscs living in water with high nickel concentration may contain relatively large amounts of nickel (IPCS/WHO, 1991 [128]).

The mean nickel intake of a normal adult in the Western countries was estimated to be 200-300 µg/d (IPCS/WHO, 1991 [128]). The analysis of duplicate food samples in Germany suggests an intake of about 80 µg/d (maximum 740 µg/d) (Becker et al., 1996 [132]; Schulz, 1998 [85]). Therefore, the range given by WHO should be extended to lower values.

There is considerable variation in the data on intestinal nickel absorption (1-20 %) (IPCS/WHO, 1991 [128]). WHO has adopted an absorption rate of <15 % (WHO, 1997 [130]). Intestinal absorption of nickel from drinking water is estimated to be around 25 % (IPCS/WHO, 1991 [128]).

In the following tables 2.3.4 and 2.3.5, an absorbed daily dose of nickel is calculated. In addition, a “low” and a “high” estimate are given. The latter values are not intended to represent the extremes of the possible range of exposure, instead, they should represent values to which a significant proportion of the population is probably exposed.

For adults, a reference body weight of 60 kg and a reference value of 2 l/day for water consumption according to U.S. EPA recommendations (EPA, 1988 [9]) are assumed.

For children, a reference body weight of 15 kg is assumed. Therefore, instead of the reference drinking water rate of 1 l/day for a 10-kg child used by EPA‘s Office of Drinking Water

(EPA, 1988 [9]), a daily water consumption of 1.5 l is used. This does not change the absorbed dose per kg and day. The amount of food is assumed to be 50 % of that of an adult.

Table 2.3.4: Calculation of the absorbed daily dose of nickel. Source: Drinking water

Exposure [1]	Concentration in water (µg/l)	Absorption (%)	Other assumptions	Absorbed dose (ng Ni / (kg•d))
Adults				
low	0.1	25	body weight: 60 kg	0.8
average	1	25	consumption of drinking water:	8.3
high	20	25	2 l/d	167
Children				
low	0.1	25	body weight: 15 kg	2.5
average	1	25	consumption of drinking water:	25
high	20	25	1.5 l/d	500

1) For the “high” exposure estimate, the provisional EC drinking water limit value of 20 µg/l is used

Table 2.3.5: Calculation of the absorbed daily dose of nickel. Source: Food

Exposure	Amount ingested (µg Ni /d)	Absorption (%)	Other assumptions	Absorbed dose (ng Ni / (kg•d))
Adults				
low	50	15	body weight:	125
average	150	15	60 kg	375
high	600	15		1500
Children				
low	25	15	body weight:	250
average	75	15	15 kg	750
high	300	15		3000

Soil and Dust

In young children, uptake of house dust or soil/sand of playing grounds may also be a source of nickel exposure.

In the following table 2.3.6, an average absorbed daily dose of nickel is calculated. In addition, a “low” and a “high” estimate are given. The latter values are not intended to represent the extremes of the possible range of exposure, instead, they should represent values to which a significant proportion of the population is probably exposed.

For adults, a reference body weight of 60 kg according to U.S. EPA recommendations (EPA, 1988 [9]) is assumed. For children, a reference body weight of 15 kg is assumed.

Table 2.3.6: Calculation of the absorbed daily dose of nickel. Source: Soil and dust

Exposure	Concentration in soil/dust (µg Ni / g)	Absorption (%)	Other assumptions	Absorbed dose (ng Ni / (kg•d))
Adults				
low	2	15	body weight: 60 kg	0.5
average	20	15	average soil/dust intake:	5
high	100	15	0.1 g/d	25
Children				
low	2	15	body weight: 15 kg	10
average	20	15	average soil/dust intake:	100
high	100	15	0.5 g/d	500

For the average soil and dust intake of a 15-kg child, a value of 0.5 g/d is used. This value represents the 95th percentile for long-term soil intake of children up to 6 years old and includes pica activity (Ruck, 1990 [15]). For adults, the most often reported value for soil and dust intake is 0.1 g/d (Ruck, 1990 [15]).

For the absorption rate of nickel from soil and dust after oral uptake, a value of 15 % is assumed, corresponding to the intestinal absorption of nickel from food.

Estimation of the total absorbed nickel dose

In the following table 2.3.7, the “low”, “average” and “high” estimates for individual exposure sources are combined from tables 2.3.2-6. The simple addition of “low” and “high” values, respectively, may result in rather extreme total values, since the variabilities for each source of nickel are largely independent of each other, i.e., a high nickel dose through diet is not necessarily connected with a high dose of nickel through drinking water or a low nickel concentration in drinking water need not be connected with a low nickel concentration in air.

Table 2.3.7: Calculation of the absorbed daily dose of nickel, in ng Ni / (kg•d)

	Adults			Children		
Source	low (% of sum)	average (% of sum)	high (% of sum)	low (% of sum)	average (% of sum)	high (% of sum)
Air	0.17 (<1)	0.83 (<1)	2.5 (<1)	0.27 (<1)	1.33 (<1)	4.0 (<1)
Cigarette smoking	8.3 (6)	33 (8)	100 (6)	-	-	-
Drinking water	0.8 (<1)	8.3 (2)	167 (9)	2.5 (1)	25 (3)	500 (12)
Food	125 (93)	375 (88)	1500 (83)	250 (95)	750 (85)	3000 (75)
Soil and Dust	0.5 (<1)	5 (1)	25 (1)	10 (4)	100 (11)	500 (12)
Sum	135	422	1795	263	876	4004

An average absorbed daily dose of nickel of 400 ng / (kg•d) for adults and 800 ng / (kg•d) for children is calculated. Under average circumstances, the oral uptake of nickel via food contributes the largest amount to the total dose. On average, nickel uptake via ambient air contributes less than 1 % to the total absorbed nickel dose. The contribution of smoking usually amounts to less than 10 % of the absorbed nickel dose.

2.3.2.2 Kinetics And Metabolism

Lung deposition of nickel compounds depends on particle size with higher deposition for smaller particles. There are considerable differences in bioavailability of nickel compounds. Insoluble nickel compounds, such as nickel oxide and metallic nickel, seem to be retained in the lungs for a longer time, whereas the more soluble nickel salts are absorbed. They are also solubilized in the fluids and mucus cleared from the lungs by the mucociliary mechanisms into the alimentary tract (IPCS/WHO, 1991 [128]).

There is considerable variation in the data on intestinal nickel absorption (1-20 %) (IPCS/WHO, 1991 [128]). WHO has adopted an absorption rate of <15 % (WHO, 1997 [130]). Intestinal absorption of nickel from drinking water is estimated to be around 25 % (IPCS/WHO, 1991 [128]).

2.3.2.3 Health Effects Of Nickel

Essentiality

Nickel seems to be an essential trace element in plants, animals, and probably in humans, too. However, effects of nickel deficiency on human health have not been demonstrated, possibly because of the ubiquitous occurrence of nickel in food and drinking water (IPCS/WHO, 1991 [128]; NIPERA, 1999 [133]).

In laboratory animals, nickel deprivation induces anemia through reduced absorption of iron. Nickel may also influence the metabolism of calcium and zinc. Furthermore, the element appears to be an important component of some proteins and enzymes. A dietary nickel deficiency can lead to reproductive effects in the form of reduced litter sizes and decreased viability of the newborn.

Nickel seems to be involved in the regulation of the tone of blood vessels. A rise in serum nickel associated with childbirth has been reported. This may indicate a physiological role of the element in controlling atonic bleeding or promoting placental separation through effects on uterine vasoconstriction and uterine smooth muscle. However, this rise in serum nickel has not been confirmed by other investigations (IPCS/WHO, 1991 [128]). On the other hand, vasoconstriction of the coronary vessels would be an adverse effect in patients with myocardial ischemia.

Non-cancer Effects

The general impression from the published literature is that acute toxicity is a minor risk from nickel or its compounds, with the exception of nickel carbonyl (IPCS/WHO, 1991 [128]).

Severe lung damage has been recorded after inhalation of nickel carbonyl at workplace concentrations. In the non-occupational environment, however, the presence of nickel carbonyl has not been demonstrated.

Mucosal irritation and asthma have been reported after occupational exposure to inorganic nickel compounds and allergic dermatitis in workers as well as in the general population (WHO, 1997 [130]).

In workers who accidentally ingested drinking water contaminated by nickel sulfate and nickel chloride, elevated urine-albumin concentrations suggesting a mild transient nephropathy have been found. The albumin levels returned to normal on the fifth day after exposure (IPCS/WHO, 1991 [128]).

Generally, data on non-cancer health effects of nickel in humans are extremely scarce, with the only exception of dermal exposure. Therefore, most of the available information refers to animal data.

Effects on the respiratory system

Nickel significantly depressed normal ciliary activity in a hamster tracheal ring assay following in vivo exposure to 100 µg Ni/m³ as nickel chloride for 2 h (IPCS/WHO, 1991 [128]).

Bingham et al. (1972 [134]) exposed rats to aerosols of either nickel chloride at 109 µg/m³ (50 µg Ni/m³) or nickel oxide at 120 µg/m³ (95 µg Ni/m³) for 12 h/day and 6 days/week. After 2 weeks of exposure, the number of macrophages in the bronchial lavage fluid was markedly increased in the NiO group, and focal infiltration by lymphocytes occured in the alveolar walls and perivascular spaces. In the nickel chloride group, the bronchial epithelium was hyperplastic with evidence of marked mucus secretion.

In the U.S. National Toxicology Program (NTP), chronic inhalation studies (for each substance tested, a 2-year study with a joint 13-week study) were carried out with male and female rats and mice exposed for 6 h/d on five days per week for 112 weeks. Nickel compounds tested were green nickel oxide (NiO, mass median aerodynamic diameter 2.2 ± 2.6 µm), nickel subsulfide (Ni_3S_2, mass median aerodynamic diameter 2.0 - 2.2 µm), and nickel sulfate hexahydrate ($NiSO_4 \bullet 6\ H_2O$, mass median aerodynamic diameter 2.2 - 2.5 µm). Endpoints under study were cancer as well as non-neoplastic effects (NTP, 1996 a,b,c [135,136,137]).

Among non-neoplastic effects observed in the NTP studies, chronic active inflammation was consistently seen in rats and mice exposed to green nickel oxide or nickel subsulfide at all concentrations tested (Ni_3S_2 ≥0.11 mg/m³, NiO ≥0.5 mg/m³). In rats and mice, effects of nickel sulfate hexahydrate were seen at ≥0.06 mg/m³ in the 2-year study. In the joint 13-week study, alveolar macrophage hyperplasia was found in 8 out of 10 female rats and in 10 out of 10 male rats (NTP, 1996 a,b,c [135,136,137]) of the 0.03 mg Ni/m³ groups, and there was an increase in chronic active inflammation in the 7-month interim evaluation in male rats and a corresponding trend in female rats (table 2.3.8).

In a 15-month interim evaluation, there was an increasing trend in the absolute lung weight of both male and female rats which was considered to be related to inflammatory lung reactions that occurred in response to the nickel exposures (Dunnick et al., 1995 [138]) (table 2.3.8).

Table 2.3.8: Nonneoplastic Lesions of the Lungs of Rats in the 13-Week Study, in the 7-Month Interim Evaluation, and in the 2-Year NTP Inhalation Study of Nickel Sulfate Hexahydrate

Concentration	0 mg/m^3	0.12 mg/m^3 (0.03 mg Ni/m^3)	0.25 mg/m^3 (0.06 mg Ni/m^3)	0.5 mg/m^3 (0.11 mg Ni/m^3)
13-Week Study, male rats				
Chronic Active Inflammation	0/10	0/10	0/10	2/10
Macrophage Hyperplasia	0/10	10/10	10/10	10/10
7-Month Interim Evaluation, male rats				
Chronic Active Inflammation	0/5	4/5	4/5	5/5
Macrophage Hyperplasia	0/5	1/5	5/5	5/5
2-Year Study, male rats				
Chronic Active Inflammation	14/54	11/53	42/53	46/53
Macrophage Hyperplasia	7/54	9/54	35/53	48/53
Fibrosis	3/54	6/53	35/53	43/53
13-Week Study, female rats				
Chronic Active Inflammation	0/10	0/10	0/10	4/10
Macrophage Hyperplasia	0/10	8/10	10/10	10/10
7-Month Interim Evaluation, female rats				
Chronic Active Inflammation	0/5	2/5	4/5	5/5
Macrophage Hyperplasia	0/5	2/5	4/5	5/5
2-Year Study, female rats				
Chronic Active Inflammation	14/52	13/53	49/53	52/54
Macrophage Hyperplasia	9/52	10/53	32/53	45/54
Fibrosis	8/52	7/53	45/53	49/54
15-Month Interim Evaluation, male rats				
Lung weight	2.12 g	2.48 g	2.50 g	3.00 g
15-Month Interim Evaluation, female rats				
Lung weight	1.37 g	1.57 g	1.49 g	1.82 g

Increased mortality due to non-malignant respiratory disease has been reported in nickel refinery **workers** with more than 5 years of exposure, and pneumoconiosis has been reported after 12-20 years of exposure. No details on nickel compounds or exposure levels were given (WHO, 1997 [130]).

Allergic asthma has been reported among workers in the plating industry after exposure to nickel sulfate (WHO, 1997 [130]).

Muir et al. (1993, [139]) carried out a study designed to investigate whether the inhalation of nickel subsulfide and nickel oxide is associated with fibrosis in the lungs in nickel sinter plant workers. No information on nickel concentrations was given in the original publication. In chest radiographs from 745 workers, the prevalence of small irregular opacities was selected as the outcome of interest. The workers were monitored as part of a voluntary surveillance medical programme which started in 1973, i.e., 10 years after the sinter plant at Copper Cliff in Sudbury, Ontario, ceased its operation (1948-1963). No information was provided on the percentage of workers who participated in the programme, or how successful the authors were in obtaining radiographs of workers who died or left the programme for other reasons. Furthermore, control films were randomized, but no data on the prevalence of opacities in the control films were reported. There was considerable variation in the results of five readers who classified the radiographs. The authors conclude that the prevalence was within the range identified in cigarette smokers or in workers exposed to dusts of low fibrogenicity, but no information on smoking prevalence was provided. Four of the five readers found a significantly higher score for irregular opacities if exposure time was ≥ 5 years compared to workers with shorter exposure time.

Renal effects

Tubular lesions resulting in aminoaciduria and proteinuria have been produced in experimental animals under conditions of exposure to various nickel compounds (≥ 0.8 mg Ni/m^3) (as reviewed in Lewis and Caldwell, 1999 [129]).

Endocrine effects

Nickel seems to influence glucose regulation in experimental animals after parenteral nickel application (IPCS/WHO, 1991 [128]).

Effects of nickel on thyroid function were reported in one study by Lestrovoi et al. (1974 [140]). Nickel chloride administered to rats orally or by inhalation, significantly decreased iodine uptake by the thyroid, the effect being more pronounced if nickel was inhaled (IPCS/WHO, 1991 [128]). This effect - described to occur under continuous exposure to concentrations of 0.5 mg/m^3 and 0.005 mg/m^3 but not at 0.001 mg/m^3 for 2 to 12 weeks - was reversible after 4 weeks (Lestrovoi et al., 1974 [140]).

Immune system and defence mechanisms

The phagocytic activity, the size of alveolar macrophages and the number of macrophages with more than one nucleus were increased in rats after 4 months of continuous inhalation of nickel oxide at 25 µg Ni/m^3 which was the minimal concentration tested (Spiegelberg et al., 1984 [141]).

Dermal effects

Allergic skin reactions are the most common health effect of nickel. In a Danish study, about 2 % of the male and 11 % of the female population showed a positive skin reaction (patch test) to nickel sulfate (Nielsen and Menné, 1993 [142], as quoted by WHO 1997 [130]). Nickel content in and nickel release from consumer products (regulated by Nickel Directive 94/27 EC) with direct prolonged dermal contact are and possibly nickel in food and water (after dermal sensitization) may be critical for the dermatological effect. However, there is no evidence that airborne nickel causes allergic reactions in the general population. A Consensus Position resulting from the NiPERA Dermal Nickel Sensitization Workshop (March 1997, Brussels [143] was as follows:

„The induction of nickel sensitization by the oral or inhalation routes is unlikely; and in practice, this is rarely observed. The elicitation of a systemic dermal reaction in already sensitized individuals varies considerably and could occur when these individuals are exposed to high levels of soluble nickel species by these routes. However, this rarely if ever occurs.“

Reproduction and development

Nickel has been shown to cross the human placenta; it has been found in both the fetal tissue and in the umbilical cord serum, where the average concentration from 12 newborn babies was in good accordance with that in their mother´s serum immediately after delivery (IPCS/WHO, 1991 [128]).

Data on the reproductive and developmental effects of nickel in human beings are scarce. No data could be identified by IPCS/WHO, 1991 [128]. In a Russian nickel refinery with male and female workers, the percentage of pregnancies with complications was increased, especially abortion, and structural malformations in infants were increased, too, if compared with local female construction workers without occupational exposure to nickel. Nickel sulfate concentrations were 0.2 mg/m³ in the electrolysis department and 0.13 mg/m³ in the electrolytic purification department of the refinery (Chashschin et al., 1994 [144]).

Genotoxicity

In an overview of data on genotoxicity tests of nickel and nickel compounds, IPCS/WHO (1991 [128]) conclude that nickel compounds are generally inactive in bacterial assays, but active in systems using eukaryotic organisms, and that positive responses were observed regardless of the nickel compound tested.

Data on genetic effects in exposed workers are scarce and don´t provide a clear picture (IPCS/WHO, 1991 [128]).

As reviewed in the Canadian Environmental Protection Act Assessment (Health and Environment Canada, 1994 [145]), there is some weak evidence of genotoxicity in limited epidemiological studies. Although there may have been concomitant exposure to other compounds in these studies, the common predisposing factors in the various groups of workers examined appear to be the groups of nickel compounds. In addition, there is some supportive evidence of carcinogenicity and genotoxicity of these forms of nickel in principally limited studies in animal species.

The report by Lewis and Caldwell prepared for CONCAWE [129] summarises that the in vitro and in vivo genotoxicity data indicate that some forms of nickel are genotoxic. The authors conclude, however, that taken together with human genetic toxicology studies, the weight of the evidence indicates nickel is unlikely to be genotoxic to humans by the inhalation route of exposure.

Carcinogenicity

In the chronic inhalation studies of the U.S. National Toxicology Program mentioned above, male and female rats and mice were exposed for 6 h/d on five days per week for 112 weeks. Nickel compounds tested were green nickel oxide (NiO), nickel subsulfide (Ni_3S_2), and nickel sulfate hexahydrate ($NiSO_4 \bullet 6\ H_2O$).

With respect to the inhalation carcinogenicity bioassays in mice, negative results were found for nickel subsulfide and nickel sulfate. Nickel oxide gave equivocal results. Therefore, the results in mice are uninterpretable with respect to differences in the carcinogenic potential of the respective compounds.

With respect to the inhalation carcinogenicity bioassays in rats, the classification of the results was as follows (NTP, 1996 a,b,c [135,136,137]): There was

- **"some evidence"** in male rats based on lung adenoma or carcinoma (1/54 at 0; 1/53 at 0.5 mg/m^3; 6/53 at 1 mg/m^3; 4/52 at 2 mg Ni/m^3 as **NiO**) and on benign or malignant pheochromocytoma (27/54 at 0; 24/52 at 0.5 mg/m^3; 27/53 at 1 mg/m^3; 35/52 at 2 mg Ni/m^3 as NiO),
- **"some evidence"** in female rats based on lung adenoma or carcinoma (1/53 at 0; 0/53 at 0.5 mg/m^3; 6/53 at 1 mg/m^3; 5/54 at 2 mg Ni/m^3 as **NiO**) and on benign or malignant pheochromocytoma (4/51 at 0; 7/52 at 0.5 mg/m^3; 6/53 at 1 mg/m^3; 18/53 at 2 mg Ni/m^3 as NiO),
- **"clear evidence"** in male rats based on lung adenoma or carcinoma (0/53 at 0 mg/m^3; 6/53 at 0.11 mg/m^3; 11/53 at 0.73 mg Ni/m^3 as $\mathbf{Ni_3S_2}$) and on benign or malignant pheochromocytoma (14/53 at 0 mg/m^3; 30/52 at 0.11 mg/m^3; 42/53 at 0.73 mg Ni/m^3 as Ni_3S_2,
- **"clear evidence"** in female rats based on lung adenoma or carcinoma (2/53 at 0 mg/m^3; 6/53 at 0.11 mg/m^3; 9/53 at 0.73 mg Ni/m^3 as $\mathbf{Ni_3S_2}$) and on benign pheochromocytoma (2/53 at 0 mg/m^3; 7/53 at 0.11 mg/m^3; 36/53 at 0.73 mg Ni/m^3 as Ni_3S_2,
- **"no evidence"** in rats in the case of **nickel sulfate hexahydrate**.

However, the California EPA, Office of Environmental Health Hazard Assessment (OEHHA, 1999 [146]), draws attention to the exposure conditions during these NTP bioassays. Due to the higher toxicity of nickel sulfate hexahydrate, relatively low exposure concentrations had to be chosen resulting in a low nickel burden of the lungs, whereas in the case of Ni_3S_2 and NiO, clearly higher exposure concentrations could be applied, resulting in – especially in the case of NiO – a much higher lung burden even in the low exposure group. Therefore, according to the

OEHHA, the result of “no evidence” in the case of nickel sulfate hexahydrate, when contrasted to the results obtained for nickel subsulfide and nickel oxide, is not sufficient to reliably distinguish, even with respect to the rat lung, the carcinogenic potential of nickel sulfate from either nickel subsulfide or nickel oxide.

Studies that link nickel uptake from the environment and cancer incidence in the general population are not available. There is agreement that nickel refinery workers exposed by inhalation to various nickel compounds in the past are at a significantly higher risk for cancer of the lungs and the nasal cavity than the non-occupationally exposed population (WHO, 1997 [130]; Shannon et al., 1991 [147]; Oller et al., 1997 [148]; Slooff et al., 1992 [149]).

Studies of industrial secondary and end users of nickel have generally not been positive, but the exposure levels have been less than 1 mg Ni/m³ both for particulate and soluble nickel compounds (WHO, 1997 [130]).

The ICNCM study (Doll, 1990 [150]) tried to give a complete overview of the then available information on nickel effects based on cohorts of a total of 80,000 workers (see table 2.3.9). It was pointed out that respiratory cancer risk was seen among workers exposed to a mixture of oxidic and sulfidic nickel at very high concentrations, and exposure to large concentrations of oxidic nickel in the absence of sulfidic nickel was also associated with increased lung and nasal cancer risk. Confounding by exposure to other substances like arsenic and sulfur dioxide could not always be excluded. The main conclusion was that it appears that more than one form of nickel gives rise to lung and nasal cancer. There was no evidence that metallic nickel was associated with increased lung and nasal cancer risks, and no substantial evidence was obtained to suggest that occupational exposure to nickel or any of its compounds was likely to produce cancers elsewhere than in the lung or nose. Another conclusion was that the evidence from this study suggests that respiratory cancer risks are primarily related to soluble nickel at concentrations in excess of 1 mg Ni/m³ and to exposure to less soluble forms at concentrations greater than 10 mg Ni/m³. With excess risks being confined to these high levels of exposure and the absence of any evidence of hazard from metallic nickel, it can be concluded according to the authors that the risk to the general population from exposure to the extremely small concentrations (less than 1 µg Ni/m³) to which it is exposed in the ambient air is minute, if indeed there is any risk at all.

Table 2.3.9: Overview of the nickel exposed groups of workers included in the ICNCM study (Doll, 1990 [150]).

	Study populations	Cohort size	Follow-up until
1	Mond/INCO nickel refinery, Clydach, South Wales	2.521	1984
2	Falconbridge Nickel Mines, Ontario	11.594	1984
3	Hanna Nickel Smelting Company, Oregon	1.510	1983
4	Huntington Alloys, West Virginia	3.208	1982
5	INCO, Ontario, Sudbury	50.458	1984
6	INCO, Ontario, Port Colborne	4.288	1984
7	Falconbridge Nickel Refinery, Kristiansand, Norway	3.250	1984
8	Oak Ridge Gaseous Diffusion Plant, Tennessee	813	1982
9	Outokumpu Oy Nickel Refinery, Finland	129	1987
10	Societe Le Nickel, New Caledonia	(79 cases, 223 referents)	1987
11	Henry Wiggin Alloy Company, Hereford, UK	1.907	1985

Data from Falconbridge, Ontario, were in part (table 2.3.9, #2) included in the ICNCM study. The authors (Shannon et al., 1991 [147]) found a significant increase in lung cancer Standardized Mortality Ratio (SMR) overall and in miners, but they concluded that this increase did not appear consistent with an occupational etiology. However, based on a lung cancer SMR of 100 for a cumulative exposure of less than 0.1 mg/m³ x years Ni, the SMR was increased to 137 for those with a higher cumulative exposure to all forms of nickel.

A recent update of the Finnish copper/nickel smelter and nickel refinery workers study (cf. table 2.3.9, #9) at the Outokumpu Oy Nickel Refinery (Antilla et al., 1998 [151]) is now based on a cohort of 1155 workers with a total of 21 cases of lung cancer. The follow-up period was extended to end 1995. Yearly mean workplace concentrations were mainly in the range of 0.1-0.8 mg/m³. After 1991, exposure was reduced by modifications at the nickel refinery and the more systematic use of effective respirators and protective masks. The authors conclude that among employees in the nickel refinery, where the primary source of exposure was nickel sulfate, there was an elevated risk for nasal cancer and also for lung and stomach cancer.

A follow-up of the Falconbridge nickel refinery, Kristiansand, cohort (cf. table 2.3.9, #7) until 1993 showed an excess risk of lung cancer in association with exposure to soluble forms of nickel and a multiplicative effect of smoking and exposure to nickel. The authors concluded that it is not possible to state with certainty which specific nickel compounds are carcinogenic, but a significant excess risk was found for workers exposed to soluble nickel alone or in combination with other forms of nickel (Andersen et al., 1996 [151a]).

This new information confirm the conclusion of the ICNCM study (Doll, 1990 [150]) that more than one form of nickel gives rise to lung cancer. However, with respect to the conclusion that respiratory cancer risk is primarily related to soluble nickel at concentrations in excess of 1 mg Ni/m³ and to exposure to less soluble forms at concentrations greater than 10 mg Ni/m³, the concentrations given in the Doll report are not confirmed and may possibly need downward correction.

At present, several cancer risk estimates for nickel compounds exist. WHO (1997 [130]) concludes that “based on the most recent information of exposure and risk estimated in industrial populations an incremental risk at a concentration of 1 µg/m³ of 3.8×10^{-4} can be given. The concentrations corresponding to an excess lifetime risk of 1:10,000, 1:100,000 or 1:1,000,000 are about 250, 25 or 2.5 ng/m³, respectively.” It is not explicitly mentioned which are the nickel compounds this unit risk refers to.

U.S. EPA calculates an inhalation unit risk estimate of 2.4×10^{-4} based on 3 cohorts (Copper Cliff, Clydach, and Kristianssand) with a range of estimates from 1.1×10^{-5} to 4.6×10^{-4}. This estimate concerns nickel refinery dust. The U.S. EPA estimate is close to an estimate of 2.5×10^{-4} provided by CEPN (1997 [152]). For nickel subsulfide, U.S. EPA calculates an inhalation unit risk estimate of 4.8×10^{-4}.

The classifications of nickel and nickel compounds by several organizations are given in table 2.3.10.

Table 2.3.10: Classification of nickel and nickel compounds with respect to carcinogenicity. For the exact meaning of the classifications, see footnote in Table 2.1.13 of Chapter 2.1.2.3

Nickel species	Organization			
	IARC	EC	US EPA	NTP-BSC [116]
Metallic nickel	2B	3		Reasonably anticipated to be a human carcinogen
Soluble nickel compounds	1			Known to be human carcinogen*
$NiSO_4$		3		
Oxidic nickel	1			Known to be human carcinogen*
NiO, Ni_2O_3, NiO_2, NiO_3, $Ni(OH)_2$		1		
Sulfidic nickel	1		A	Known to be human carcinogen*
NiS, Ni_3S_2		1		
Nickel carbonyl	1	3	B2	Known to be human carcinogen*

*) The upgrade of nickel compounds to “known to be human carcinogen” proposed by the NTP-BSC is still pending

2.3.2.4 Human Biomonitoring

Data from the German Environmental Surveys do not include nickel in blood or in urine.

Human biomonitoring data were provided by a review of published reports of nickel concentrations in human serum or plasma, whole blood, and urine (Templeton et al., 1994 [153]). Smith-Sivertsen et al. (1997 [154]) studied nickel in urine of inhabitants of a municipality in northern Norway located close to two Russian nickel refineries. The authors concluded that nickel exposure attributable to air pollution from the refineries was of minor importance for the exposure to nickel of people living in the municipality they studied. A small compilation of biomonitoring data is provided by Ewers et al. (1993 [155]). The data are summarized in table 2.3.11.

Table 2.3.11: Human biomonitoring data concerning nickel (in µg/l) in adults

Sample	Average	Range	Reference Value (95 percentile)	Data Source
Serum/plasma	0.14-0.63 0.2-0.5	<0.05-1.3	1.0	Templeton 1994 [153] Ewers 1993 [155]
whole blood	0.34-2.3 0.2-0.5	<0.05-3.8 1.0	1.0	Templeton 1994 [155] Ewers 1993 [155]
urine	0.9-4.1 2-5 0.6-0.9	0.1-10	10	Templeton 1994 [153] Ewers 1993 [155] Smith-Sivertsen 1997 [154]

2.4 Effects Of Arsenic, Cadmium And Nickel On Terrestrial Ecosystems

2.4.1 Introduction

2.4.1.1 Effects On Flora

Deposition of heavy metals (HM) is generally the result of anthropogenic activities and to a lesser extent due to geogenic origin (i.e. volcanic eruptions). These metals are liberated to the atmosphere by manifold industrial activities and depending on particle size and the gravitation field of the earth. They are more or less rapidly deposited, leading to a direct contamination of vegetation or after periods of accumulation in soils to an indirect contamination of plants via root uptake.

Heavy metals have to be differentiated into those elements essential for plant nutrition, exhibiting phytotoxic effects only in relatively high concentrations (Cu, Fe, Mo, Zn, Co, (Ni)) and into the non-essential elements like As, Cd, Cr, Hg, Pb and Tl which, due to frequent use in industrial processes, are deposited even in remote ecosystems and exhibit a potential phytotoxic risk. Amount, availability and element-specific mobility determine the degree of plant contamination via roots or leaves and hence the entrance into the biological chain. They are passed on in the ecosystems to other organisms at higher trophic levels by the uptake of contaminated plant material. Besides the direct phytotoxic properties of heavy metals, the transfer of toxicologically relevant compounds like cadmium into the foodchain is of specific relevance. However, plants differ not only with respect to their accumulation characteristics, but also in the target organ of accumulation. In leaves as edible plant parts, heavy metals are generally accumulated to a larger extent than in fruits or seeds.

Heavy metal contamination of plants occurs directly via the path

ambient air ⇨ plant
or indirectly via
soil ⇨ plant

by dry or wet deposition of particulate matter or suspended particles. The direct uptake of HM by above-ground plant parts is important only in the vicinity of specific sources, whereby morphological features (i.e. hairy versus smooth or waxy leaves) of plants influence particle retainment and uptake of heavy metal ions. Furthermore, impaction of heavy metals which are either retained by forest species or washed off is a significant way of forest soil contamination, in addition to heavy metal input by wet deposition experienced only at open field sites.

The most important pathway of As, Cd, and Ni uptake relates, however, to the soil/root system, since heavy metals are accumulated in the rooting zone of soils even in remote areas due to their persistency and long-term deposition. Plant uptake is greatly influenced by the pH-value of the soil solution and specific sorption characteristics (organic matter and clay content as well as iron oxides). On an ecosystem level, soil acidification by wet deposition of acidic substances can enhance mobility of heavy metals in soils, namely cadmium, leading to increased plant availability as well as increased heavy metal leaching into the groundwater system.

The phytotoxic potential of heavy metals is determined besides their availability in soil by the distribution within different compartments of the plant. Due to specific genetic disposition, some plant species are capable to tolerate high contents of heavy metals in soil (Galmeiflora) or to reduce heavy metal uptake via roots or even tolerate high tissue concentrations by inactivation due to inorganic or organic complexation, just to name some mechanisms of tolerance. As a consequence, large differences in heavy metal tolerance are found in plants.

Most heavy metals react due to their chelating properties by enzyme inhibition or blockage, whereby the strength of electronegativity of the specific element is important. Changes in permeability of cell membranes as well as the formation of insoluble, sulfidic compounds in tissues can lead to disturbances of plant metabolism. Furthermore, essential and non-essential heavy metals are in competition for enzymatic binding sites when taken up by the roots or into the cell, and relatively small amounts of, e.g, cadmium can act strongly toxic. Specific, element-related symptoms on above-ground plant parts are rarely observed. Broad leaf plants show generally chlorosis similar to iron deficiency symptoms, observed usually in older aerial plant parts. On an ecosystem level, phytotoxicity of heavy metal contaminants can lead to reduced biomass production, altered species composition and thus changes in structure and biodiversity of the habitat. (for literature see: Guderian, 1986 [156], Bergmann, 1993 [157], Allaway, 1999 [158]).

2.4.1.2 Effects On Fauna

Since soil is the major sink with respect to heavy metal deposition, considerations on possible faunistic effects are restricted to soil organisms. Unpolluted soils generally have a great variety of soil organisms which are vital with respect to (i) decomposition of organic matter, (ii) mineralisation of nutrients, and (iii) cycling of elements. Depending on the heavy metal element, the content of soils, and the bioavailability, organisms such as nematodes, springtails, isopods, mites and earthworms may be deleteriously affected by HMs in the soil. Heavy metals are taken up either by dermal contact and/or oral feed of contaminated soil particles or organic matter. The latter seems to be the most important pathway with respect to differential exposure to metals. Since fungal hyphae are known to accumulate HMs, soil organisms feeding on these are particularly exposed.

Decreases in species density and depressed biological activities have been observed in heavily polluted soils, partly leading to an accumulation of epigeic organic matter due to reduced mineralisation. However, changes in soil communities are also caused by specific predator-prey interactions, when certain predators increase in number due to, e.g., favourable environmental conditions, decreasing certain prey communities. Evaluations of persistent pollutants on soil organisms are therefore extremely complex and a very demanding task.

Moreover, most studies are done under controlled conditions or - when done in the field - usually with short duration. Besides pollution as influential factor, population and exposure dynamics driven by external factors like climate, above-ground vegetation and edaphic factors, however, demand long-term observations in order to get an understanding of major causal relationships.

Furthermore, variable bioavailability of metals in the environment, dynamic exposure processes, tissue distribution, accumulation, remobilisation and excretion processes complicate estimations of dose-response relationships. Even though research efforts have increased during the recent decades, our knowledge on the effects of heavy metals accumulated in soil organisms is more or less rudimentary and thus assessment of possible ecological risks is limited (Bargaghi, 1998 [159]).

2.4.2 Arsenic

2.4.2.1 Flora

Plants

Adverse effects on vegetation were recorded near gold mines at concentrations in air >3.9 µg As /m^3 (NRCC, 1978 [160]). Terrestrial plants may accumulate arsenic by root uptake from the soil or by absorption of airborne arsenic deposited on the leaves. The lowest concentration of arsenic in soil associated with effects was reported to be about 20-30 mg As/kg dry weight (Slooff et al., 1990 [161]; Hesse et al., 1990 [162]; WHO, 1999 [163]). Biomagnification of arsenic does not occur in plants. In crops grown on uncontaminated soil containing about 10 mg As /kg dry matter, arsenic concentration varied from 0.001 to 0.014 mg As/kg fresh weight. In a heavily contaminated mining area with soil concentrations of 144-892 mg As/kg dry matter, concentrations in crops ranged from 0.01 to 0.93 mg As/kg fresh weight (Slooff et al., 1990 [161]; Hesse et al., 1990 [162]). Depressed crop yields were recorded at 3 to 28 mg water-soluble As/l water, or about 20-85 mg total As /kg soil (Eisler, 1994 [164]). Concentrations of about 50 µg As /l can be toxic to certain freshwater algae (WHO, 1999 [163]).

2.4.2.2 Fauna

There is only a small number of publications concerning the effects of arsenic on soil organisms. Geiszinger et al. (1998 [165]) investigated the arsenic concentrations of soil and earthworms at six sites in Austria. Total arsenic concentrations ranged from 3.2 to 17.9 mg/kg dry weight in the worms and 5.0 to 79.7 mg/kg dry weight in the soil samples. There was no strict correlation between the total arsenic concentrations in the worms and the soil.

2.4.3 Cadmium

2.4.3.1 Vascular Plants

Natural cadmium concentrations in vascular plants range between 0.05 -3 µg/g dw (Kloke, 1973 [166]) and are strongly correlated with the soil cadmium content (Allaway, 1999 [158]). Cadmium is non-essential for plant growth (Bergmann, 1993 [157]). Normal soil contents are in the range of 0.01 – 0.30 µg/g (Bowen, 1966 [167]).

Besides industrial emissions, Cd contents in agricultural soils are frequently increased by application of sewage sludge and/or phosphate fertilizers; Cd soil contents of up to 200 µg/g have been observed (Bergmann, 1993 [157]). Mobility of cadmium increases with decreasing pH value, and is also dependent on the organic matter content, whereby increases in the latter will decrease mobility (Sauerbeck, 1989 [168]). Liming is therefore an appropriate method to reduce cadmium availability for plants (Sauerbeck, 1989 [168]).

Phytotoxic effects resulting in reduced biomass or growth can be observed when tissue concentrations of agricultural crops are in the order of 5 -10 µg/g dw. Concentrations below 2 µg/g dw, however, are found to stimulate growth (Balsberg-Pahlsson, 1989 [169]). Cd accumulation in monocotyledones like grasses or cereals is relatively low in comparison to leaves of many vegetable species (dicotyledones) (Sauerbeck, 1989 [168]).

Symptoms on above-ground plant parts like discoloration of leaves, wilting or specifically stunted growth are rarely observed in the field and are generally associated with concentrations higher than those mentioned above (Bergmann, 1993 [157]; Allaway, 1999 [158]). Therefore, with regard to plant growth or biomass production, quantitative aspects of Cd contamination are of minor relevance in comparison to qualitative aspects. El-Bassam (1978 [170]) reports that leaves of spinach and salad may contain up to 100 µg/g dm without any visible symptoms; these are concentrations, however, which are very relevant with respect to the food chain. With respect to health aspects, Cd concentration in vegetables should be < 1 µg/g dm and hence phytotoxic effects need not to be specifically addressed with respect to limit values.

2.4.3.2 Forests

No literature was available describing phytotoxic effects of cadmium on forest trees. Landold et al. (1989 [171]) carried out a survey of heavy metal contamination in spruce stands in Switzerland. They found that the mean needle content from branches of the upper tree part was 0.14 µg Cd/g dm, ranging from 0.05 to 1.60 µg/g dm. They also concluded that Cd values are influenced by deposition processes since generally higher values were found closer to areas with industrial activities.

Cadmium deposition in open field plots in North-Rhine Westphalia in remote areas have decreased very much from 1984 to 1993 from >1,1 µg/m^2*d to < 0,8 µg Cd/(m^2*d) (Schulte and Gehrmann, 1996 [172]). Measurements at the Egge Mountains, 180 km north-east of the Ruhr-area in Germany, showed mean values during 1986-1988 of 1,00 µg/(m^2*d) and about 2.27 and 1.24 µg/(m^2*d) at the edge of forest and within the forest, respectively (Prinz, 1990 [173]), demonstrating that impaction doubles deposition in comparison to the open field. Since cadmium mobility in soils increases with decreasing pH values, the ongoing deposition of acidic substances into forest ecosystems will keep Cd rather mobile and hence Cd accumulation in forest soils is very limited, but Cd has to be considered a serious contaminant for drainage systems (Johansson et al., 1995 [174]). It is known that Cd and other heavy metals are accumulating in ombrotrophic ecosystems. However, no quantitative data are available at present. Even though information is limited and dose-effect relationships for forest species are lacking, the conclusion made for vascular plants applies also for forests.

2.4.3.3 Fauna

Cadmium concentrations from up to 36.3 mg/kg have been measured in invertebrates (Daunderer, 1992 [175]). For annelids, a cadmium concentration of 3-12.6 mg/kg dry weight has been shown (IPCS, 1992 [87]). Ma et al. (1983 [176]) analysed soil and earthworms at varying distances from a zinc-smelting plant. Cadmium concentrations ranged from 0.1 to 5.7 mg/kg for the soil and 20 to 202 mg/kg for the worms, and there was a correlation between decreasing distance from the smelter and increasing cadmium levels. The bioconcentration factor of invertebrates reaches up to 100. Morgan and Morgan (1988 [177]) sampled earthworms from one uncontaminated site and fifteen metal-contaminated sites in the U.K. Cadmium concentrations in the worms ranged from 8 to 1786 mg/kg dry weight. They were generally higher than the soil levels, and the total soil cadmium explained 82 to 86 % of the variability in earthworm cadmium concentrations. The authors found some evidence that cadmium accumulation was suppressed in extremely organic soils.

2.4.4 Nickel

2.4.4.1 Vascular Plants

The toxic properties of Ni to corn and bean plants have been demonstrated as early as 1893 by Haselhoff, using solution culture techniques (Hutchinson, 1981 [178]). According to various studies in the seventies, Ni is considered as a plant essential element. Normal nickel concentrations in plants are < 10 µg/g dm and according to Vanselow (1966, cited in Hutchinson, 1981 [178]), nickel contents in leaves of most crop plants are below 2 µg/g dm (El-Bassam, 1978 [170]). Ni contents in soils range from 5 to 500 µg/g dm under natural conditions, depending very much on the origin of the bedrock material (Hutchinson, 1981 [178]). Contents of several 1000 µg/g dm are found in Serpentine soils in Italy, Scotland and the Balkans just to name some (Bergmann, 1993 [157]).

Nickel emissions are associated with metal refining processes. A famous example of Ni contamination of the environment happened in the vicinity of the INCO Nickel smelters in Sudbury, Ontario, Canada. Natural vegetation was totally devastated by emissions of sulfur dioxide and soils became more or less infertile due to heavy metals accumulation from smelting operations. For example, Ni concentrations found in plant tissue 60 km downwind were still elevated up to 40 µg/g dm (Hutchinson, 1981 [178]). Only recent extensive efforts in soil amelioration allow recolonization of vegetation (Gunn et al., 1995 [179]). Addition of sewage sludge to soils is a further major man-made Ni contaminant (Sauerbeck, 1989 [168]). There is a linear relationship between Ni content in soil and Ni accumulation in plant material, and mobility of Ni in soil is increasing with decreasing soil pH value. Furthermore, organic matter content as well as sorption properties are influencing factors (Sauerbeck, 1989 [168]). Liming is therfore considered as an appropriate means to reduce Ni uptake via roots (Bergmann, 1993 [157]). In the presence of organic matter, comparatively high Ni toleration by plants is associated with formation of organic Ni complexes, featuring a high stability and therefore not available for plant uptake (Bergmann, 1993 [157]).

According to El-Bassam (1978 [170]), plant tissue concentrations of 50 µg/g dm are associated with visible toxicity symptoms. According to a literature study carried out by Sauerbeck (1989 [168]), production of agricultural crops is reduced when plant tissue Ni concentrations range between 20 and 100 µg/g dm. Very recent evaluations carried out by the German Bund/Länderarbeitsgruppe Bodenschutz (LABO, 1998 [180]) associate phytotoxic effects with tissue concentrations of 45 µg/g dm. To avoid possible yield reductions of agricultural crops by nickel accumulated in agricultural soils, a soil Ni value of 1500 µg Ni/kg dm (extracted by NH_4NO_3) has been established as “check value”, where further investigations are recommended to be undertaken. The LABO group further suggests that Ni soil concentrations should not exceed 1900 µg/g dm in grassland used for any kind of animal production. They recommend in such cases specific measures to reduce Ni availability in soil in order to avoid further transfer of Ni into the biological chain.

To avoid Ni accumulation in agricultural soils with respect to possible phytotoxic effects, deposition of Ni should not exceed 4 mg Ni/(m^2d). Calculations are based on the following principle assumptions (Liebe et al., 1997 [181], Prinz & Bachmann, 1999 [182]):

- a *check* value of 1500 µg Ni/kg dm (extracted by NH_4NO_3)
- a background Ni value of 9-44 mg/kg in soils with loose stony material
- a layer density for agricultural soils of 1.5 t/m^3
- an accumulation horizon of 0.3 m
- an accumulation time of 200 years.

The deposition value is rather high due to the low mobility of Ni in soils, the relatively low background values in soils as well as the relatively low phytotoxicity.

2.4.4.2 Forests

No effect-related information was found for forest trees. Landold et al. (1989 [171]) carried out a survey of heavy metal contamination in spruce stands in Switzerland. They found that the mean needle value from twigs of the upper tree part was 5.16 µg Ni/g dm, ranging from 0.3 to 21.2 µg/g dm. However, differences between adjacent trees were rather high, indicating a great variance in Ni tissue contents. According to Schulte and Gehrmann (1996 [172]), the wet deposition in remote areas of North-Rhine Westphalia, Germany, ranges around 10 - 15 g Ni/(ha*yr) in 1984, and 5 and 10 g Ni/(ha*yr) in 1993, respectively. Again it can be generally said that Nickel availability in forest will increase with the input of acidic substances; however, no evaluation can be made with respect to possible effects on trees or terrestrial ecosystem level.

2.4.4.3 Fauna

In general, there are only few data on the effects of nickel - apart from data from laboratory experiments - available. Nickel levels in terrestrial and also aquatic organisms vary over several orders of magnitude, according to the species, the analysed tissues and environmental factors. Neuhauser et al. (1985 [183]) evaluated the impact of heavy metals on the soil ecosystem. They used the earthworm *Eisenia foetida* as a test organism. Following a 14-day exposure to nickel nitrate in artificial soil, the LC_{50} was calculated to be 757 mg/kg. Ma (1988 [184]) extrapolated an EC_{50} of 20 mg/kg nickel for *Lumbricus terrestris*. The bioconcentration factor of soil organisms for nickel is generally low (BCF 1 to 2).

2.4.5 Conclusions

The knowledge of possible effects of As, Cd, and Ni on terrestrial ecosystems is still rather limited and furthermore restricted to single compartments, i.e. plants or parts of the edaphon, for which some dose-effect relationships have been derived. Direct effects on vegetation by aerial heavy metal impact are rare and restricted to a very limited number of sources. Long-term effects are more related to heavy metal accumulation in soils. However, considering anthropogenic sources and some recent results from long-term observations on the deposition of heavy metals in reclaimed loess soils in North-Rhine Westphalia, only cadmium accumulated over an observation period of about 30 years (Delschen, 1999 [185]), while no such trend was observed for Ni. From the perspective of phytotoxicity and harmful effects to the edaphon, only cadmium remains to be considered as relevant. For the considerations also given in chapter 2.5.2, a deposition value of 5 µg/(m^2d) for cadmium will also cover the protection of terrestrial ecosystems.

2.5 Deposition

2.5.1 Introduction

For persistent compounds such as heavy metals or non-volatile halogenated organic pollutants, there is no simple one source - one receptor relationship, by which the transfer from the source to the environment could be described. Quite different and mutually interfering paths have to be considered when following the way of such a pollutant from the emission to the uptake by receptors, which are situated more or less close to the sources.

For systemicly acting pollutants like cadmium, the oral uptake from food or soil (children) can be more important than the inhalation, taking the carcinogenic effects on the respiratory tract apart. The input of persistent pollutants into vegetation and soils predominantly occurs via deposition of dust particles. In the long term, accumulation of metal compounds in soil can cause problems by increased uptake and contamination of plants. In the short term, dust deposits also cause contamination of above-ground plant parts. This can enhance transfer to humans via contact - children having contact with plants, bare soil or objects and take up heavy metals via contaminated hands - or by the consumption of vegetables.

Taking into account the levels of arsenic, cadmium and nickel compounds in the environment (see chapter 1.4), their toxicity and some other aspects, cadmium is without any doubt the most relevant metal for oral uptake. In chapter 2.1 it has been demonstrated that the main concern for arsenic is refered to its carcinogenic effects on the lung by inhalation, and that oral uptake is of minor importance with respect to this endpoint. Also for nickel, the risk evaluation is dominated by effects on the respiratory system. Consequently, only cadmium will be considered in the following for deriving proposals for deposition limit values. However, the principles of the methods outlined here are generally applicable for persistent pollutants.

The derivation for the local scale (chapter 2.5.2) is predominantly based on experiences made in Germany and Belgium, whereas Sweden and the Netherlands have chosen a different approach of looking into the widespread accumulation of cadmium and other persistent compounds in soils. This approach will be outlined in chapter 2.5.3. For European standard setting, these experiences should be compared with data from other countries. Partly because of the lack of published data and partly because of the limited time available, this could not be achieved by the Working Group. It is recommended to set up an international Working Group, for instance within the framework of the CAFE programme, which is specifically charged with examining the effects of deposition of heavy metals, including lead, and of persistent organic compounds on a European scale.

2.5.2 Derivation Of Deposition Standards For Local Scales

The paths which are important for a comprehensive and integrated management of emitted pollutants are shown in Figure 2.5.1. Already the effluents of installations have to be partitioned into deposited waste, released sewage and emissions into the air (see Figure 2.5.1). Only the latter path will be considered in some more detail.

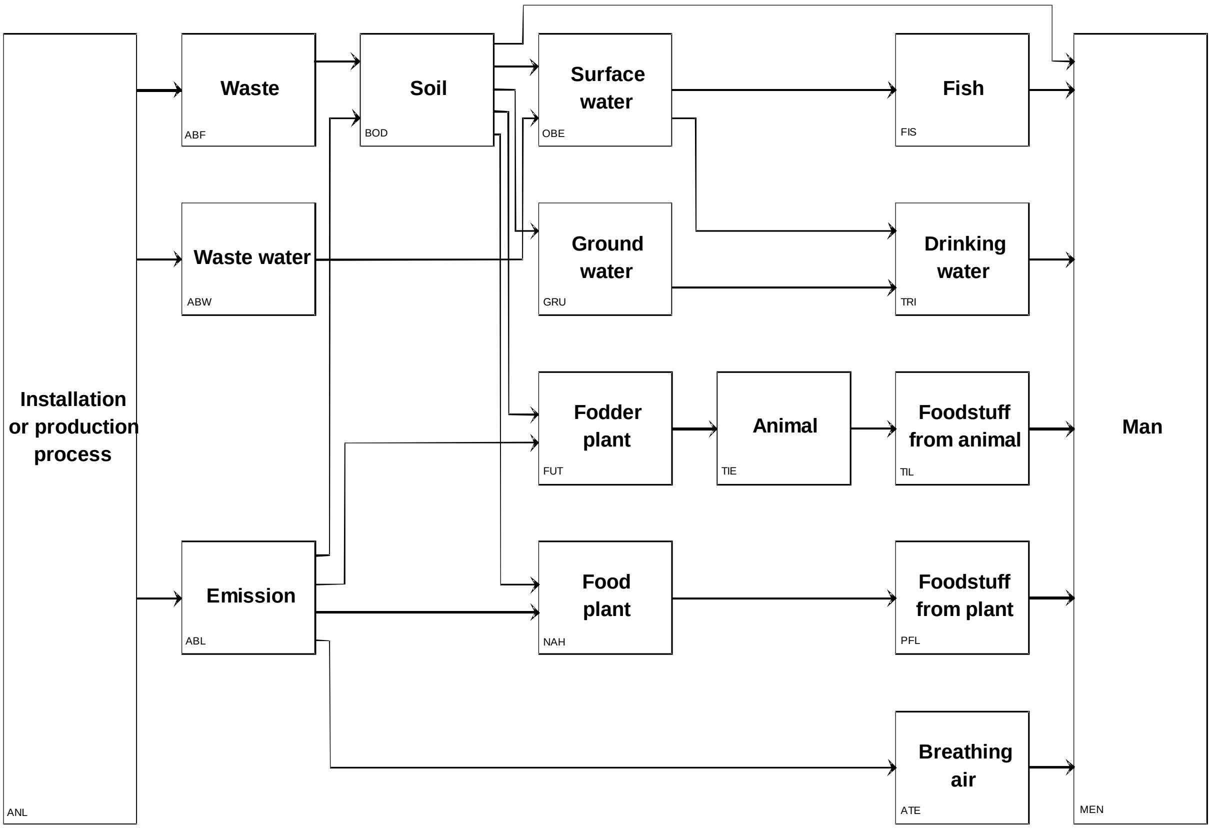


Figure 2.5.1: Model for the integrated management of emitted pollutants

The model is based on the following principles:

- The model is stream-oriented. Pollutants are transfered quantitatively from one compartment to the next one within given time-intervals. If physico-chemical transformations take place, they will mainly occur in the form of mobilisation and demobilisation. The pH value exerts a significant influence on these parameters in soils.

However, even more important are the effects of intermediate accumulation and release. There are some difficulties of dealing with these parameters on the time-axis.

- The model does not cover all possible impacts on the environment, but it is focussed on human health. The endpoint of all relevant transfers are effects on the human organism. Consequently, other possible ecotoxic effects like those on the edaphon of soils or the accumulation of persistent pollutants within soils are considered as less relevant within this context. It has to be mentioned, however, that for high concentrations of pollutants in soils and for high deposition rates, growth disturbances and visible damage to plants may not be neglected; they are covered in chapter 2.4. Likewise, grazing cattle may also be endangered. Nevertheless, the standards derived below are mainly based on the risk to human health by the uptake of contaminated food, which may occur either for the public in general or more specifically for garden owners close to sources. As has been already mentioned in chapter 2.4, this pathway is the most sensitive one and will afford lower standards than considering ecotoxic effects such as damages to plants only.

- The model predominantly adresses local pollution levels near sources or in agglomerations. Typical scales are areas from several hundred square meters (e.g. gardens) to several square kilometers.

At least near sources, depositions and concentrations are not necessarily closely correlated, as they represent different size spectrums of the particulate matter which, in addition, may be emitted by different sources within a factory. For example, the coarse dust connected with high depositions is mainly caused by fugitive emissions such as transport processes or resuspension from stock piles. Consequently, high deposition rates of coarse particles can be combined with only moderate heavy metal concentrations in ambient air, which are mainly caused by fine particles (see chapter 1.2). Limiting cadmium concentrations in ambient air only may thus underestimate the risk posed by oral uptake of vegetables or soil (by playing children) in the vicinity of industrial sources.

The derivation of deposition standards presented in the following is mainly focussed on the risks to human health caused by oral uptake of contaminated food supplies or soils in regions close to sources. Possible ecotoxic effects in remote regions such as widespread transboundary air pollution and accumulation in soils are not explicitely taken into account (cf. Chapter 2.5.3).

It has to be borne in mind that the quantitative relationships used for the derivation below are generally chosen as conservative conventions out of the whole range of possible values. One cause of the variations occurring in the real world is, for example, the different pH value in soils. However, for the derivation of deposition limits, this variation had to be somewhat simplified and condensed from ranges to figures, because otherwise a whole set of different deposition limit values would result, for example for agricultural soils with different compositions. Such a set would be hardly operational for the risk manager.

2.5.2.1 Dust accumulation On The Above-Ground Biomass

The following assumptions are used as starting points:

- The acceptable or tolerable dose of cadmium uptake by man is set to 0.75 - 0.95 µg (kg bw)$^{-1}$ d^{-1} (bw stands for body weight, d for day). This dose was originally defined by the JECFA [186] as a provisional tolerable weekly intake (PTWI) for an adult, i. e. 400 - 500 µg p^{-1}w^{-1} (p stands for an adult person, w for week), but transformed here to a daily basis and a 75 kg body-weight for an average adult. The currently accepted dose, published by JEFCA in 1996 [187], amounts to 1 µg (kg bw)$^{-1}$d^{-1} and is comparable to the assumption made above.

Tolerable dose	0.75 ... 0.95 µg (kg bw)$^{-1}$d^{-1}

- This dose has to be alloted to the different uptake routes. This task is extremely difficult because the relative importance of the uptake routes may change from one case to the other. Therefore, conventions are necessary including corresponding uncertainty factors. The uptake by inhalation is considered for this purpose as small and set equal to zero. Therefore, the whole tolerable dose is reserved for the partial oral dose for vegetables.

Partial dose air	0,00 µg (kg bw)$^{-1}$d^{-1}

Partial oral dose (vegetables)	0,65 .. 1,00 µg (kg bw)$^{-1}$ d^{-1}

- In the sense of a worst case assumption it is estimated that garden owners consume 250 g leafy vegetables from their own production per day.

Transfer plant ⇒ man	250 g fw d^{-1}

(fw stands for fresh weight)

- Taking a percentage of 10 to 15 % dry matter from the fresh weight and the assumptions given above as starting points, the maximum allowable cadmium concentration in vegetables can be calculated to be 2 µg (g dm)$^{-1}$. This plant limit corresponds to the recommendation of the German authorities (BGVV, Berlin) for the cadmium content in vegetables and also to the Belgian limit value for vegetables (see below).

Plant limit	2 µg (g dm)$^{-1}$

- It is further assumed that this concentration may be caused half by uptake from the air and half by uptake from the soil via roots (dm stands for dry matter). This results in a value of 1 µg (g dm)$^{-1}$.

- The transfer factor air ⇒ plant is highest for leafy vegetables and fodder plants, defined here as [188]:

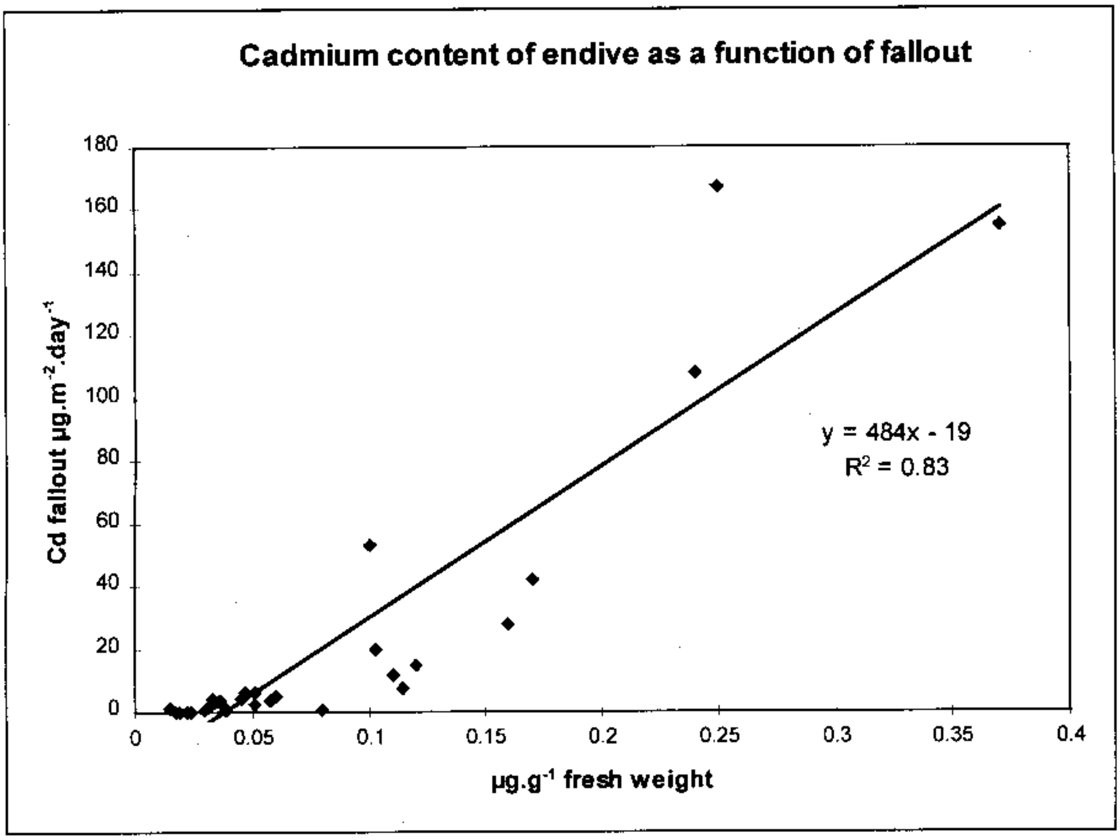
Transfer air ⇒ plant	10 [µg m^{-2}d^{-1}] : 1 [µg (g dm)$^{-1}$]

- On basis of this transfer factor for air ⇒ plant and considering the above aspects, the following maximum deposition can be derived:

Resulting deposition limit for cadmium	10 µg m^{-2} d^{-1}

Using an experimental rather than the theoretical approach presented above, the Belgian Centrum voor Onderzoek in Diergeneeskunde en Agrochemic (CODA) derived a range of tolerable cadmium depositions of 5 - 100 µg/$m^{-2}d^{-1}$ for different leafy crops such as spinach, lettuce, endive, lambs lettuce, celery and curled kale. Lettuce ranked at the upper end, curled kale at the lower end of this range [189].

The vegetables were grown in containers in unpolluted soil in the periphery of Hoboken, near a lead copper smelter. After exposure, the vegetables were harvested and analyzed for their cadmium content. By means of deposition measurements which were performed simultaneously at the sites of exposure, linear regressions correlating cadmium deposition and cadmium contents in the different vegetables (unwashed) could be established. Two examples (endive and lambs lettuce) are shown in Figure 2.5.2 [189]. Taking the Belgian limit value for vegetables (0.2 µg$(gfw)^{-1}$, for curled kale 0.1 µg$(gfw)^{-1}$) and using the linear regressions, the said range of 5 - 100 µg/$m^{-2}d^{-1}$ can be derived [189].



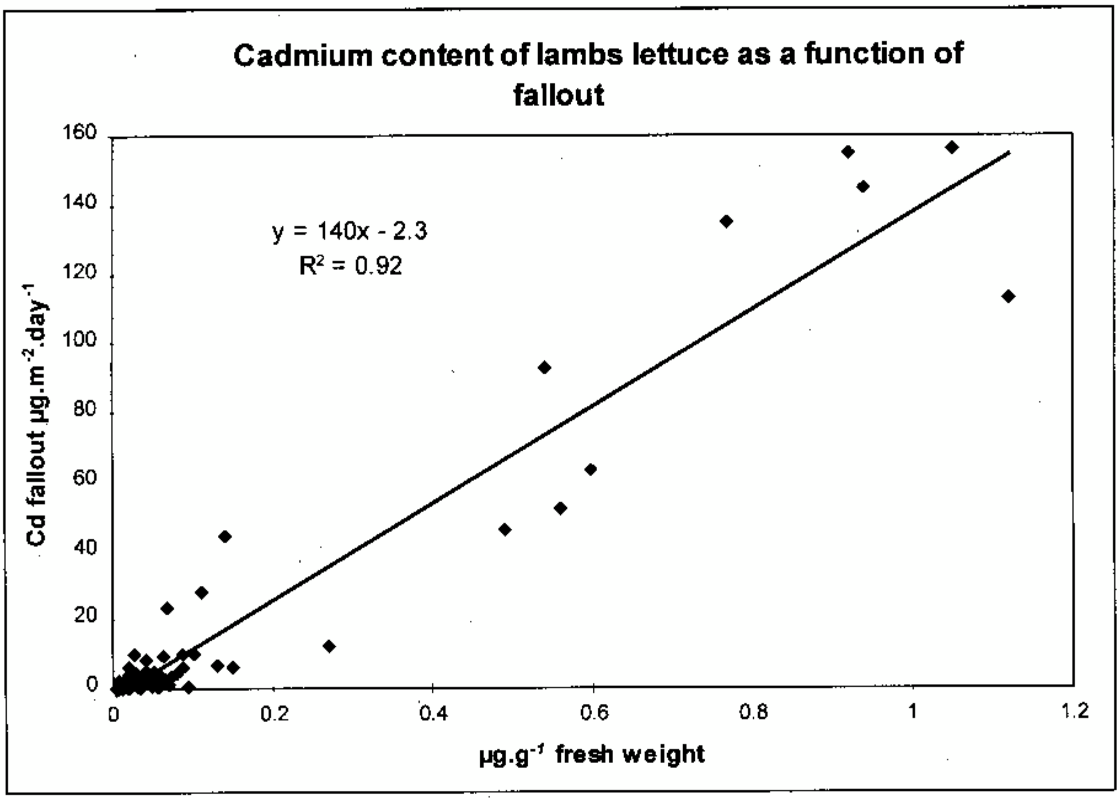


Figure 2.5.2: Correlation of cadmium content in vegetables grown in unpolluted air and cadmium deposition near Hoboken, Belgium

The Belgian limit value for vegetables based on fresh weight closely corresponds to the German plant limit of 2 µg(gdm)$^{-1}$ (dry weight), and also the resulting deposition limit falls within the same range.

However, it should be borne in mind that the derivation of the deposition limit so far only covers the short-term dust accumulation of cadmium on the above-ground biomass, and neglects the long-term effects on the soil or the edaphon.

2.5.2.2 Cadmium Uptake Of Vegetables From The Soil

In order to take into account the uptake of cadmium by vegetables from the soil, the following transfer factor [190] sets the starting point:

Transfer soil ⇒ plant	[2,5 µg (g dm)$^{-1}$] : [1 µg (g dm)$^{-1}$]

- Using the above mentioned assumption that the concentration in plants may be caused half by uptake from the air and half by uptake from the soil via roots, this transfer factor results in limiting the soil concentration to:

Soil limit	2.5 µg (g dm)$^{-1}$

- The transfer factor air ⇒ soil is calculated on the basis of 100 years exposure time, a soil density of 1.3 t m^{-3}, related to dry weight, 20 to 25 cm mixing depth for arable land and 100 % persistency:

Transfer air ⇒ soil	4 [µg m^{-2}d^{-1}] : [µg (g dm)$^{-1}$]

- The high persistency of 100 % is a worst case assumption and holds definitely not true for forest soils, particularly under conifers. Due to the low pH value, cadmium is more mobile within forest soils.

With these assumptions, the above derived maximum deposition of 10 µg m^{-2} d^{-1} results in a maximum soil concentration of 2.5 µg (gdm)$^{-1}$. To take into account the existence of particularly high soil burdens which cannot be ruled out close to sources, a safety factor of 2 should be applied and leads to the following proposal based on the oral uptake from vegetables:

Deposition limit	5 µg m^{-2} d^{-1}

2.5.2.3 Additional Effects Which Should Be Adressed

A number of additional effects should be considered when setting a deposition limit:

- According to several experiments [191], the yield in a spectrum of several crops is reduced on the average by 12 % when dusted with 100 to 230 µg m^{-2} d^{-1} for an exposure time of 17 to 45 days. Because of the sigmoid deposition-effect curve, the above defined maximum cadmium deposition would correspond to yield losses of less than 1 %. Therefore, the vegetation can also be considered as sufficiently protected by the limit value derived above.

- Heavy metals including cadmium also show toxic effects on plant roots, especially in the first developing stages, but at much higher concentrations of hundreds of µg (g dm)$^{-1}$ than considered here [192]. Also cattle is sufficiently protected from the uptake of contaminated forage if the above derived deposition limit value is met.

- The influence of cadmium depositions on cadmium concentrations in groundwater under forest soils as most sensitive target is also an important issue which has to be addressed. In acidic soils, as most forest soils are, cadmium taken up by the soil percolates nearly quantitatively to the groundwater horizon because of its high mobility. Roughly estimated, a cadmium deposition of 1 µg m^{-2} d^{-1} over open field is equivalent to 2 µg m^{-2} d^{-1} under canopy [193]. According to experiments in a 35 years old stand of Norway spruce, the resulting cadmium concentrations in seeping water collected by lysimeters in 25 cm depth range under these conditions between 1.1 and 3.1 ng ml^{-1}. The limit for the cadmium concentration in groundwater can be set according to the EC directive EG 80/778 to be 5 ng ml^{-1}. It can be concluded that the deposition limit derived above is definitely too high for those sensitive areas where groundwater is used for drinking water supply. For this reason and following the precautionary principle, the limit value derived for the oral uptake of vegetables should be modified for those sensitive areas.

Another important aspect is the protection of the soil, where the accumulation of persistent toxic compounds should be limited or prevented. This may be an upcoming issue for EC legislation and has been recently addressed by the German ordinance for soil protection and contaminated sites [194]. The following new features have been introduced:

- A background contamination was taken into consideration as well as an exposure period of 200 years.

- Two types of thresholds for soil concentrations were introduced:
  "trigger values" and "action values". "Trigger values" demand further investigations when exceeded. "Action values" are levels calling for immediate remediation measures without further investigations, if exceeded. The values for cadmium are as follows: a “trigger value” of 10 mg (kg dm)$^{-1}$ Cd, extractable by aqua regia, for playgrounds of children; an “action value” of 0.04 – 0.1 mg (kg dm)$^{-1}$ Cd, extractable by ammonium nitrate, for agricultural land raising vegetables and crops as well as for gardens; an “action value” of 20 mg (kg dm)$^{-1}$ Cd, extractable by aqua regia, for pasture land. The resulting deposition limits correspond roughly to ranges from 2.5 µg m^{-2} d^{-1} (sensitive crops, playground for children) to 16 µg m^{-2} d^{-1} (pastures) [195]. Taking the lower bound of this range would result in a limit value for cadmium deposition of 2.5 µg m^{-2} d^{-1}.

- A limit for see page water for the protection of groundwater is set to be 5 ng ml^{-1} (“trigger value”). This leads, however, to the same conclusions as already presented above.

Summarizing all aspects discussed above, a deposition limit of 2.5 µg m^{-2} d^{-1} can be considered as a generally applicable limit for cadmium deposition which guarantees far-reaching safety for man and the environment including sensitive targets as the protection of groundwater or children's playgrounds. It must be stressed, however, that this limit does not prevent cadmium to accumulate within soils, even though the accumulation will be rather slow. A prevention of cadmium accumulation affords a much higher level of protection and is considered in chapter 2.5.3.

If the principal aim is to protect from the oral uptake via vegetables in agglomerations and industrial areas where the most sensitive compartments of the ecosystem do not occur, a limit value of 5 µg m^{-2} d^{-1} applies.

The EEB is of the opinion that the starting point of the derivation, the currently accepted tolerable cadmium dose of 0.75 - 0.95 µg(kg bw)$^{-1}$d^{-1}, is too high and should be lowered to less than 0.5 µg(kg bw)$^{-1}$d^{-1}. This point of view is based on the conclusions given by Järup et al. [110] (1998), that from a life-long average exposure to cadmium via food of 70 µg per day (corresponding to the present tolerable dose), a percentage of 7 % of the adult general population would be expected to develop cadmium-induced tubular damage. For high-risk groups, the percentage would be even higher (up to 17 %). Consequently, the EEB considers a deposition limit of 2.0 µg $m^{-2}d^{-1}$, as already applied in Switzerland, as a reasonable and generally applicable limit, which has to be met in agglomerations and in industrial areas.

Depending on the goods to be protected, the majority of Working Group recommends to set a limit value for cadmium deposition for local scales within the following range:

2.5 - 5 µg m^{-2} d^{-1}

2.5.3 Widespread Accumulation Of Cadmium In Soils

It has been pointed out in subchapter 2.5.2.3 that the proposed deposition limit of 2.5 - 5µg $m^{-2}d^{-1}$ for local scales will not protect from a slow accumulation of cadmium within soils, which, depending on the background concentration, may reach critical levels after one or several centuries. To prevent any accumulation, the cadmium intake into the soil by all routes (fertilizers, deposition etc.) must not exceed the outflows.

Cadmium balances in agricultural soils have been examined in Sweden [196,197] (table 2.5.1) and the Netherlands [198]. Cadmium levels in agricultural soils in Sweden vary between 0.2 and 0.4 mg Cd kg^{-1} top soil; both higher and lower values can be found. Corresponding figures for most other EC countries are in the same range.

Table 2.5.1: Example for balance calculations of Cd input and output for some agricultural soils in southern Sweden (µg Cd $m^{-2}year^{-1}$)

	Soil No.				
Inflows	1	2	3	4	5
Atmospheric deposition	35	37	60	37	60
P-fertilizers	15	15	28	28	20
Manure, lime	67	16	2	6	67
Outflows					
Leaching	6	6	6	6	6
Crops	35	16	21	10	67
Increase top soil (% $year^{-1}$)	0.12	0.049	0.11	0.092	0.12

It can be taken from table 2.5.1 that Cd deposition (35 - 60 µg $m^{-2}year^{-1}$, corresponding to 0.096 - 0.16 µg $m^{-2}d^{-1}$) outweighs the input from P-fertilizers even in southern Sweden (average input of 20 µg $m^{-2}year^{-1}$ Cd caused by an average application of P from about 8 kg P ha^{-1}). The other sources are manure and lime.

Several factors are influencing the uptake of cadmium by crops, the most important are the cadmium content in the top soil and the pH. As can be inferred from the table, the input of cadmium gives rise to a slow increase of the cadmium levels.

The outflows presented in table 2.5.1 vary between 16 and 73 µg Cd $m^{-2}year^{-1}$. If half of this outflow is alloted to the input by fertilizers and half to the input by deposition, the acceptable atmospheric deposition consistent with no accumulation will be about 10 to 40 µg Cd $m^{-2}year^{-1}$, corresponding to 0.027 - 0.11 µg Cd $m^{-2}d^{-1}$.

Similar results have been obtained in the Netherlands [198] by an evaluation of the wash out of cadmium from clay and other soils, compare table 2.5.2 [198]. For clay soils, a wash out of 1 - 2 gramme cadmium per hectare and year was determined. For other soils, the wash out is higher. Because clay soils often occur in the Netherlands, this soil was taken as the basis for a Dutch non legal binding target value. To prevent accumulation of cadmium in all kinds of soils, the lower bound of the wash out range for clay soils was taken: 1 g Cd $ha^{-1}year^{-1}$, corresponding to 100 µg Cd $m^{-2}year^{-1}$ (0.27 µg Cd $m^{-2}day^{-1}$) [199].

Table 2.5.2: Leaching of Cd to be expected from Dutch soils at equilibrium with the Cd concentrations in the soils given in the last row of the table

Type of soil	Leaching (g Cd•ha^{-1}year^{-1})	Corresponding Cd concentrations in the soils (mg Cd kg^{-1})
Sand poor in humus	4 - 6	1.3 - 2
Humous sand and sandy clay	2 - 5	0.6 - 1.7
Clay	1 - 2	0.3 - 0.7
Peat	5 - 7	1.7 - 2.3

The range derived to prevent any accumulation is about one order of magnitude (Netherlands) and more than one order of magnitude (Sweden) lower than the toxicology-based deposition limit for the local scale, and also much lower than the depositions currently measured in urban areas of central and western Europe (compare table 1.14 in chapter 1.4.2). This holds true also for some rural areas. It should be kept in mind, however, that the leaching rate supposed in Table 2.5.1 for Sweden (6 µg Cd m^{-2}year^{-1} or 0.02 µg Cd m^{-2}day^{-1}) is much lower than the leaching rate supposed in the Dutch data in Table 2.5.2 (1-2 g Cd ha^{-1}year^{-1} or 0.3-0.6 µg Cd m^{-2}day^{-1}) and that the Dutch calculation does not include outflows via crops which, in the Swedish examples, amount to 2-11 times the outflow by leaching.

The Working Group recommends that cadmium balances should be examined also for agricultural soils in other countries with different climatic and geological conditions and, possibly, different application of fertilizers. This work should be coordinated by the Working Group already mentioned above, for instance in the framework of the CAFE process.

The big gap between current deposition levels and a steady state assumption in many European areas underlines the need for a significant further reduction of cadmium input into soils with the aim to avoid any accumulation, following the precautionary principle. Taking into account that the general intake of cadmium by food from 10 - 20 µg Cd day^{-1} has only a narrow margin of safety even in Sweden to cadmium intakes which can result in a slight increase in early signs of kidney dysfunction for risk groups such as women with low iron levels, a long-term policy to further reduce the cadmium deposition and other inputs into soil and crops is definitely called for.

On the other hand, the Working Group has some doubts whether limit values which refer to large scales (for example the EMEP grid width) and which are so far below current levels in many urban and even some rural areas are an effective policy instrument. The Working Group feels that the development of a joint EC policy for cadmium in products, in fertilizers and for the reduction of cadmium emissions to air and water together with a close cooperation with UNECE is the strategy which should be followed.

2.6 Proposals For Limit Values In Air

2.6.1 Introductory Remarks

It must be recognised at the outset that there is no perfect way to derive limit values for air pollutants. Any procedure chosen necessarily includes a number of uncertainties. For example, there will be uncertainties in the extrapolation between species, the assessment of exposures in epidemiological studies, and the extrapolation from workers to the general public. Furthermore, there is a deficit in the knowledge about the shape of the dose-response function at concentrations much lower than those employed in the studies which are available. These deficits and uncertainties have to be acknowledged in the process of setting limit values.

As a starting point for their work, the Working Group used the most recent health-based assessments published by the World Health Organization. In some areas, additional material has emerged since the WHO assessments were performed. Where appropriate, this material has been considered by the Working Group.

2.6.1.1 Non-Cancer Effects

According to the WHO proposals for the derivation of guidance values for health-based exposure limits (IPCS/WHO, 1994 [200]), an uncertainty factor of 10 is used to consider inter-species differences. This factor of 10 corresponds to two factors of slightly more than 3 (exactly the square root of 10), i.e., 3.2 for toxicokinetics (uptake, distribution, excretion) and 3.2 for toxicodynamics (specific effects). Another factor of 10 is applied for inter-individual differences (sensitive subgroups). Using LOAEL instead of NOAEL, the application of an additional uncertainty factor (3, 5 or 10) is proposed by WHO. Also, exposure time has to be taken into account adequately. The use of a separate uncertainty factor to allow for uncertainties in the database is also under discussion, e.g., a factor of 3 in case of missing data about effects on reproduction. The uncertainty factors mentioned here are default factors which may be modified based on scientific evidence.

2.6.1.2 Carcinogenic Effects

To harmonise the process of deriving limit values for carcinogenic air pollutants with the procedure used in the EC Directive on Drinking Water, the Working Group was given the task to consider that the additional lifetime risk of cancer should be kept to less than one in a million.

The European Commission has published a Technical Guidance Document with regard to performing risk assessments for carcinogens and other substances [201]. This document differentiates between genotoxic and non-genotoxic carcinogens: „**Genotoxic carcinogens** induce cancer as a consequence of the **direct** interaction of the substance, or an active metabolite, with DNA“ [201, p. 116]. In this case, a threshold cannot be identified, and extrapolation of the dose-response function to zero is used. In the document it reads further: „**Non-genotoxic carcinogens** are believed to exert their carcinogenic effects through mechanisms other than genotoxicity“ and „It is generally assumed that these mechanisms can be associated with threshold doses, and it may be possible to define no-effect levels for the underlying toxic effects of concern“ [201, p. 117]. Therefore, if a lack of genotoxic activity were convincingly established and a NOAEL identified from the experimental data then this level could be used in setting a concentration limit for the carcinogen in question.

However, the technical guidance document, on another page, gives a definition of genotoxicity in general which is not in full accordance with the above mentioned definitions: „Genotoxicity is a broader term and refers to potentially harmful effects on genetic material, which may be mediated directly or indirectly, and which are not necessarily associated with mutagenicity. Thus, tests for genotoxicity include tests which provide an indication of induced damage to DNA (but not direct evidence of mutation) via effects such as unscheduled DNA synthesis (UDS), sister chromatid exchange (SCE) or mitotic recombination, as well as tests for mutagenicity“ [201, p. 101]. Therefore, if there are carcinogens which have harmful effects on genetic material which are mediated indirectly, these carcinogens are **not** defined as being **genotoxic carcinogens** inspite of their general genotoxicity.

With respect to carcinogenicity, the potential health risk is usually described as the **unit risk**, which - in the case of inhalation - is defined as the additional risk due to lifetime exposure to a chemical compound at a mean concentration of 1 µg/m³. The estimate of this additional risk can be given in two different ways, either as a maximum likelihood estimate (MLE) or (which is the case more frequently) as the upper bound of the 95 % confidence interval of the slope of the extrapolated/modelled exposure-effect curve at the concentration of 1 µg/m³. The MLE provides the ”most accurate” estimate, but it does not reflect the amount of inherent uncertainty. With increasing uncertainty of the estimate, e.g., if the data base is relatively small, the upper bound of the 95 % confidence interval will become higher. If risk estimates are based on the latter, the estimate will be more on the „safe side”, but an overestimation of the risk is more probable than in the case of using the MLE.

For low concentrations, linear extrapolation to zero is usually used. In the case of arsenic, cadmium and nickel, this leads to concentrations in the nanogramme/m³ range. These concentrations are several orders of magnitude below those at which experimental or epidemiological data are available to derive the dose-response function. In many cases, biological concentration-effect relationships are S-shaped, i.e., they have a sub-linear shape in their lower part (the extreme form of sub-linearity would be a threshold). If the dose-response function is sub-linear, then the method of linear extrapolation will overestimate the ”true” risk. If, in contrast, it is supra-linear, linear extrapolation will underestimate the risk. It is essential to note that for the elements in question (like for many others), the exact shape of the dose-response function at low concentrations (nanogramme/m³ range) is not known.

An alternative to the unit risk approach for deriving air quality standards has been used by the Expert Panel on Air Quality Standards in the UK for several genotoxic carcinogenic pollutants (benzene, 1,3-butadiene and polycyclic aromatic hydrocarbons (PAHs)). The rationale behind this approach has been published (Maynard et al., 1995 [202]). It is based on identifying a level in a reasonably sized epidemiological study at which it is difficult to demonstrate a clearly increased risk. It is, of course, acknowledged that for a genotoxic carcinogen this level does not represent a true threshold and that a large enough (but probably non-practicable) epidemiological study might well demonstrate that there is still a risk at that level. However, on a pragmatic basis, this level is then used as a starting point to which uncertainty factors are applied. The remaining level of risk is not defined but is supposed to be probably very small. This method has uncertainties, too, but does not give the false impression of accuracy of the unit risk factor approach.

It must be accepted that no method will give an accurate estimate of the risk level as the shape of the dose-response function at concentration levels lower than those encountered at the workplace is unknown.

2.6.1.3 Speciation

In air, an element can occur in different chemical forms or species but measurements very often only provide concentration data for the total amount of this element without any separation into the different species or compounds. This has important consequences for estimating the carcinogenic risk posed to the population as different species and compounds may have different carcinogenic potency.

Basically, this applies to all three elements under consideration here, but it has particular relevance to nickel where the available epidemiological evidence comes from occupational settings where workers may be exposed to different nickel species compared to the general population. Thus, in the case of exposure to As, Cd, and Ni in air where there can be different species, it is important to consider how the „one-in-a-million principle for an individual carcinogen“ can be applied.

Due to practical reasons (cost and feasibility), almost all measurements of elements in air do not differentiate between species. This is likely to remain the case for the foreseeable future. Thus, it would not make much sense to define limit values for single compounds or species of an element. Nevertheless, the toxic potential and the relative abundance of the various species are taken into consideration where such information is available. It is obvious that limit values based solely on the most toxic compound or the compound with the highest carcinogenic potency will overestimate and „err on the safe side” with respect to health risks. However, it is not possible to quantify precisely the error involved.

2.6.1.4 Steps To Derive A Limit Value

Based on the above mentioned considerations, the Working Group has chosen to derive a limit value for each element according to the following steps:

1. Derive a limit value based on non-cancer effects.
2. Derive an appropriate limit value for cancer effects (taking into account genotoxicity, one-in-a-million excess lifetime risk, alternative approaches, uncertaintities)
3. Compare the cancer and non-cancer approaches to see whether the two approaches give compatible limit values.
4. If necessary, use expert judgement to arrive at a reasonable compromise that provides an appropriate level of protection.

2.6.2 Limit Value For Arsenic

2.6.2.1 Limit Value Based On Non-Cancer Effects

Starting point

Following inhalation of arsenic, the most relevant non-cancer effects are irritation of the upper respiratory tract, peripheral neuropathy and cardiovascular effects, such as Raynaud‘s disease and increased blood pressure. The lowest arsenic concentration at which these effects have been found after exposure at the workplace over several years was 50 µg As/m^3 (Table 2.6.1). This concentration is taken as the LOAEL.

Trivalent arsenic has a much higher affinity to sulfhydryl groups and is therefore more active than the pentavalent compounds. One might, therefore, consider the definition of separate limit values for trivalent and pentavalent arsenic compounds. However, as there is a significant in vivo conversion between the two valencies, limit values should be based on the most active form: trivalent arsenic (de Wolff & Edelbroek, 1994 [22]).

Uncertainty factors

The exposure conditions encountered at the workplace have to be transformed into a chronic exposure of the general population. If mechanistic or physiological considerations do not preclude to do so, this is usually done by linear extrapolation. Assuming 8 working hours per day and 225 working days per year, the correction factor amounts to 24/8 x 365/225 which is 5 in a rounded form.

Table 2.6.1: Summary of toxic effects in humans after occupational inhalation exposure to inorganic arsenicals

Health endpoints	Effect	Lowest observed effect level (concentration)	Reference
Respiratory effects	irritation of upper respiratory tract in workers exposed to arsenic dusts	0.1-1 mg As/m^3	Ide and Bullough, 1988 [25]; Perry et al., 1948 [26]
Neurological effects	after inhalation of inorganic arsenicals, peripheral neuropathy in workers	0.05 mg As/m^3	Blom et al., 1985 [31]; Lagerkvist and Zetterlund, 1994 [30]
Gastrointestinal effects	nausea and anorexia in one worker (but not in another) exposed to arsenic trioxide dust; no other studies with quantitative exposure data available	0.11 mg As/m^3	Ide and Bullough, 1988 [25]
Cardiovascular effects	smelter workers exposed to arsenic trioxide dusts have a higher incidence of Raynaud‘s disease and increased constriction of blood vessels in response to cold	0.05-0.5 mg As/m^3	Lagerkvist et al., 1986; 1988 [37,38]
Skin effects	hyperkeratoses and hyperpigmentation are common in people exposed by the oral route, but have very rarely been reported after inhalation exposure	no data	ATSDR, 1998 [8]
Haematological effects	anaemia is often noted in humans exposed by the oral route, but has not been observed after inhalation exposure	no data	ATSDR, 1998 [8]

To extrapolate from the lowest concentration at which effects have still been observed (LOAEL) to a concentration without any observed adverse effects (NOAEL), it has been proposed to use an uncertainty factor between 3 and 10 (WHO, 1994b [200]). In the case of arsenic, effects on several organs/systems (neurological and cardiovascular effects) are found to start at concentrations of 50 µg/m³ (see Table 2.6.1). An uncertainty factor of 10 is judged to be adequate because effects seen on several organs/systems suggest that the appropriate uncertainty factor for the extrapolation from LOAEL to NOAEL should be at the upper range of factors proposed for this extrapolation step.

The usual default value of 10 is introduced to account for the variability within the human population (including children, elderly and ill people) (WHO, 1994b [200]).

Limit value

Using the above-mentioned factors of 5, 10, and 10 (= 500), a limit value for the arsenic concentration in ambient air of 50 µg/m^3 : 500 = **100 ng As /m³ based on non-cancer effects** can be proposed.

Proposals made by other Organisations

The U.S. EPA has not established a Reference Concentration for inorganic arsenic.

In the framework of their Hot Spots Program, the Californian EPA has published a draft with the derivation of an Inhalation Chronic Reference Exposure Level for inorganic arsenic for public comments (OEHHA 1999 [203]. Based on a LOAEL of 200 µg As/m³ (exposure for 4 hr/day during gestational days 9-12) with reduction in fetal weight in mice (Nagymajtenyi et al., 1985 [204]) as the critical effect, a REL of 0.03 µg As/m³ was proposed.

IPCS had the intention to give an accurate and balanced presentation of critical data relevant to the development of hazard characterisation and exposure-response analysis. However, they did not intend to provide quantitative estimates of risks or their uncertainties or guideline values for human exposure (IPCS, 1999 [67]).

2.6.2.2 Limit Value Based On Carcinogenic Effects

Route of exposure and carcinogenicity

There is ample evidence in the literature that arsenic is a human carcinogen. The target organ varies depending on the route of exposure. Oral uptake of arsenic has been associated with skin cancer, whereas inhalation is considered to be the route which causes malignancies of the lung. Any limit value for arsenic in air should, therefore, be related to lung cancer risk in the general population.

Genotoxicity and shape of the dose-response relationship

With regard to the mechanism of action, there are differing opinions on the question of genotoxicity of arsenic and on the shape of the exposure-response relationship. However, as information on mechanisms is mainly based on dose-response functions from *in vitro* studies, extrapolation to *in vivo* conditions may be questionable.

The observed inhibition of DNA-repair enzymes and the induction of chromosomal aberrations and cell proliferation (Rudel et al., 1996 [47]; ATSDR, 1998 [8]) can be classified as indirect genotoxic mechanisms of arsenic. DMA (dimethylarsinic acid) was found to inhibit

DNA synthesis and to induce chromosomal aberrations (Chan and Huff, 1997 [205]). However, there are other observations that suggest a radical mechanism for DNA damage by DMA (Chan and Huff, 1997 [205]). The findings that DMA increases the formation of superoxide anion and hydroxyl radicals and that DMA itself can form the dimethylarsenic peroxyl radical, which can directly damage DNA, might argue against a threshold hypothesis.

A recent review (Clewell et al., 1999 [206]) states that no single hypothesis for the mechanisms of inorganic arsenic carcinogenicity has widespread support. Inorganic arsenic has repeatedly been shown to act as a comutagen in vitro and as a cocarcinogen in vivo; it is clastogenic, producing chromatid aberrations, but does not produce point mutations at single gene loci. The authors propose a cocarcinogenic mode of action in which inorganic arsenic acts primarily on intermediate cells deficient in cell cycle control at a late stage in a preexisting carcinogenic process. This interaction would enhance genomic fragility and accelerate conversion of premalignant lesions to more aggressive, clinically observable tumors. An indirect effect of inorganic arsenic on DNA repair would be consistent with the expectation of a nonlinear dose-response rather than the linear dose-response traditionally assumed for mutagenic carcinogens.

A paper by Kirsch-Volders et al. (2000 [206a]) describes the theoretical background of possible threshold considerations for carcinogens. The conclusions drawn by the authors of this paper are carefully worded and end with the following statement: "If data are available, which show that the mechanism(s) assumed to be responsible for the carcinogenic effect do(es) not occur at a dose below a certain level and that the effect can be discerned from spontaneous event, a real threshold might be suggested." However, such data are not available in the case of arsenic.

When evaluating carcinogenicity data after oral exposure to arsenic via drinking water, Byrd et al. (1996 [207]) found that skin cancer prevalence was a highly non-linear function of arsenic dose rate suggesting the existence of a threshold. However, kidney and bladder cancer showed linear dose-response relationships, but this aspect is of limited weight because according to the authors, it cannot be ruled out that these cancers were caused by other chemicals correlated in concentration with arsenic.

Under contract with U.S. EPA, Eastern Research Group convened an Expert Panel on Arsenic Carcinogenicity on May 21 and 22, 1997. Based on epidemiological studies, the Expert Panel concluded that arsenic is a human carcinogen via the oral and inhalation routes. They agreed that arsenic and its metabolites do not appear to directly interact with DNA, and that for each of the modes of action regarded as plausible, the dose-response would either show a threshold or would be nonlinear. At low doses, the dose-response would likely be truly nonlinear, i.e., with a decreasing slope as the dose decreased. However, at very low doses such a curve might be linear but with a very shallow slope, probably indistinguishable from a threshold (Eastern Research Group, 1997, as quoted by U.S. EPA IRIS Substance file - Arsenic, inorganic [208]). It should be mentioned that these statements are presented in the IRIS Substance file in the chapter concerning carcinogenicity of oral exposure to arsenic.

In the view of an IPCS draft, support for a non-linear relationship is provided by studies on arsenic metabolism (saturation of methylating enzymes) and genotoxicity. In addition, the IPCS draft argues that if arsenic is essential for humans as this has been shown for animals, the dose-response curve cannot pass through zero exposure (IPCS, 1999 [67]). However, no explanation is given why essentiality should necessarily mean that there is a threshold for carcinogenicity.

On the other hand, **supralinearity** was discussed by Hertz-Picciotto and Smith (1993 [75]). They concluded that all of the epidemiological studies with quantitative data are consistent with a supralinear dose-response relationship. However, the authors discuss confounding from smoking and measurement errors especially at high concentrations as possible reasons for a supralinear shape of the dose-response curve (cf. Viren and Silvers, 1994 [76]). It should be kept in mind that a flattening of the dose-response curve at relatively high cumulative exposures does not necessarily mean that there is supralinearity at environmental exposures, too. A known **supra**linear (upper) part as well as a **sub**linear lower part at concentrations relevant to non-occupational exposure may be part of the same sigmoidal curve.

Lubin et al. 2000 [209] performed an update of the Montana copper smelter data. They describe a significant, linear increase in the excess relative risk of respiratory cancer with increasing exposure to inhaled airborne arsenic. The data points and their confidence intervals are consistent with a linear relationship (Figure 2 in [209]). However, a sigmoidal curve seems to provide a fit much better than the linear one.

Unit risk approach

Human data on effects of occupational exposure to arsenic mainly refer to 2 cohorts in the U.S. (Anaconda and Tacoma cohorts) and a more recent one in Sweden (Rönnskär cohort). The U.S. EPA based a unit risk estimate on data from the Anaconda and the Tacoma smelter cohorts. For the Anaconda smelter, a unit risk of 2.56×10^{-3} $(\mu g/m^3)^{-1}$ was derived, for the Tacoma smelter a unit risk of 7.19×10^{-3} $(\mu g/m^3)^{-1}$ was used based on Enterline and Marsh (1982 [72]). The final unit risk estimate was the geometric mean of these two estimates, i.e., 4.29×10^{-3} $(\mu g/m^3)^{-1}$ (Viren and Silvers, 1994 [76]; IRIS, 1999 [208]). There is no obvious reason why neither the Tacoma update nor the Rönnskär data have been used by U.S. EPA in their recent risk estimate.

In contrast, WHO made use of the more recent data. In a first step in 1994, WHO incorporated the data on workers exposed at the Rönnskär smelter. For three groups of workers exposed to average airborne arsenic levels of 0.05, 0.15 and 0.30 mg/m^3, relative risks of 2.01, 3.53 and 4.8, respectively, were determined and unit risks of 3.77×10^{-3}, 3.1×10^{-3} and 2.4×10^{-3} were calculated. Together with risk estimates based on the Tacoma and Anaconda cohorts, WHO estimated a lifetime unit risk of 3×10^{-3} (WHO, 1994a [77]).

During the further course of the update and revision process of the WHO Air Quality Guidelines for Europe, WHO largely adopted the view of Viren and Silvers (1994 [76]) and their pooled estimate based on updated Tacoma estimates (1.28×10^{-3}), Anaconda estimates (2.56×10^{-3}) and Rönnskär estimates (0.89×10^{-3}) and thus derived a lifetime unit risk of 1.43×10^{-3} which was rounded up to 1.5×10^{-3} (WHO, 1997 [2]).

Although a dose-response relationship has been shown to exist for lung cancer and occupational exposure to arsenic, the exact shape of the curve - and hence the shape of its lower part

- is unknown. A linear extrapolation from the unit risk estimate recommended by the WHO of 1.5×10^{-3} $(\mu g/m^3)^{-1}$ so as to satisfy the one-in-a-million excess lifetime cancer risk criterion, would result in a limit value of 0.66 ng As/m³ air.

Threshold approaches

- A **UK approach** [210] starts from the lowest dose level groups with significant increase of lung cancer analysed in the cohort studies (Rönnskär and Anaconda cohorts). The midpoints of these dose levels were 125 µg/m³ x years (< 250 µg/m³ x years, taken as 0-250 µg/m³ x years, midpoint taken as 125 µg/m³ x years, Rönnskär cohort, Järup et al., 1989 [32]) and 415 µg/m³ x years (< 10 mg/m³ x months or < 833 µg/m³ x years, taken as 0-833 µg/m³ x years, midpoint taken as 415 µg/m³ x years, Anaconda cohort, Lee-Feldstein, 1986 [74]). Since risk was increased even at these levels, a safety factor of 10 was applied to obtain a level at which one would expect that increased risks would be difficult to detect in a reasonably sized epidemiological study. As discussed in the UK comments, the level of increased risk in the Swedish study might require a safety factor greater than 10 but this need is seen to be counterbalanced due to the greater number of smokers amongst smelter workers compared with the general population. Dividing the midpoints by 10 gives a level of 12.5 - 41.5 $\mu g/m^3$ x years.

  Workers are only exposed 8 hours a day, 5 days a week and 48 weeks of the years. To adjust for the fact that the general population will be exposed all the time for a lifetime, division by a further factor of 4.5 is required (8/24 x 5/7 x 48/52). This gives 2.7 to 9.2 $\mu g/m^3$ x years. A cumulative exposure of 2.7 to 9.2 $\mu g/m^3$ x years is equivalent to 2.7 to 9.2 $\mu g/m^3$ for 1 year or 0.039 to 0.131 $\mu g/m^3$ for 70 years. Using another factor of 10 for sensitive groups gives a proposed limit value of around 4 to 13 ng/m^3.

  In this UK approach, arsenic is not classified as a non-genotoxic carcinogen. On the basis of the principle that levels of genotoxic carcinogens in the atmosphere should not be allowed to rise, the final proposed limit value would be 2.5 ng/m^3 corresponding to UK levels of arsenic in background urban areas.

- **Industry** argues starting from workplace observations. In occupational regulations, limit values for inorganic arsenic have been set between 10 and 50 µg/m³. For example, in 1996 ILO (International Labour Organization) concluded that there is consistent evidence from numerous epidemiologic studies linking lung cancer excesses with occupational exposures of smelter workers to arsenic, this evidence being conclusive that arsenic is a human carcinogen. Based on data from Enterline et al. (1987 [73]) indicating a significant excess of lung cancer risk for workers exposed to a mean level of 0.2 mg/m³ of arsenic, a TVL-TWA of 0.01 mg/m³, as arsenic, is recommended by ILO.

  Extrapolation (from 15 years of work to lifetime, from 8 to 24 hours/d, from 240 to 365 days/year; this results in an extrapolation factor of 21.3) in combination with an uncertainty factor of 10 for inter-individual sensitivity differences would result in „estimated safe values" of 47-235 ng/m³ (i.e., 10-50 µg/m³ divided by 213). Based on the argument that pulmonary exposure at workplaces with up-to-date industrial hygiene practices should not exceed 100 µg/m³ averaged over an 8 h shift, an „estimated safe value" of 70 ng/m³ is presented (i.e., the midpoint between 47 and 100 ng/m³).

> Based on the argument that Järup et al. (1989 [32]) found little increased risk of lung cancer due to exposure to arsenic below 15 mg/m³ x years, a LOAEL of 47 µg/m³ is derived by industry. With an uncertainty factor of 10 for inter-individual sensitivity differences, this results in an “estimated safe value” of 470 ng/m³.
>
> Another argument was that in 1993, the Health Council of the Netherlands defined a health based limit for inhalatory exposure of the workplace. This was defined at 5 µg/m^3 and is still valid. The Dutch Institute for Public Health and the Environment then derived a limit value of 500 ng/m^3 for the general population, being one tenth of the occupational standard.
>
> Based on these arguments, industry proposes a safe effects range between 50 and 500 ng/m³. A concentration of 50 ng As/m³ which is the lowest value of this range (for both carcinogenic and non-carcinogenic effects) is proposed as a limit value for arsenic in ambient air.

The industry proposal of 50 ng/m³ is considerably higher than the range of 4-13 ng/m³ derived according to the „alternative UK approach”. In these two „threshold based” approaches, the main difference concerns the starting point. Industry uses a cumulative exposure of 15 mg/m³ x years with the argument that below this cumulative dose the increase of lung cancer risk is not dose-related. The UK approach starts from 125 - 415 µg/m^3 x years as a LOAEL because there is a statistically significant increase in lung cancer risk. The original data are shown in Figure 2.6.1.

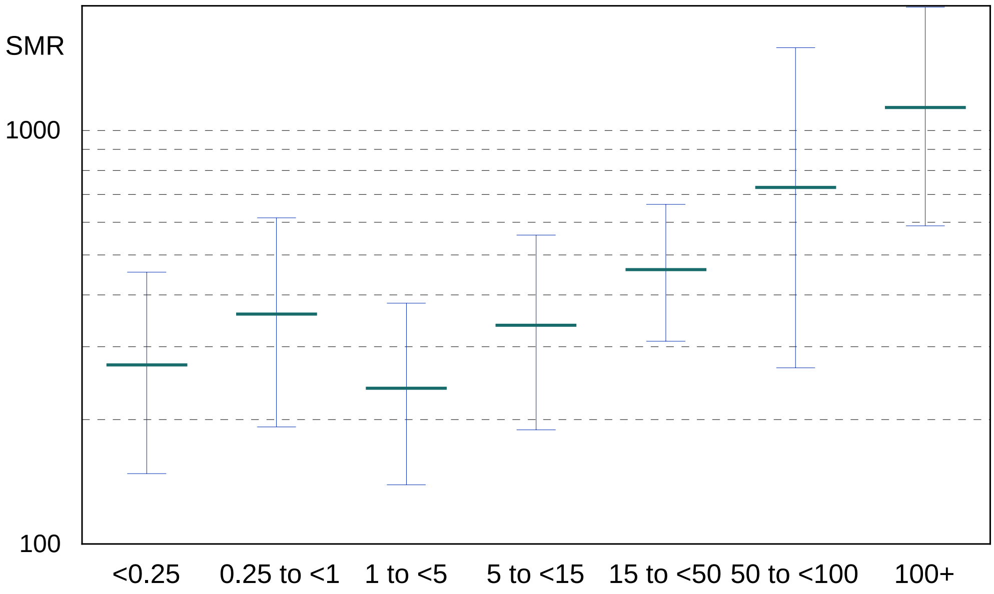


Figure 2.6.1: Lung cancer risk (Standardised Mortality Ratio SMR, given with 95 % C.I., logarithmic scale) among Rönnskär smelter workers in relation to cumulative arsenic exposure (in mg/m³ x years).

Due to the relatively small numbers of lung cancers in the groups, the confidence intervals are wide. In all groups, however, the lower bound of the confidence interval is higher than 100. An increase in risk over the whole range of cumulative exposure is compatible with the data shown in Figure 2.6.1. If the three Rönnskar groups with the lowest cumulative exposure are combined as is done in Figure 2.6.2, a continuous increase can be seen. The relative risk in this combined new lowest exposure group (< 5 mg/m³ x years) is increased (SMR < 100) but lower than in the next group, i.e., there is a dose-response relationship over the whole range of cumulative exposure. The confidence intervals given in Figure 2.6.1 show that a continuous increase of risk over the whole range of cumulative exposure is compatible with the data. Due to the fact that the starting points differ by a factor of 36-120, it is not surprising that after the next derivation steps which are not very different, the two approaches arrive at different levels. It should be mentioned, however, that the starting point selected by the UK approach - based on the Rönnskär and the Anaconda cohorts - is in good agreement with the results of the Tacoma cohort, too, where the midpoint of the lowest cumulated exposure group was 405 µg/m³ x years. In this group, lung cancer mortality was increased by 54 %, but this increase was not statistically significant (Enterline et al., 1995 [34]).

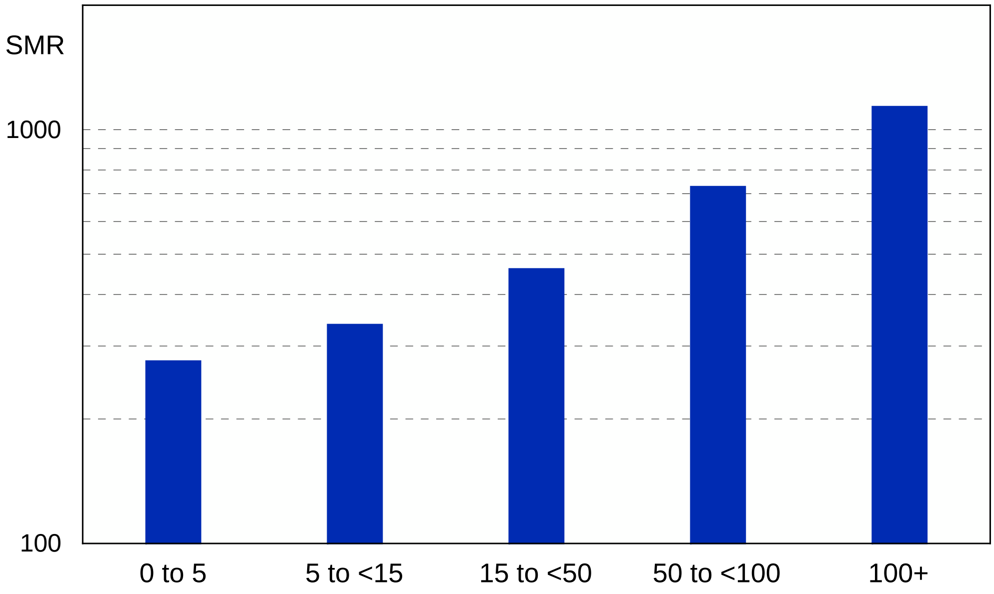


Figure 2.6.2: Lung cancer risk (Standardised Mortality Ratio SMR, logarithmic scale) among Rönnskär smelter workers in relation to cumulative arsenic exposure (in mg/m³ x years). In contrast to Figure 2.6.1, the three groups with the lowest exposure are combined

The situation in The Netherlands as described by industry does not seem to be a very strong argument because it is not indicated clearly how these values are derived. However, a factor of 10 between workplace and ambient concentrations does not seem to be acceptable keeping in mind that a factor of about 5 already results from the different exposure times during the year without consideration of the relation between years of work and years of life.

2.6.2.3 Proposed Limit Value For Arsenic

Although the point is still the subject of scientific debate, there is some evidence in the literature that at least part of the mechanisms by which arsenic acts as a carcinogen may be indirect ones, implying that for these mechanisms a safe threshold does exist and that linear extrapolation leads to an overestimation of risk. However, at present, there is not sufficient evidence to reasonably exclude the possibility that arsenic may act as a genotoxic agent, too.

On the basis of the above considerations, the Working Group concludes that the limit value of 100 ng/m³ derived based on non-cancer effects (see section 2.6.2.1) does not provide sufficient protection with respect to cancer. On the other hand, the Working Group feels that the unit-risk-based approach applied is likely to overestimate the ”true” risk, but obviously this cannot be quantified precisely. However, the Working Group believes that the ”pseudo threshold” approach proposed by the UK yields values (ranging 4-13 ng/m³) to be in the range of the suggested uncertainty. Given the current concentrations of arsenic in ambient air in Europe, a limit value near the lower bound of this range seems to be appropriate.

Therefore, the majority of the Working Group proposes a limit value in the range of 4-13 ng/m³ as an annual mean for arsenic in air.

With respect to the discussion on genotoxicity of arsenic, and as low-dose-linear models may be more appropriate when a carcinogen acts in concert with other exposures and processes that cause a background incidence of cancer, the EEB regards a proposal of 3 ng/m³ as one first step to a further reduction by a future revision of this limit value.

Industry, on the other hand, is of the opinion that a limit value of 50 ng/m³ could provide sufficient protection with respect to cancer as well as non-cancer endpoints.

2.6.3 Limit Value For Cadmium

2.6.3.1 Limit Value Based On Non-Cancer Effects

Starting point

The kidney is the critical organ with respect to long-term occupational or environmental exposure to cadmium. The revised WHO AQG value for cadmium of 5 ng/m³ was set in the range of current ambient levels with the aim of preventing any further increase of cadmium in agricultural soils that would be likely to increase the dietary cadmium intake of future generations.

Thun et al. (1991 [99]) analysed the pooled data from seven epidemiological studies that examined renal tubular proteinuria as a function of cumulative cadmium exposure in occupational settings. They concluded that the prevalence of renal dysfunction may increase at cumulative exposures between 100 and 499 µg/m³ x years, but that it was impossible to identify a no-effect level with certainty given the quality of data available to them. For the workplace, the authors recommended an 8-hour permissible exposure limit of 5 µg/m³ corresponding to a cumulative exposure of 225 µg/m³ x years during 45 years of work. They stated, however, that this value should be regarded as providing little or no safety margin against tubular proteinuria in some workers.

The WHO discussed the key occupational exposure studies (summarised by Thun et al., 1991 [99]) and identified a critical cumulative dose of 100 µg/m³ x years for the occurrence of renal effects from which the LOAEL can be extracted and used to derive a limit value. Moreover, taking into account the ratios of PM_5 to TSP given by Lauwerys et al. (1974 [96]) for several workplaces, the cumulative exposure levels in the studies used by Thun et al. (1991 [99]) may in fact have been lower, which may give further support to this WHO estimate which represents the lower bound of the range discussed by Thun et al. (1991 [99]).

It is proposed, therefore, that the starting point in deriving a limit value for non-cancer renal dysfunction should be a LOAEL equivalent to an accumulated occupational exposure of 100 µg/m³ x years.

This approach is supported by a recent draft, in which the California EPA derived a Chronic Reference Exposure Level based on a study of Lauwerys et al., 1974 [96]. CalEPA identified a LOAEL of 21 µg/m³ respirable cadmium (mean exposure time 27.8 years) and a NOAEL of 1.4 µg/m³ respirable cadmium (mean exposure time 4.1 years) [211]. The corresponding cumulative exposures are 580 and 6 µg/m³ x years, respectively.

Uncertainty factors

The workplace exposure level must be converted into an equivalent continuous lifetime exposure in order to derive a limit value for the general population. Therefore, the occupational LOAEL is extrapolated from 8 hours to 24 hours, from 225 working days to 365 days and distributed over an average human lifetime of 75 years. The overall conversion factor is 0.0027 (8/24 x 225/365 x 1/75). Consequently , by applying this factor, the LOAEL (occupational) of 100 µg/m³ x years can be converted to a LOAEL (continuous) of 270 ng/m³.

Reversibility and extrapolation from LOAEL to NOAEL

It has been argued that the initial onset of microproteinuria (as may occur in the general population and associated with a level of 2µg/g creatinine in urine), is in fact a reversible, non-adverse effect and not associated with a progressive and irreversible renal dysfunction. Studies by Hotz et al. (1999 [109]) and Roels et al. (1997 [108]) have been cited to support this argument. This would mean that the factor required to extrapolate from the LOAEL above to a NOAEL could be less than the usual value of 10. Some members of the Group would go further to say that this first, limited microproteinuria should be considered as a reversible non-adverse effect, and consequently, the level of 2µg/g creatinine in urine be considered a NOAEL to which an additional safety factor of 3 can be applied.

However, this approach raises some fundamental questions. If an effect is reversible after cessation of exposure, but persisting if exposure continues, what is the relevance of this reversibility? Does reversibility make an effect a non-adverse one? If a person is continuously exposed to a concentration level that leads to a “reversible” effect, then we cannot be sure that the “reversible” effect may not be an intermediate stage on the way to more critical and irreversible dysfunction.

The majority of the Working Group concludes that these doubts concerning reversibility in practice do not permit to classify the functional renal changes as being non-adverse. Since, in summary, an uncertainty factor of 2 seems to be too small, and on the other hand a factor of

10 may be not fully justified, a factor of 5 is proposed for the extrapolation from LOAEL to NOAEL. This leads to a NOAEL (continuous) of 54 ng/m³.

Interindividual sensitivity

When deriving a limit value from the NOAEL it is common practice to introduce an uncertainty factor of 10 to provide protection for those individuals who may be particularly sensitive to the substance in question. This factor may be modified if appropriate scientific evidence is available. Based upon the conclusions of the Cadmibel study (Buchet et al., 1990 [101]), industry argues that an uncertainty factor of 5 is appropriate. Keeping in mind, however, that women may be at higher risk than men because iron deficiency increases intestinal cadmium resorption, that early signs of renal effects are detected in large population groups already at cadmium-in-urine levels of 0.5-2 µg/g creatinine (Järup et al., 1998 [110]), that diabetic patients may be more susceptible to the renal effects of cadmium (Buchet et al., 1990 [101]), and that increased urinary cadmium levels may be also associated with increased risk of bone fractures in women and height loss in men at relatively low levels of exposure, which may have important health implications for the elderly (Staessen et al., 1999 [111]), an intraspecies uncertainty factor of less than 10 does not seem to be justified. Applying these factors to the above mentioned NOAEL (continuous) of 54 ng/m³ leads to a limit value of 5 ng/m³ based on renal effects.

In a report prepared for U.S. EPA, TERA (Haber et al., 2000 [212]) tried to address potential differences between occupational and general populations. They found no evidence to support the hypothesis that the general population is more sensitive than workers to the kidney effects of cadmium, there was even some suggestion that the general population may be less sensitive than workers. The authors state that the reliability of any conclusions is limited by the limited amount of data for the general population. However, more important limitations may be due to the lack of individual data with respect to age and urinary excretion, the questionable use of geometric means when defining adversity instead of using individual data, and the questionable approach of “normalizing” data by dividing the response in all of the exposed groups by the response in the corresponding control group of the respective study without consideration of different levels of exposure in the control groups. Therefore, this report cannot invalidate the need of using an uncertainty factor for interindividual differences in sensitivity when starting from occupationally exposed groups.

Model-based approach

- The U.S. EPA is in the process of revising their risk assessment for cadmium. An external review draft is publicly available (EPA, 1999a [95]), but this is still a draft at this stage and does not reflect the official position of the U.S. EPA.

  The study by Buchet et al. (1990 [101]) has been chosen as the basis for a revised, and as yet provisional, Reference Concentration (RfC) because the study relates to the general population (including sensitive subpopulations) exposed both orally and by inhalation. A modified model by Oberdörster (1990 [91]) was used. It relates urinary cadmium excretion to inhalation and oral exposure, based on the data of Buchet et al. (1990 [101]), with a uri-

> nary cadmium excretion of 2.7 µg/day as a starting point. As described in the U.S. EPA draft, the model associates a cadmium concentration in ambient air of 650 ng/m³ with a 10 % probability of an adverse renal effect in the general population at the age of 70. This level has been taken as a NOAEL in the draft. As the study population included sensitive individuals, no need was seen to introduce any uncertainty factors and so a RfC of 650 ng/m³ has been derived, based on the assumption of an oral daily intake of cadmium of 10 µg/person. In case the oral intake amounts to 20 µg/person, the corresponding air concentration is reduced to 500 ng/m³ (EPA, 1999a [95]).

Given that there is a 10 % probability of an adverse renal effect in the general population at the age of 70, it is difficult to assume a concentration of 650 ng/m³ to be a NOAEL. It would be more appropriate to consider this to be a LOAEL. From this and using an uncertainty factor of 10 one can derive a NOAEL of 65 ng Cd/m³. If a factor of 5 is used, one arrives at a NOAEL of 130 ng Cd/m³. If it is accepted that the study population already includes sensitive individuals, an intraspecies uncertainty factor is not required (i.e., the factor is 1). However, persons with iron deficiency or diabetics might not be adequately protected. Furthermore, one also has to consider the wide and log-normal distribution of cadmium intake and kidney cortex concentration in the population. As discussed by Elinder and Järup (1996 [213]), even small increases in the average daily intake of cadmium - say from 15 to 20 µg cadmium/day - will result in a clear increase in the share of individuals exceeding the critical level of 50 µg/g cadmium in kidney cortex: from about 4 % to 9 % in nonsmokers and from 16 % to 23 % in smokers. Therefore, an uncertainty factor up to 10 should be used.

The various approaches are summarised in Table 2.6.2.

Table 2.6.2: Proposals for deriving a limit value for cadmium in the air, based on non-cancer effects. For explanation of extrapolation steps and uncertainty factors used, see text above in this chapter 2.6.3.1

Step	Working Group	Industry position	Model-based Approach (US EPA draft)
Data base	Occupational	Occupational	General population
LOAEL (occupational)	100 µg/m³ x years [88, 99]	100 µg/m³ x years [88, 99]	
LOAEL (continuous)	270 ng/m³	270 ng/m³	650 ng/m³ [95, 101]
Uncertainty factor LOAEL → NOAEL	Factor 5	Factor 3	Factor 5-10
NOAEL (continuous)	54 ng/m³	90 ng/m³	65-130 ng/m³
Interindividual variation	Factor 10	Factor 5	Factor 1-10
Limit value (non-cancer)	5 ng/m³	18 ng/m³	6.5 ng/m³ -130 ng/m³

2.6.3.2 Limit Value Based On Carcinogenic Effects

Route of exposure and carcinogenicity

The IARC as well as Health and Environment Canada [123a] have classified cadmium and cadmium compounds as a human carcinogen having concluded that there was sufficient evidence for cadmium to produce lung cancer in humans and animals exposed by inhalation. The current external review draft of the cadmium risk assessment from the U.S. EPA [95] has classified cadmium as a probable human carcinogen by inhalation exposure, whereas the NTP Board of Scientific Counselors Report on Carcinogens Subcommittee has recommended to upgrade cadmium and cadmium compounds to “known to be human carcinogen” [116]. This – still pending - recommendation is supposed to be included in the 9th Report on Carcinogens which is due in 2000.

Unit risk approach

In the revision of the air quality guidelines, the WHO (1997 [88]) felt unable to recommend a reliable unit risk estimate because of the controversial debate on the influence of confounding arsenic exposure in the available epidemiological studies. Nevertheless, WHO cites two existing risk estimates with respect to lung cancer. Based on rat studies (Takenaka et al., 1983 [115]), a unit risk of 9.2×10^{-2} $(\mu g/m^3)^{-1}$ has been derived, whereas human data yielded a unit risk of 1.8×10^{-3} $(\mu g/m^3)^{-1}$ (Thun et al., 1985 [117]). WHO states that generally, if human data are available, these data are more reliable because in this case there is no need for interspecies extrapolation. Therefore, in the case of cadmium, animal data suggesting a higher risk should not be used.

It may be discussed wether or not the concerns regarding the possible confounding by exposure to arsenic are of practical relevance because the environmental exposure to cadmium is usually combined with some exposure to arsenic, too. Therefore, the exposure conditions of the general population in the surroundings of cadmium emitting plants may be similar to the conditions in the occupational studies with respect to concomitant exposure to arsenic.

In the case of cadmium, the main data base for the unit risk derivation is a cohort of workers exposed to cadmium at a U.S. cadmium production facility. In 1976, investigators at the National Institute for Occupational Safety and Health (NIOSH) showed an increase in lung cancer mortality in this cohort (NIOSH cohort). Follow-up studies have been published by Thun et al. (1985 [117]) and by Stayner et al. (1992 [118] and 1993 [214]).

According to the U.S. EPA web site (EPA, 1999b [215]), EPA calculated an inhalation unit risk estimate of 1.8×10^{-3} $(\mu g/m^3)^{-1}$. This is the unit risk quoted by WHO (1997 [88]). It is based on the NIOSH cadmium cohort according to Thun et al. (1985 [117]). In the external review draft (EPA, 1999a [95]), EPA continues to base risk estimates for lung cancer on the NIOSH cadmium cohort. However, in the review draft, the data as described by Stayner et al. (1992 [118]) are used.

An advantage of using the more recent Stayner data of the NIOSH cohort is the extended follow-up time. However, a methodological problem is the choice of the reference population (within-cohort comparison or U.S. population). In the „old“ still „official“ EPA unit risk estimate the U.S. population has been chosen as the reference population. In the new external review draft (1999a [95]), a within-cohort comparison is applied. This different approach (different reference population, extended follow-up period) results in a unit risk of 2.45 x 10^{-3} (Maximum Likelihood Estimate) or 4.15 x 10^{-3} (95 % upper bound) (see 2.6.1.2). However, as discussed by Sorahan and Lancashire (1997 [119]), there are still many open questions concerning causality and dose-response relationship, which may be in part due to the relatively low number of lung cancer cases (n = 24, among them 3 who could not be included) in the NIOSH study.

Genotoxicity

With respect to genotoxicity, there are some parallels between cadmium and arsenic. The results of genotoxicity tests do not give sufficient evidence to move away from the conservative default assumption that cadmium and cadmium compounds are genotoxic. A plausible explanation would be that several mechanisms are contributing to the overall effect, suggesting linear as well as nonlinear partial components. In this case, linear extrapolation is likely to overestimate the „real“ effect, and some kind of sublinearity should result as an overall exposure-effect relationship. A threshold might be possible, too, but at present evidence is not strong enough to suggest adoption of a threshold hypothesis. Therefore, as cadmium and cadmium compounds may be - at least in part - genotoxic, it is prudent to extrapolate linearly from the available unit risk estimates quoted above (1.8 or 2.45 or 4.15 x 10^{-3}) to a cadmium concentration associated with an excess lifetime risk of lung cancer of one-in-a-million. This leads to a concentration range of 0.24-0.55 ng/m³. This range is significantly below currently measured concentrations in non-rural areas of Europe.

2.6.3.3 Proposed Limit Value For Cadmium

It must be remembered that WHO (1997 [88]) has refrained from recommending a quantitative cancer risk estimate because of the uncertainties concerning qualitative and quantitative aspects of possible cancerogenicity of cadmium. The Working Group believes that these uncertainties and the uncertainty associated with the extrapolation from (the unit risk reference point of) 1 µg/m³ to considerably lower concentrations at the nanogramm/m³ level means that the 0.24-0.55 ng/m³ range based on the unit-risk approach is likely to be overprotective.

The EEB is of the opinion that, as in the case of arsenic, with respect to the genotoxicity of cadmium and as low-dose-linear models may be more appropriate when a carcinogen acts in concert with other exposures and processes that cause a background incidence of cancer, a proposal of 2.5 ng/m³ corresponding to the upper bound of the urban background values in Europe can be regarded as one first step to a further reduction by a future revision of this limit value.

In summary, the majority of the Working Group believes that an annual mean concentration level of 5 ng/m³ as derived from non-cancer effects provides also an appropriate level of protection from cancer risk due to exposure to cadmium. This value is identical with the new WHO AQG value.

2.6.4 Limit Value For Nickel

2.6.4.1 Limit Value Based On Non-Cancer Effects

Starting point

Non-cancer effects of nickel are seen in the respiratory tract, the immune system, and on endocrine regulation. The non-cancerous dermal reactions are very important, too. However, there is no clear evidence of an influence of airborne nickel or nickel compounds on skin reactions, at least in the general population.

In experimental animals, effects on the respiratory system are the best documented non-cancer effects. Due to a lack of well-documented human data, animal data have to be used. The Working Group agreed that the starting point in the derivation of a limit value for non-cancer effects of nickel should be the bioassay of nickel sulfate hexahydrate by the "National Toxicology Program" in the U.S. (NTP, 1996b [136]). The authors of the NTP study concluded: „Respiratory toxicity in the lung of rats exposed to nickel sulfate hexahydrate occurred for the most part in 0.25 and 0.5 mg/m³ rats and was characterized by fibrosis, hyperplasia, and alveolar proteinosis; these lesions were considered to be the various components of chronic active inflammation. In mice, treatment-related lung lesions were diagnosed as inflammation, hyperplasia, proteinosis, and cellular infiltration; these lung lesions were observed primarily in 0.5 and 1 mg/m³ mice." This conclusion may be interpreted as the statement of a LOAEL of 0.25 mg/m³ (0.25 mg/m³ of nickel sulfate hexahydrate, equivalent to 0.06 mg/m³ nickel). However, an explicit statement with respect to a NOAEL cannot be found in the study report.

There has been much discussion within the Working Group whether the observed increase of fibrosis that occurred in the low exposure group of the NTP study (i.e., control = 3/53 male rats or 6 % and 0.03 mg Ni/m³ = 6/53 male rats or 11 %) is compatible with classifying 0.03 mg Ni/m³ as being a NOAEL. A reason for the classification as a NOAEL could be that this increased rate of fibrosis was not accompanied by an increase in chronic active inflammation, a condition which may be an intermediate stage in the development of fibrosis. In addition, analysis of control data from 56 NTP studies demonstrated a historical control range of response for lung fibrosis from 0/50 to 8/50 animals.

On the other hand, there are several reasons that suggest effects at concentrations lower than 0.06 mg Ni/m³. Table 2.6.3 demonstrates a trend of increasing lung weight with increasing exposure concentration, which is most pronounced in the 15-month evaluation (unfortunately, data for 2 years are not available from the NTP study). An increase in lung weight may be considered to be related to inflammatory lung reactions that occurred in response to the nickel exposures (Dunnick et al., 1995 [138]). Table 2.6.4 shows the fibrosis data in the context of other respiratory endpoints and the high percentage of animals concerned at 0.06 mg Ni/m³. Table 2.6.5 demonstrates that in female mice statistically significant effects were observed at all exposure concentrations studied.

Table 2.6.3: Relative Lung Weight of Rats (mg Lung Weight / g Body Weight, mean ± standard error) at Interim Evaluations of the NTP Study of Nickel Sulfate Hexahydrate

Male Rats						
			Concentrations			
Table	n	Evaluation	0 (0)	0.12 (0.03)	0.25 (0.06)	0.5 (0.11)
F2	10	13-Week	4.13 ± 0.14	3.82 ± 0.06	4.53 ± 0.19	5.28 ± 0.13*
F3	5	7-Month	3.93 ± 0.15	4.16 ± 0.18	4.39 ± 0.13	4.77 ± 0.08*
F4	5	15-Month	4.38 ± 0.26	5.12 ± 0.25	5.32 ± 0.27	6.39 ± 0.55*
Female Rats						
			Concentrations			
Table	n	Evaluation	0 (0)	0.12 (0.03)	0.25 (0.06)	0.5 (0.11)
F2	10	13-Week	5.18 ± 0.11	5.20 ± 0.09	6.05 ± 0.17*	7.06 ± 0.29*
F3	5	7-Month	5.10 ± 0.05	5.35 ± 0.26	5.17 ± 0.22	6.24 ± 0.20*
F4	5	15-Month	4.81 ± 0.22	5.41 ± 0.36	5.27 ± 0.20	6.36 ± 0.36*

The column „Table“ indicates the names of those tables in the NTP Technical Report 454 [136] which contain the data used here. Concentrations in mg/m³ nickel sulfate hexahydrate, in brackets in mg Ni/m³. The asterisk* marks statistical significance of the increase

Table 2.6.4: Non-neoplastic Lesions of the Lung of Rats in the 2-Year Inhalation Study of Nickel Sulfate Hexahydrate (Table 14 of NTP TR 454 [136])

		Concentrations			
Group	Endpoint	0 (0)	0.12 (0.03)	0.25 (0.06)	0.5 (0.11)
Male Rats	Inflammation, Chronic Active	14/54	11/53	42/53*	46/53*
	Macrophage Hyperplasia	7/54	9/53	35/53*	48/53*
	Fibrosis	3/54	6/53	35/53*	43/53*
Female Rats	Inflammation, Chronic Active	14/52	13/53	49/53*	52/54*
	Macrophage Hyperplasia	9/52	10/53	32/53*	45/54*
	Fibrosis	8/52	7/53	45/53*	49/54*

Concentrations in mg/m³ nickel sulfate hexahydrate, in brackets in mg Ni/m³. Animals with lesions/total number of animals. The asterisk* marks statistical significance of the increase

Table 2.6.5: Non-neoplastic Lesions of the Lung of Mice in the 2-Year Inhalation Study of Nickel Sulfate Hexahydrate (Table 27 of NTP TR 454 [136]).

Group	Endpoint	0 mg/m^3 (0 mg/m^3 Ni)	0.25 mg/m^3 (0.06 mg/m^3 Ni)	0.5 mg/m^3 (0.11 mg/m^3 Ni)	1 mg/m^3 (0.22 mg/m^3 Ni)
Male Mice	Inflammation, Chronic Active	1/61	2/61	8/62*	29/61*
	Bronchialization	1/61	4/61	19/62*	39/61*
	Macrophage Hyperplasia	6/61	9/61	35/62*	59/61*
Female Mice	Inflammation, Chronic Active	1/61	7/60*	14/60*	40/60*
	Bronchialization	0/61	9/60*	32/60*	45/60*
	Macrophage Hyperplasia	7/61	24/60*	53/60*	59/60*

Animals with lesions/total number of animals. The asterisk* marks statistical significance of the increase

The situation can be summarised as follows. In mice, there is a LOAEL of 0.06 mg Ni/m^3 demonstrated in the NTP 2-year inhalation study of nickel sulfate hexahydrate. In rats, there are clear adverse effects at 0.06 mg Ni/m^3. With respect to lung fibrosis, there is a slight increase in male rats at 0.03 mg Ni/m^3 in the 2-year study which is not statistically significant. However, in male rats there is an increasing trend in lung weight for the 15-month interim evaluation (Figure 2.6.3). These results indicate possibly adverse effects at 0.03 mg Ni/m^3, and therefore 0.03 mg Ni/m^3 may be not a NOAEL in rats. This means that the LOAEL for mice is 0.06 mg Ni/m^3, the LOAEL for rats is probably lower than 0.06 mg Ni/m^3, and a NOAEL has neither been found for rats nor for mice in the NTP study of nickel sulfate hexahydrate.

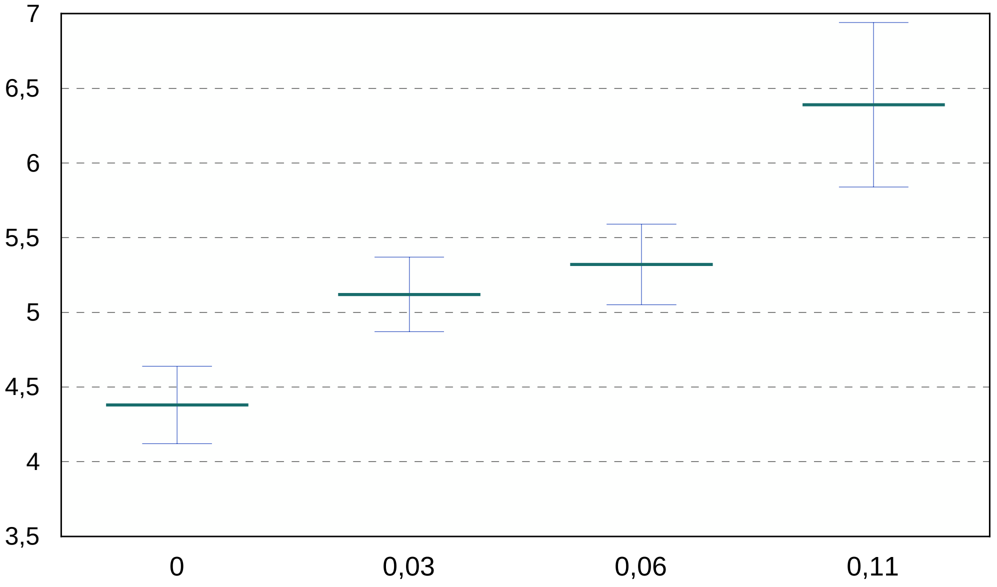


Figure 2.6.3: Relative Lung Weight of Male Rats (mg Lung Weight / g Body Weight, mean ± standard error) at the 15-Month Interim Evaluation of the NTP Study of Nickel Sulfate Hexahydrate [136] (cf. Table 2.6.3 above).
X-axis: exposure concentration in mg Ni/m³, Y-axis: rel. lung weight.

On behalf of the Metal Finishing Association of Southern California, U.S. EPA and Health Canada, TERA (Toxicology Excellence for Risk Assessment) has prepared a toxicological assessment of soluble nickel salts (TERA, 1999 [216]). The TERA assessment was subjected to an external peer review process. The reviewers agreed with the TERA decision to select the NTP study (NTP, 1996 a,b,c [135, 136, 137]) as the key study and lung fibrosis as the critical effect. This view has also been adopted by the Californian EPA/OEHHA in deriving Chronic Reference Exposure Levels for nickel compounds (Air Toxic Hot Spots Program) (OEHHA, 2000 [217]).

TERA defined the lowest exposure concentration studied (0.027 mg Ni/m³, rounded 0.03) as the NOAEL for lung effects in rats. However, the majority of the Working Group had the impression that the Figures A1 and A2 of the TERA report - although difficult to read due to the need to multiply the numbers of the y-axis by 100 - clearly suggest effects (lung fibrosis and active inflammation) in male rats starting at levels lower than 0.03 mg Ni/m³.

As shown above and discussed in the Working Group, there are reasons to presume that there are effects in rats at a concentration of 0.03 mg Ni/m³. Therefore, 0.03 mg Ni/m³ should not be called a real NOAEL for rats. In mice, the lowest concentration studied (0.06 mg Ni/m³) was associated with effects. This means that there is a LOAEL for mice of 0.06 mgNi/m³. In summary, the Working Group proposes not to use 0.03 mg Ni/m³ as a NOAEL, but to use 0.06 mg Ni/m³ like a LOAEL for effects in mice and rats as a starting point.

Uncertainty factors

Extrapolation from LOAEL to NOAEL

The choice of the uncertainty factor from LOAEL to NOAEL should not only consider that effects decrease between 0.06 and 0.03 mg Ni/m³, but also that a high percentage of animals is affected at 0.06 mg Ni/m³, and that at least female mice showed effects at any concentration tested.

Furthermore, a study by Glaser et al. (1986 [218]) showed severe lung damage in rats after continuous exposure to 60 and 200 µg/m³ nickel oxide. Only one rat per group survived until the end of this 2-year study. This might indicate more severe effects of continuous exposure in comparison to the intermittent exposure during the NTP studies.

Therefore, in a conservative approach, a factor of 10 is proposed to extrapolate from LOAEL to NOAEL. The next steps are shown in Table 2.6.6.

Extrapolation from animals to humans

The default factor of 10 which is often used for animal-to-human extrapolation can be seen as being composed of roughly equal parts related to differences between animals and humans concerning toxicodynamics (factor 3) and toxicokinetics (factor 3) (cf. section 2.6.1.1). In some calculations (e.g. by TERA [216]), dosimetric adjustment is applied to the NOAEL to account for toxicokinetic differences, otherwise a default factor of 3 for toxicokinetics can be used. It is argued (e.g., by TERA, but without giving references for this statement) that comparisons of occupational exposure data and data from animal studies indicate that humans are less sensitive than rodents to the respiratory effects of inhaled soluble nickel sulfate. This would support a toxicodynamic factor of 1, resulting in a total factor of 3 for interspecies extrapolation. This question was discussed in the TERA reviewers meeting, too. It was pointed out by the TERA authors that „while the exposure concentrations of nickel are higher in the occupational studies, the pulmonary concentrations received are not necessarily greater than those that the laboratory animals received“, cf. *ITER* Peer Review Meeting Summary, page 8, which is part of the TERA assessment [216]. In this context, it is also important to consider that some of the endpoints studied in rats cannot be studied in living humans (e.g., results of chest radiographs cannot be compared with those of histological examinations). Consequently, the suggested higher sensitivity of rats may be questioned, especially if there is a lack of adequate epidemiological studies in humans. It should be added that the Californian EPA has used an uncertainty factor of slightly more than 10 [217] (cf. Table 2.6.6).

It should be taken into account, too, that neither a multigeneration reproduction study with inhaled soluble nickel nor developmental studies are available.

Considering the total situation, the Working Group proposes not to reduce the interspecies uncertainty factor of 10.

Proposals made by other bodies

In the **TERA** risk assessment, a Reference Concentration for the protection of human health (including sensitive individuals) of 200 ng Ni/m³ has been proposed as an annual average using 30 µg/m³ as a NOAEL to start from [216].

The **California Environment Protection Agency** has published chronic reference exposure levels (RELs) for nickel compounds and nickel oxide (OEHHA, 2000 [217]). For nickel compounds, the concentration of 0.03 mg Ni/m³ from the NTP study cited above was defined as a NOAEL, and a REL of 50 ng Ni/m³ was derived. For nickel oxide, a REL of 100 ng Ni/m³ was derived.

Industry point of view

Industry argues that the calculation of an ambient air limit value for nickel should be based on the results of the NTP bioassay of nickel sulfate hexahydrate (NTP, 1996b [136]). In the view of the industry members of the Working Group, this study established a NOAEL of 0.03 mg Ni/m^3 in male rats, although a marginal (not significant) increase in the rate of fibrosis occurred in the low exposure group of the NTP study (i.e., control = 3/54 animals or 6 % and 0.06 mg Ni/m^3 = 6/53 animals or 11 %). They argue that a causal relationship with exposure to nickel sulfate hexahydrate is not supported because there is no increase in chronic active inflammation (a condition related to the formation of fibrosis) in the group exposed to 0.06 mg Ni/m^3 compared to the control group. In addition, analysis of control data from 56 NTP studies demonstrated a historical control range of response for lung fibrosis from 0/50 (0 %) to 8/50 (16 %) animals. The NTP nickel sulfate hexahydrate study should also be chosen as the key study because results of animal studies show that the insoluble nickel compounds present in ambient air (e.g., nickel oxides) are less irritating than nickel sulfate hexahydrate at equal concentrations of nickel.

Starting from 0.03 mg Ni/m³ and using uncertainty factors of 10 for interspecies extrapolation and 10 for intrahuman variability results in a value of 50 ng Ni/m³. Since the NTP study is a chronic carcinogenicity study and a NOAEL was obtained in the NTP study, no additional uncertainty factors are needed. However, this calculation is said to be unduly conservative. Comparing the exposure concentrations that result in adverse effects in rats to the (10 to 100-fold higher) concentrations that workers are exposed to in the workplace without any adverse effects indicates that rats are more sensitive than humans to the respiratory effects of inhaled nickel compounds. Thus, the data support a toxicodynamic factor of 1, resulting in a total factor of 3 (i.e., the default factor for toxicokinetics) for interspecies extrapolation. Calculating the limit value with an overall uncertainty factor of 30 instead of 100 gives a limit value for nickel of 160 ng Ni/m^3. An independent peer reviewed assessment using the NTP nickel sulfate hexahydrate carcinogenicity study calculated a protective air limit of 200 ng Ni/m^3 (TERA, 2000 [216]). According to these arguments, an air limit value between 50 and 160 ng Ni/m^3 would be protective of human health since it is based on: (1) the most sensitive endpoint for toxicity, (2) the nickel compounds which are more potent with regard to pulmonary toxicity (water soluble nickel compounds), and (3) the most sensitive species (rats). This industry view is presented in Table 2.6.6, too.

Limit value

Table 2.6.6 summarises three approaches to derive limit values for nickel in the air.

Table 2.6.6: Derivation of a limit value for nickel based on non-cancer effects using data of the NTP studies [135, 136, 137] as a starting point

Step	WG Proposal	California EPA	Industry
LOAEL (rat, non-continuous)	60 µg Ni/m³	60 µg Ni/m³	60 µg Ni/m³
Uncertainty factor LOAEL to NOAEL	10		
NOAEL (rat, non-continuous)	6 µg Ni/m³	30 µg Ni/m³	30 µg Ni/m³
Uncertainty factor expos. time	6	5.6	6
NOAEL (rat, continuous)	1 µg Ni/m³	5.4 µg Ni/m³	5µg Ni/m³
Uncertainty factor interspecies	10	3 x 3.4	3 - 10
NOAEL (human, continuous)	100 ng Ni/m³	0.5 µg Ni/m³	500 - 1600 ng/m³
Uncertainty factor intraspecies	10	10	10
Limit Value (human, non-cancer)	10 ng Ni/m³	50 ng Ni/m³	50 - 160 ng Ni/m³

Considering all the above mentioned arguments, the Working Group proposes a limit value for non-cancer effects in the range of 10-50 ng Ni/m³ as an annual mean.

2.6.4.2 Limit Value Based On Carcinogenic Effects

Route of exposure and carcinogenicity

In the EC classification, nickel oxide, nickel monoxide, and nickel sulfide are classified as Group 1 (known human carcinogens), whereas nickel, nickel carbonate, nickel hydroxide, nickel sulfate, and nickel tetracarbonyl are classified as Group 3 (possible carcinogens). IARC has classified nickel compounds as Group 1 human carcinogen and metallic nickel as possible human carcinogen (Group 2B). Carcinogenicity is documented for inhalation exposure. Health and Environment Canada (1994 [145]) confirmed this IARC view, and the NTP Board of Scientific Counselors [116] recommended to upgrade nickel and nickel compounds including soluble nickel compounds to “known to be human carcinogen” in the 9th Report on Carcinogens (still pending).

In the chronic inhalation studies of the US National Toxicology Program there was “clear evidence” with respect to carcinogenicity in male and female rats based on lung adenoma or carcinoma for nickel subsulfide, “some evidence” in male and female rats based on lung adenoma or carcinoma for NiO, and “no evidence” in rats and mice in the case of nickel sulfate hexahydrate (NTP, 1996 [135, 136, 137].

Given that all of the available epidemiological evidence has been obtained under occupational conditions, there has been much discussion as to whether the workers and the general population are exposed to the same nickel compounds. The International Committee on Nickel Carcinogenesis in Man (CNCM, Doll Report 1990 [150]) came to the conclusion that more than one nickel species gives rise to concern with respect to lung and nasal cancer. Therefore, the argument that nickel subsulfide is only present at workplaces but not in the atmosphere cannot disprove the necessity of a limit value for nickel in the air.

Human data generally should be given more weight than animal data because their use excludes the need of interspecies extrapolation. Therefore, the results of the NTP study cannot invalidate the workplace findings that more than one nickel species appears to have cancinogenic properties.

The recently published TERA risk assessment concluded that the carcinogenic potential of inhaled soluble nickel compounds could not be determined because of the conflicting evidence in the literature. TERA argued, however, that soluble nickel is not carcinogenic in itself but acts so as to increase the cancer risk associated with exposure to other forms of nickel [216].

Genotoxicity

In the framework of the NTP nickel studies, nickel oxide was tested for induction of micronuclei in normochromatic erythrocytes (NCE) of male and female mice exposed by inhalation for 13 weeks. The compound did not induce an increase in the frequency of micronucleated NCEs in peripheral blood samples. Nickel sulfate (500 to 800 µg/mL) was tested for induction of trifluorothymidine resistance in L5178Y mouse lymphoma cells. A positive response was observed in the absence of S9. The test was not performed with S9.

Water soluble nickel compounds generally have been found to induce effects in certain kinds of mammalian genotoxicity assays. In particular, these effects include mutagenic responses and DNA damage *in vitro*, chromosomal effects including aberrations and sister-chromatid exchanges *in vitro* and *in vivo*, and carcinogenic transformation of mammalian cells *in vitro*. However, responses in many of these cases were weak and occurred at toxic doses. Considering these results, the TERA assessment [216] concludes that there is no clear evidence either for or against water soluble nickel compounds being genotoxic carcinogens (cf. section 2.6.1.2).

In summary, the available information is not sufficient to permit a clear classification of nickel compounds as being non-genotoxic carcinogens. Therefore, under precautionary aspects the existence of a threshold should not be assumed.

Unit risk approach

The U.S. EPA has estimated the lifetime cancer risk from exposure to nickel refinery dust as 2.4×10^{-4} based on 3 cohorts (Copper Cliff, Clydach, and Kristianssand) with a range from 1.1×10^{-5} to 4.6×10^{-4}. This estimate concerns nickel refinery dust. Based upon the assumption that nickel dust contains 50 % nickel subsulfide, the U.S. EPA has estimated a unit risk of 4.8 x10^{-4} (µg/m³)$^{-1}$ for nickel subsulfide.

The Centre d´Etude sur l´Evaluation de la Protection dans le domaine Nucléaire (CEPN) performed a risk assessment for nickel based upon respiratory cancer in humans and animals using a linear non-threshold approach (Lepicard et al., 1997 [152]). The epidemiological studies of occupational exposure led to a unit risk estimate of 2.5 x 10^{-4} (µg/m³)$^{-1}$. To account for the physical and chemical differences between nickel refinery workers and the general population, adjustments were made to this value using the results of animal studies. In the view of the CEPN authors, this permitted to distinguish between nickel oxide and nickel subsulfide. They derived unit risk estimates for lung cancer of 4.0 x10^{-5} (µg/m³)$^{-1}$ for nickel oxide and 3.0 x10^{-4} (µg/m³)$^{-1}$ for nickel subsulfide.

The WHO has recommended a unit risk of 3.8 x 10^{-4} (µg/m³)$^{-1}$ based on a study of nickel refinery workers from Falconbridge in Norway [130], where a significant excess risk was found for workers exposed to nickel including soluble nickel.

It is essential to bear in mind that the monitoring data describing the workplace situation - especially as far as they concern the situation some decades ago - are very incomplete. The percentage of nickel occurring in the small particle fraction seems to have been very low in earlier times. Therefore, the concentrations of respirable nickel associated with excess risk of lung cancer may have been lower than one would expect from the available concentration data. This would mean that the unit risk estimates given might underestimate the lung cancer risk in humans.

Threshold approach

Although the available information is not sufficient to permit a clear classification of nickel compounds as being non-genotoxic carcinogens and therefore under precautionary aspects the existence of a threshold should not be assumed, on request of the Steering Group, the Working Group looked into the possibility of applying some kind of threshold approach comparable to the one described for arsenic in the case of nickel, too.

The International Committee on Nickel Carcinogenesis in Man (CNCM, Doll Report, 1990 [150]) stated „that there was no definitive evidence of increased cancer risk associated with exposure to metallic nickel, oxidic nickel or sulfidic nickel at concentrations of less than 1 mg Ni/m³“ and that the „risk to the general population from exposure to extremely small concentrations (less than 1 µg/m³) to which it is exposed in the ambient air is minute, if indeed there is any risk at all“.

If the starting point in deriving a limit value is the assumption that the 1 mg Ni/m³ level from the Doll report is a LOAEL, then the NOAEL in the same occupational setting can be derived by dividing the LOAEL by a factor of 10. The NOAEL in the occupational setting must be extrapolated to the general population, i.e., from 8 hours to 24 hours, from 225 days to 365 days, from 40 years to 75 years (8/24 x 225/365 x 40/75). The resulting NOAEL(continuous) of 10.9 µg Ni/m³ is further reduced by a factor of 10 to account for the possibility of sensitive individuals. This yields a limit value of 1.1 µg Ni/m³ (1100 ng Ni/m³).

A slightly different approach (also using a threshold concept) has been proposed by CONCAWE (Lewis and Caldwell, 1999 [129]). This approach starts from 1 mg/m³ of soluble nickel compounds as a LOAEL under workplace conditions. With a combined adjustment factor of 155, including factors for years exposed (70/7.2), hours exposed (168/40), breathing rate (0.75/1.0), and susceptible subpopulation (5.0), this LOAEL for workplace conditions is adapted to continuous exposure of the general population. This results in a LOAEL for the population of 1 mg/m³ / 155 = 0.006 mg/m³ or 6 µg/m³. CONCAWE proposes an additional adjustment factor of 10 for the extrapolation from LOAEL to NOAEL to obtain a level of 0.6 µg Ni/m³ (600 ng Ni/m³).

In any threshold approach, the choice of the starting point is a crucial step. If one agrees with the Doll report conclusions, then a concentration of 1 mgNi/m³ is to be selected. However, in preparing the 1990 Doll report, only part of the Falconbridge results as updated by Shannon et al. (1991 [147]) could be used. The data published by Antilla et al. (1998 [151]) on the occurrence of excess lung cancer at relatively low concentrations have not been available at all at that time.

In the Shannon et al. paper [147], the first group of workers with an increase in lung cancer has an estimated cumulative exposure of 0.1-0.3 mg/m³ x years. However, due to the relatively small number of lung cancer cases, the increase in the lung cancer rate does not reach statistical significance. If nevertheless these data are used, the starting point can be the mean exposure of this group, i.e., 0.2 mg/m³ x years. Formally following the steps as described in the UK „pseudo threshold“ approach for arsenic [210] (cf. Chapter 2.6.2.2), a factor of 10 for extrapolation to a concentration at which no effects could be detected in an epidemiological study, a factor of 4.5 for annual time of exposure, the use of a factor of 70 (years of life) and a factor of 10 for sensitive groups result in a concentration of 6 ng/m³.

A synopsis of the three “treshold-based approaches” described above is given in Table 2.6.7.

Table 2.6.7: Three different “threshold-based apporaches” as described above

	Based on Doll report [150], factors according to Thun et al. [99]	CONCAWE [129]	Approach based on Shannon et al. [147]
Starting point	1 mg/m³	1 mg/m³	0.2 mg/m³ x years
LOAEL to NOAEL	10	10	10
Exposure time	8/24 h/d 225/365 d/y	40/168 h/w	4.5
Work to lifetime	40/75	7.2/70	1/70
Breathing rate		0.75	
Sensitive groups	10	5	10
Limit value	1100 ng/m³	600 ng/m³	6 ng/m³

Up to now, little speciated monitoring of nickel in ambient air has been undertaken. Therefore, it is not possible at this stage to reach any conclusion regarding likely qualitative differences in nickel exposure between the general population and nickel refinery workers. CONCAWE (Lewis and Caldwell, 1999 [129]) has, however, stated that the most common forms of nickel in ambient air are nickel sulfate, nickel oxide and complex nickel-ferric oxide. More specifically, according to CONCAWE, 50 % of total nickel in air is soluble nickel, up to 8 % is nickel oxide and the remainder is in the form of complex nickel oxides. Citing the CEPN study [152], CONCAWE states that nickel subsulfide may be present in the atmosphere at extremely small concentrations. However, recent measurements performed in Germany suggest the possibility that concentrations of nickel subsulfide in ambient air are higher than previously expected (cf. Chapter 1).

2.6.4.3 Proposed Limit Value For Nickel

Considering all the above mentioned arguments, the Working Group proposes a limit value for non-cancer effects in the range of 10-50 ng Ni/m³ as an annual mean.

The three available unit risk estimates relating to cancer induced by exposure to nickel compounds are 3.8×10^{-4}, 2.4×10^{-4} and 2.5×10^{-4} $(\mu g/m^3)^{-1}$ from the WHO, U.S. EPA and CEPN, respectively. When combined with the “one-in-a-million” excess lifetime risk criterion, these estimates give a range of possible limit values for protection from cancer of 2.6 - 4 ng/m³. For reasons already given, the Working Group has accepted that these values may overestimate the true risk by about one order of magnitude. The lower bound of the range of concentrations which can be derived using a “threshold approach” is 6 ng/m³ (see Table 2.6.7). It is possible that the true cancer risk of the general population is overestimated because of the possibility that nickel refinery workers are exposed to different nickel species than individuals in the public at large.

Thus, a limit value in the range 10-50 ng/m³ as derived from non-cancer effects can be judged compatible with the aim of limiting the excess lifetime cancer risk to not more than one in a million. The majority of the Group proposes a limit value at the lower end of this range as an annual mean of total airborne nickel.

> The following three **reservations** have been notified:
>
> **WHO:**
> „WHO (1997) derived a unit risk of 3.8×10^{-4} per µg/m³ for excess lung cancer caused by nickel compounds. This corresponds to a concentration of 2.5 ng Ni/m³ associated with an excess life time risk of one in a million. In view of the possible overestimation of the risk by applying a linear extrapolation and the apparent difference in nickel species regarding their carcinogenic activity, the lower end of the range (10 ng Ni/m³) is considered to provide sufficient protection of the general population to the carcinogenic effects of nickel compounds in ambient air.”

EEB:

"Also in the case of nickel the EEB proposes to take special care of the precautionary principle that levels of possible genotoxic carcinogens should not be allowed to rise, and to use roughly the upper bound of the urban background values of 10 ng Ni/m^3 as limit value".

Industry:

"The industry members of the Working Group disagreed with the recommendation of 10 ng/m^3 as a limit value. This disagreement was based upon the following issues:

1. Interpretation of the NTP Nickel Sulfate Hexahydrate Study low dose group effects:
   Industry, the NTP, the California EPA, and the members of the TERA Risk Assessment peer review have all identified the 0,03 mg/m^3 exposure level as a NOAEL in this study. The Working Group defined 0.03 mg/m^3 as a LOAEL. The difference in the proposed 10 ng/m^3 limit value and the industry-supported 50 ng/m^3 proposal are entirely based upon this issue. Due to disagreement on the definition of the study NOAEL level at 0.03 mg Ni/m^3, the next highest dose of 0.06 mg Ni/m^3 (a LOAEL) was used by the Working Group to derive the 10 ng Ni/m^3 limit value. Since this was a LOAEL, an extra 10-fold safety factor was applied for LOAEL to NOAEL extrapolation. Industry disagreed with this approach which resulted in a 5-fold increase in the Overall Uncertainty Factor hence, the difference in between the 10 and 50 ng Ni/m^3 limit value proposals.

2. Threshold-based carcinogenesis should be considered.
   The TGD [201] defines a "genotoxic carcinogen" as having a direct action on DNA. The available data demonstrate that the nickel ion has a very low affinity for DNA and hence should be handled as a threshold carcinogen within the definition in the TGD. A threshold-based extrapolation shows a threshold as occurring between 600 and 1100 ng Ni/m^3. Therefore, there should be no concern for carcinogenicity at ambient air concentrations and the limit value for nickel should be based solely on non-carcinogenic respiratory inflammation.

3. Alternatively, the Linear Extrapolated Risk Estimate for nickel subsulfide would have to be modified in ambient air.
   The low or non-existent level of nickel subsulfide in ambient air should also be considered. There are two main issues, (i) the carcinogenic potency of nickel subsulfide is at least an order of magnitude higher than that of nickel oxide (i.e., NTP data), and (ii) the risk factors derived by the U.S. EPA, WHO, etc. are all based upon nickel subsulfide exposure. Consequently, the occupational cancer risk of nickel based on a linear extrapolation should be modified when applied to ambient air. Specifically, the risk should be reduced by the relative maximum concentration of nickel subsulfide (i.e., ~ 30 %) in ambient air and a minimum 10-fold potency would need to be applied to the linear risk extrapolation to generate a linear based risk estimate for ambient air. The result would be a cancer limit value at a risk level of 1:1,000,000 above 100 ng Ni/m^3. This also lends credence to the conclusion of #2 above.

   Taking these issues into account, industry maintains that a limit value of 50 ng Ni/m^3 would be more than adequately protective of the health of the general public."

It has been discussed in the Working Group without unanimous approval that under the precautionary principle the current concentrations of carcinogenic compounds in ambient air should not rise. Therefore the lower end of the range given is suggested as a limit value for the general population. In the immediate vicinity of specific industrial sources, however, a higher value within the range proposed might be considered as a temporary exception.

2.6.5 Summary Of Limit Values

The following Table 2.6.8 summarises the proposed limit values.

Table 2.6.8: Summary of Limit Value Proposals

Element	As	Cd	Ni
Limit value (based on non-cancer effects)	100 ng/m³	5 ng/m³	10-50 ng/m³
Limit value based on cancer, unit risk approach	0.66 ng/m³	0.24-0.55 ng/m³	2.6-4 ng/m³
Limit value based on cancer, threshold approach	4-13-50 ng/m³		6-1100 ng/m³
Limit value proposal	4-13 ng/m³	5 ng/m³	10-50 ng/m³

2.7 Summary Of Key Points And Recommendations

2.7.1 Arsenic, Effects On Human Health

Under average circumstances, the oral uptake of arsenic via food and drinking water contributes the largest amount to the total dose. On average, arsenic uptake via ambient air contributes less than 1 % to the total absorbed arsenic dose.

The organic arsenicals found in seafood, such as arsenobetaine and arsenocholine, have been studied by several researchers and have been found to be of low toxicological significance.

The skin is a target organ in people exposed to inorganic arsenical compounds. Hyperkeratoses and hyperpigmentation are common in people orally exposed, but have very rarely been reported after inhalation exposure. Gangrene of the extremities, known as Blackfoot disease, is due to peripheral vascular disorder. Neuropathy and increased mortality from cardiovascular diseases have been observed in epidemiological investigations of workers exposed to high levels of airborne arsenic. A LOAEL of 50 µg/m³ for non-cancer effects can be derived from these workplace studies. Using uncertainty factors of 5 (workplace to continuous exposure), 10 (LOAEL to NOAEL), and 10 (interindividual variation) yields a limit value proposal of 100 ng/m³ based on non-cancer effects.

There is sufficient evidence that inorganic arsenic compounds are skin and lung carcinogens in humans. Both trivalent and pentavalent arsenic compounds have occurred in these exposure situations. At present the possibility cannot be ruled out that any form of inorganic arsenic may be carcinogenic. Arsenic and arsenic compounds are classified to be known human carcinogens by IARC and EC.

Lung cancer is considered to be the critical effect following exposure to arsenic via inhalation. WHO proposes a unit risk of 1.5×10^{-3} $(\mu g/m^3)^{-1}$ for arsenic.

Although the point is still the subject of scientific debate, there is some evidence in the literature that at least part of the mechanisms by which arsenic acts as a carcinogen may be indirect ones, implying that for these mechanisms a safe threshold does exist and that linear extrapolation leads to an overestimation of risk. However, at present, there is not sufficient evidence to reasonably exclude the possibility that arsenic may act as a genotoxic agent, too.

On the basis of the above considerations, the Working Group concludes that the limit value of 100 ng/m³ derived based on non-cancer effects does not provide sufficient protection with respect to cancer. On the other hand, the Working Group feels that the unit-risk-based approach which yields a concentration of 0.66 ng/m³ associated with a one-in-a-million risk is likely to overestimate the ”true” risk, but obviously this cannot be quantified precisely. However, the Working Group believes that the ”pseudo threshold” approach proposed by the UK yields values (4 – 13 ng/m³) which are in the range of the suggested uncertainty. Taking into account the current urban background concentrations of arsenic in ambient air in Europe, a limit value near the lower bound of this range seems to be appropriate for the majority of the Working Group. The Working Group does not put forward a proposal for deposition limits for arsenic compounds.

All in all, the majority of the Working Group proposes a limit value in the range of 4-13 ng/m³ as an annual mean concentration for arsenic in air.

Inspite of the intensive discussions within the Working Group, there are still differences of opinion in respect to the proposed limit values for arsenic as well as for cadmium and nickel. Reservations by some members of the Working Group are included in chapter 2.6.

For arsenic, EEB proposes 3 ng/m³, whereas industry proposes 50 ng/m³.

2.7.2 Cadmium, Effects On Human Health

Under average circumstances, the oral uptake of cadmium via food and drinking water contributes the largest amount to the total dose. On average, cadmium uptake via ambient air contributes less than 3 % to the total absorbed cadmium dose. In smokers, however, inhalation of cigarette smoke results in an important contribution which can represent the dominant factor for the absorbed cadmium dose.

The kidney is the critical organ with respect to long-term occupational or environmental exposure to cadmium and non-cancer effects. Renal effects are usually described in relation to cadmium excretion in urine which is taken as an indicator of cumulative long-term exposure and renal cadmium burden. The WHO identified a critical cumulative dose of 100 µg/m³ x years for the occurrence of renal effects, corresponding to a continuous exposure concentration of 270 ng/m³. Taking this as a LOAEL and using uncertainty factors of 5 (LOAEL to NOAEL) and 10 (interindividual variation) results in a limit value proposal of 5 ng/m³ based on non-cancer effects which is in accordance with the WHO Air Quality Guideline value of 5 ng/m³.

IARC has classified cadmium as a human carcinogen. The EC classification of cadmium and several cadmium compounds is group 2 (substances which should be regarded as if they are carcinogenic to man). The U.S. EPA calculated an inhalation unit risk estimate of 1.8 x 10^{-3} $(\mu g/m^3)^{-1}$ which was recently proposed to be increased to 4.15 x 10^{-3} $(\mu g/m^3)^{-1}$. However, there are concerns regarding possible confounding by co-exposure to arsenic in the workplace studies in which an excess in lung cancer mortality was reported, and the importance of cadmium as a carcinogen at environmental concentrations is not generally accepted. WHO has refrained from recommending a quantitative cancer risk estimate because of the uncertainties concerning qualitative and quantitative aspects of possible carcinogenicity of cadmium.

The results of genotoxicity tests are equivocal, suggesting linear as well as non-linear partial mechanisms being involved in the carcinogenic activity of cadmium. Therefore, linear extrapolation is likely to overestimate the „real“ effect. A threshold might be possible, too, but at present evidence is not strong enough to suggest the adoption of a threshold hypothesis.

The Working Group believes that these uncertainties and the uncertainty associated with the extrapolation from (the unit risk reference point of) 1 µg/m³ to considerably lower concentrations at the nanogramme/m³ level mean that the 0.24-0.55 ng/m³ range based on the unit-risk approach is likely to be overprotective.

In summary, the majority of the Working Group believes that an annual mean concentration level of 5 ng/m³ as derived from non-cancer effects provides also an appropriate level of protection from cancer risk due to exposure to cadmium. This value is identical with the new WHO AQG value.

However, EEB proposes 2.5 ng/m³, whereas Industry proposes 18 ng/m³ based on non-cancer effects.

As cadmium compounds act as systemic pollutants and as their transfer into the food chain is of particular relevance, the Working Group is of the opinion that the concentration limit value should be supplemented by a deposition limit. Using a tolerable dose of 0,75 – 0,95 µg(kg bw)$^{-1}$d^{-1} for cadmium intake as starting point and taking into account the dust accumulation on the above-ground parts of plants, the cadmium uptake of vegetables from the soil, the protection of ground water and the uptake of soil by playing children, the majority of the Working Group recommends to set a limit value for cadmium deposition for the local scale in urban and industrialized areas in the range 2.5 – 5 µg m^{-2}d^{-1}.

However, EEB proposes a lower value for the tolerable cadmium uptake used as starting point and a deposition limit of 2.0 µg/m^{-2}d^{-1}.

An examination of the balance between cadmium input (e.g., by deposition and use of fertilizers) and output (e.g., by leaching) shows that this toxicology-based limit does not protect from a slow cadmium accumulation in soils. To prevent such slow accumulation for all types of soils and applying the precautionary principle, the cadmium input by deposition should be more than one order of magnitude lower, that is 10 - 100 µg Cd m^{-2}year^{-1} (0.03 – 0.27 µg/m^{-2}d^{-1}). Such low inputs can only be reached by a joint EC policy for the reduction of cadmium in all environmental media and a close co-operation with UNECE.

The Working Group proposes to collect and assess more data on deposition from various Member States, for instance in the frame of the CAFE project.

2.7.3 Nickel, Effects On Human Health

Under average circumstances, the oral uptake of nickel via food contributes the largest amount to the total dose. On average, nickel uptake via ambient air contributes less than 1 % to the totally absorbed nickel dose, the contribution of smoking usually amounts to less than 10 %.

Non-cancer effects are seen on the respiratory tract, the immune and defence system, and on endocrine regulation. Allergic skin reactions are the most common health effect of nickel affecting about 2 % of the male and 11 % of the female population. However, there is no evidence that airborne nickel causes allergic reactions in the general population, although this reaction is well documented in the working environment.

Due to a lack of well-documented human data, animal data have to be used as a starting point in deriving limit values. In experimental animals, effects on the respiratory system are the best documented non-cancer effects of inhalation exposure to nickel. With respect to the choice of the starting point, two options have been discussed in the Working Group, to use (i) 30 µg/m³ as a NOAEL or (ii) 60 µg/m³ as a LOAEL in combination with an uncertainty factor of 10 for the extrapolation to a NOAEL. Using uncertainty factors for extrapolation to continuous exposure (6), for interspecies (10) and intraspecies variation (10) as further steps, a limit value protective with respect to non-cancer effects of 10-50 ng/m³ can be derived.

There is agreement that nickel refinery workers exposed by inhalation to various nickel compounds in the past are at a significantly higher risk for cancer of the lungs and the nasal cavity than the non-occupationally exposed population. With the exception of metallic nickel, IARC has classified nickel as known human carcinogen. In the EC classification, nickel oxide, nickel monoxide, and nickel sulfide are classified as Group 1 (known human carcinogens), whereas nickel, nickel carbonate, nickel hydroxide, nickel sulfate, and nickel tetracarbonyl are classified as Group 3 (possible carcinogens).

The available information is not sufficient to permit a clear classification of nickel compounds as being non-genotoxic carcinogens. Therefore, under precautionary aspects the existence of a threshold should not be assumed.

The U.S. EPA has estimated the lifetime cancer risk from exposure to nickel refinery dust to be 2.4×10^{-4}, the WHO has recommended a unit risk of 3.8×10^{-4} $(\mu g/m^3)^{-1}$. When combined with the “one-in-a-million” excess lifetime risk criterion, these estimates give a range of possible limit values for nickel with respect to cancer of 2.6 - 4 ng/m³. However, an overestimation of effects is to be expected if a limit value is based on nickel in general, i.e., without speciation. Other sources of potential overestimation should be kept in mind, such as the uncertainty associated with the extrapolation from the unit risk reference point to the nanogramme/m³ level. The Working Group does not see the necessity to derive deposition limit values for nickel compounds.

In summary, a limit value in the range 10-50 ng/m³ as derived from non-cancer effects can be judged compatible with the aim of limiting the excess lifetime cancer risk to not more than one in a million. The majority of the Group proposes a limit value at the lower end of this range as an annual mean of total airborne nickel.

However, reservations were made by EEB and WHO proposing to generally select 10 ng/m³, and Industry proposing 50 ng/m³.

2.7.4 Effects On Ecosystems

The knowledge of possible effects of arsenic, cadmium and nickel compounds on terrestrial ecosystems is still rather limited and restricted to single compartments. Direct phytotoxic effects on vegetation are rarely observed and are combined with concentrations in leaves much higher than health-related levels. Long-term effects on the ecosystem are related to the accumulation of pollutants in the rooting zones of the soils, which may decrease the species density and the biological activity and may adversely influence the species composition of soil organisms. The evaluation of these effects is extremely complex and the available information is more or less rudimentary. Therefore, at present no proposals for eco limit values based on these effects can be made. From the perspective of phytotoxicity, accumulation and harmful effects on the edaphon, only cadmium seems to be relevant. However, the Working Group feels that the health-related limit values proposed for cadmium (concentration and deposition) will also be protective with respect to terrestrial ecosystems.

2.8 Literature To Chapter 2

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3. MEASUREMENT AND ASSESSMENT

3.1 Introduction And Requirements Of The Framework Directive

The council directive 96/62/EC on ambient air quality assessment and management (framework directive) [1] states in its article 1 that

- the assessment of ambient air quality in Member States on the basis of common methods and criteria and
- the adequate and comprehensive information of the public

rank under the important objectives of this directive.

The general strategy for the assessment of ambient air quality is mainly described in article 6 of the framework directive, specific requirements have to be laid down in daughter directives. For the components SO_2, NO_x, PM10 and Pb, this has been done in the first daughter directive [2], and for the second daughter directive on benzene and CO, a common position has been reached in December 1999 [3]. In order to establish an assessment system where the subsystems for different pollutants fit as much as possible together, and in order to save costs by collocation of stations whenever possible, the requirements laid down in the first and second daughter directives present important guidance also for the daughter directive on heavy metals and metalloids. Deviations from this scheme should be kept to a minimum and should be introduced only if they are justified by specific properties of the other pollutants. Consequently, the requirements of the framework directive are discussed in combination with the already existing daughter legislation [1-3].

The general assessment strategy of the framework directive has been described several times within the position papers of the pollutants already mentioned (compare, for example, [4]), so that a short outline may be sufficient here. In addition, a Working Group of the Member States together with the Commission is preparing a document giving further guidance on assessment issues.

The assessment of air quality in Member States is not based on measurements alone, but explicitely includes model calculations, emission inventories, objective estimation and monitoring as parts of an integrated system.

Notwithstanding this general principle, measurements can be regarded as „backbones“ of this system, especially for compliance checking. The monitoring efforts are reasonably differentiated according to the pollution burden within three regimes (Figure 3.1).

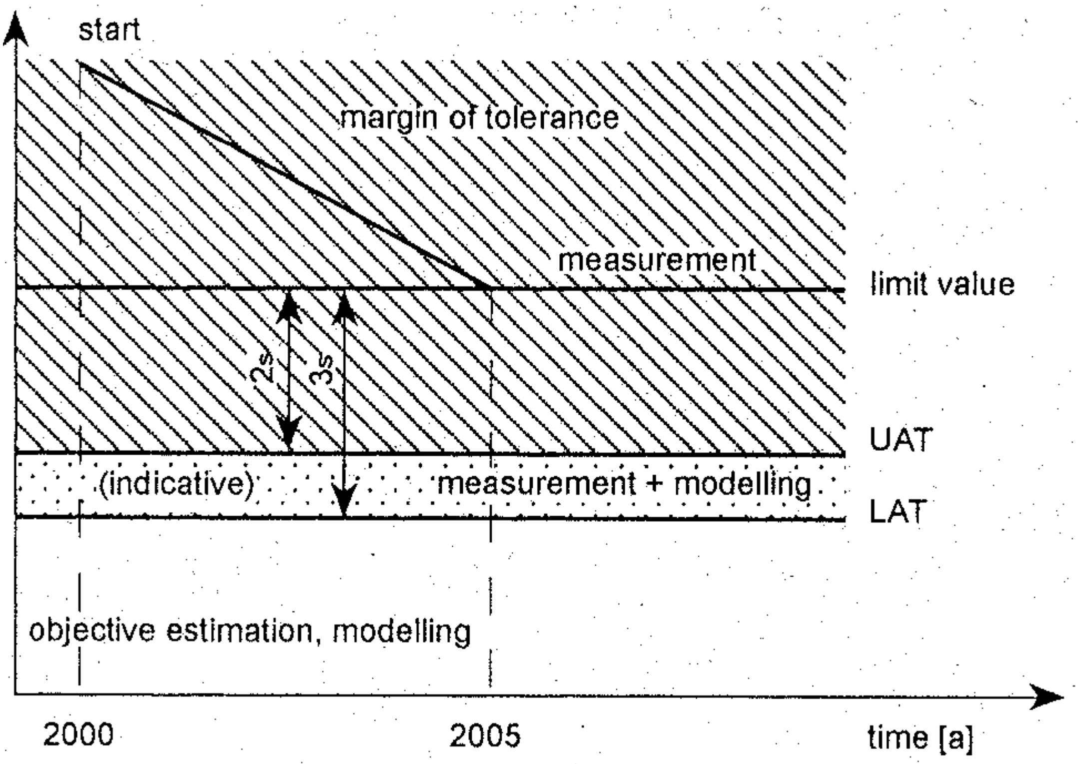


Figure 3.1: The monitoring regimes of the EC framework directive

In the regime above and close to the limit values (above the upper assessment threshold UAT) measurements are mandatory. The UAT was introduced to safeguard measurements also in those cases where the pollution burden is scarcely below the limit value, but may exceed the limit value in the near future, e.g. due to meteorological circumstances. Therefore the UAT can be defined as the limit value minus approximately twice the standard deviation of annual variations of the pollution burden. The role of the model calculations within this regime is to supplement measurements (e.g. in busy streets), to help with source reconciliation and to plan reduction measures (action plans).

The margins of tolerances also contained in figure 3.1 are important for the setting up of action plans, but do not have direct significance for the assessment.

In the second regime between the UAT and the lower assessment threshold (LAT), the monitoring efforts may be reduced (e.g. by using indicative measurements), and the measurements may be combined with and partly substituted by model calculations. The LAT can be defined as the limit value minus approximately three times the standard deviation of the interannual variability of the pollution burden (compare annex V of the first daughter directive [2]). Below the LAT, attainment with the limit values can be taken for granted. Therefore, measurements are no longer mandatory (with the exception of agglomerations) and can be fully substituted by model calculations and objective estimates. The three monitoring regimes are also important for the quality assurance.

The upper- and lower assessment thresholds (UAT, LAT) will be laid down in the daughter legislation, and it is one of the tasks of this Working Group to propose them (compare 3.2.4).

The overriding principle for measurement planning is the assessment of exposure. Therefore, measurements have to be performed at places which are representative for the exposure of the general population (e.g. urban background of agglomerations in the case of people), and at places where there is the greatest risk of exposure above the limit values (hot spots, e.g. residential areas in industrial surroundings). The exposure duration must be relevant compared with the averaging period of the limit values. For example, roadside measurements are relevant for the assessment of limit values based in hourly means, whereas limit values based on annual means should be assessed in residential quarters close to heavy traffic or industrial installations.

The measurement planning thus follows an overall strategy of stratified sampling in typical micro-environments, and is generally not directed towards spatial representativeness. However, the first daughter directive contains some guidance on spatial representativeness. Very small micro-environments in the immediate vicinity of sources shall be avoided. The measurements should be representative of at least 200 m² at traffic oriented sites, several square kilometers at urban background sites, and at least 1000 km² for sampling points targeted at the protection of ecosystems or vegetation (annex VI [2]).

Another task of this Working Group is thus to propose the micro-environments which should be monitored (dependent on routes of exposure, sources for heavy metals and metalloids and protective goods, see subchapter 3.2.1), and to describe those parts of the monitoring strategy which are particularly important for heavy metals and metalloids (compare subchapter 3.11).

In the first daughter directive, specific monitoring requirements are fixed in annex VII [2], where minimum numbers of sampling points are given for some micro-environments. The numbers depend on the population of the zones or agglomerations and on the three regimes of the pollution burden, where measurements are the sole source of information. This has been done to safeguard a comparable coverage by monitoring sites in all Member States, following the requirement of assessment by common methods and criteria.

In the case where additional information from emission inventories and diffusion modelling is available, the number of sampling points may be reduced.

Consequently, proposals have to be made for minimum numbers for sampling points in the micro-environments relevant for Cd, As and Ni (compare 3.2). In addition, it has to be checked whether the guidelines for the microscale siting of sampling points contained in annex VI of the first daughter directive also apply for metals and metalloids other than lead.

The ultimate aim of the assessment is to classify the whole territory of the Member States into zones and agglomerations corresponding to the three regimes of the pollution burden. This should preferentially be accomplished by maps showing the different zones. As the classification into zones determines the density of the monitoring network, the results should ideally be known beforehand at the stage of the network design. This is naturally impossible, and therefore zone classification and measurement network optimisation are iterative processes, starting with a preliminary assessment on the basis of available data and improving this assessment step by step.

The preliminary assessment is required by article 5 of the framework directive. A recent report from the EC gives some guidance for this first step [5], which can also be applied for metals and metalloids.

Quality assurance is of paramount importance, if comparable assessment results with known and retracable uncertainties are called for. The framework directive and the daughter legislation therefore give special attention to this subject. Important elements are data quality objectives for the required accuracy of assessment methods as well as minimum requirements for data capture and the time coverage of the measurements. These minimum requirements and the necessary accuracy can be less stringent for indicative measurements, in order to reduce monitoring costs in the two regions below the UAT (compare Figure 3.1).

The minimum requirements give valuable guidance for quality assurance and the appropriate choice of assessment methods. Data quality objectives for the assessment of metals and metalloids are discussed in chapter 3.5

Due to practical limitations, air quality measurements always have the character of spot checks. By means of continuous (or, in the case of manual sampling, quasi-continuous) measurements, it is possible to cover the variations in time completely. However, quasi-continuous daily sampling of suspended particulates with subsequent analysis of the contents of dust in the laboratory is very costly. One way to reduce these costs are intermittent measurements at fixed sampling sites (for example once per week or every third or second day). The at random measurements will reduce the accuracy of yearly statistics in relation to continuous or quasi-continuous monitoring at the same spot. If this reduction in accuracy is low (let us say ≤ 10 %), it may be acceptable. Another way to cut short costs for sampling and analysis is to prolong the sampling interval from one day to one week or even longer (compare chapter 3.3). The monitoring capacity gained by the reductions of the measurement frequency may be used to measure at two or three sites instead at one site only. In this way, the spatial resolution can be increased without additional effort. Therefore, it makes sense to look at the possibilities to use at random sampling, and to determine the loss of accuracy in dependence of the sample size. A reduction in sample size can be a very efficient means to use for indicative measurements. Again, the additional uncertainty introduced by at random sampling of a given sample size should be known. This is examined further in subchapter 3.2.3.

Finally, the use of reference methods is an important means to safeguard the comparability of monitoring results. A reference method for heavy metals and metalloids is discussed in section 3.3. It should be borne in mind that any other method can be used by Member States, provided that the equivalency to the reference method has been demonstrated (equivalence methods).

3.1.1 Specific Monitoring Requirements For Heavy Metals And Metalloids Following From The Risk Assessment (Chapter 2) And From The Emission Inventories (Chapter 1)

From the risk assessment in chapter 2, the following important conclusions for the monitoring strategy for Cd, As and Ni compounds can be drawn:

- As no acute effects from metals and metalloids have to be expected in the concentration range occurring in the European Union, the assessment of long term effects is what counts. Consequently, the limit values can be based on annual means, and monitoring of annual means will be sufficient for compliance checking. However, for other purposes such as the surveillance of fugitive emissions by industrial plants or for source apportionment as basis for action plans, it may be advisable to have monitoring data on a shorter time scale, e.g. daily means. It is therefore recommended to monitor heavy metal and metalloid concentrations on a daily basis and to calculate annual means from the corresponding time series. If compliance checking is the main purpose, it is sufficient to sample in longer intervals, e.g. on a weekly or even monthly basis by means of low volume samplers (compare chapter 3.3). In this case, the sampling efficiency must be checked and demonstrated to be equivalent to the reference method (compare chapter 3.3). It also follows from this statement that at random measurements at fixed monitoring sites should be allowed for, provided that the additional uncertainty introduced by them in comparison to quasi-continuous sampling is small enough (compare 3.2.3).

- As different uptake routes (inhalation, ingestion of vegetables, uptake of contaminated soil) can endanger human health or the environment as a whole, it is not sufficient to base the assessment on concentration measurements alone. Deposition of cadmium compounds on surfaces (e.g. leafs, soil) should be limited and assessed as well. Consequently, concentration measurements should be supplemented by deposition measurements in those cases where the possibility of high depositions has to be taken into account.

- From the discussion of sources in chapter 1 it follows that combustion processes and certain industrial facilities (e.g. secondary copper smelters) are the most relevant emitters. Traffic does not add significantly to urban background concentrations at traffic exposed sites, at least not in densely populated areas like conurbations in Western, Central and Southern Europe, where considerable background levels from a variety of combustion processes exist. Therefore, urban background and residential areas near certain industrial sources (hot spot situations) are the most relevant micro-environments to monitor. In addition, some monitoring should be performed in rural and remote areas (surveillance of ecosystems, background data).

3.2 Network Design

3.2.1 Number Of Monitoring Stations For Concentration Measurements And Siting Criteria

As stated already in the introduction of this chapter, care should be taken to design the monitoring networks for particular pollutants in such a way that they can be easily combined as sub-systems into a coherent general air quality measurement network for the framework directive and their daughter directives. Collocation of monitoring sites should be used whenever possible, to reduce monitoring costs. Consequently, the monitoring requirements laid down in the first daughter directive should be used as starting points and should only be changed if this is necessary due to specific properties or source configurations of the pollutants.

As already mentioned in chapter 3.1.1, there are three micro-environments which are relevant for the exposure to metal (other than lead) and metalloid compounds, which can be characterized as follows (table 3.1):

Table 3.1: Characterisation of micro-environments relevant for the monitoring of heavy metal (other than lead) and metalloid compounds

Site	Characterisation
Urban background	Residential areas in conurbation and towns. The sites should be representative for larger parts of the cities (several km²) and should not be directly impacted by sources (e.g. industry, power generation).
Industrial	Residential quarters directly influenced by industrial facilities like secondary copper smelters, foundries, metal processing or producing plants, metal and petrochemical refineries, power generation and waste incinerators with low outlets, ongoing work to clean up contaminated sites. For deposition, also agricultural areas and gardens near industrial sources.
Rural background and remote areas (also covered by EMEP network)	Sites located in rural areas outside built-up areas and very far away from large sources with a spatial representativeness of a few hundred up to several thousand square kilometers. In general, EMEP siting criteria [6] are valid for these sites.

Urban background

The general monitoring strategy in urban areas has been described already in the preceding position papers [e.g. 4], so that we can keep ourselves short here. If the assessment is based exclusively on measurements, a higher network density is necessary (minimum number of stations N_i). If the assessment is also backed up by emission inventories or diffusion modelling, the minimum number of stations may be reduced (N_0). The minimum number of sampling points for fixed measurement N_i laid down in annex VII of the first daughter directive [2] applies to urban background and traffic exposed sites. As traffic hot spots do generally not cause higher concentrations of arsenic, cadmium and nickel compounds, there is no need to monitor them in all agglomerations.

The minimum number N_i of sampling points laid down in annex VII can therefore be somewhat reduced, bearing also in mind that the spatial distribution of metals and metalloids in the urban background away from specific industrial sources is generally quite uniform. In the Rhine Ruhr area, for instance, the spatial variations between the stations (between 8 and 16 km apart) are generally less than a factor 2 [7].

Following these arguments, the Working Group proposes the following scheme for the minimum number of sampling points for fixed measurement N_i:

Table 3.2: Minimum number N_i of sampling points for fixed measurement for the monitoring of the urban background, where fixed measurement is the sole source of information

Population of agglomeration or zone (thousands)	If concentrations exceed the upper assessment threshold	If annual means concentrations are between the upper and lower assessment thresholds
0 to 499	1	1
500 to 999	2	1
1000 to 1999	3	1
2000 to 2749	4	2
2750 to 3749	5	2
3750 to 4749	6	3
4750 to 5999	7	3
> 6000	8	4

The sampling points should be collocated with measurement points for particulate matter and lead as much as possible (compare subchapter on microscale siting for minimum distance for collocated samplers). They should be representative for areas of several square kilometers and hence avoid the direct influence of sources. Preferentially, they should be situated in residential quarters with high population density near city centers or downtown areas and placed in open spaces away from buildings and other obstacles to enable an unrestricted air flow to the sampling head. Appropriate sites are, for example, yards of public buildings (city halls, schools, hospitals), small parks, recreational areas or squares.

In addition, it is recommended that concentration measurements of heavy metal (other than lead) and metalloid compounds should be performed at some traffic exposed sites per Member State (as a rough guidance, 1 traffic exposed measurement site per 10 Mio. inhabitants).

As has been stated already, the minimum number N_i of sampling points in table 3.2 can be further reduced if the assessment is backed up by emission inventories and diffusion modelling. In this case, the numbers proposed in table 3.2 can be reduced by 50 %. However, at least one sampling point per zone should remain.

Industrial hot spots

Network design for the compliance checking of areas near industrial hot spots has to solve two major problems:

- It is not obvious which industrial installations can cause significant exposure and possibly breaches of the limit values. There may be thousands of installations emitting metals and metalloids, but most of them (for example power plants with high stacks and efficient flue gas cleaning) will not give rise to hot spots of exposure in their surroundings. Therefore criteria are needed to establish a priority ranking of those facilities which are hot spots of exposure, and which have the greatest risk of exceeding the limit values.

- When the relevant emitters are identified, the appropriate sites and number of monitoring stations have to be selected. It has to be borne in mind that the concentration distribution in space and time can be very inhomogeneous. It is therefore necessary to take into consideration all existing information on the concentration field (e.g. diffusion modelling, results from indicative measurements) beforehand.

Nevertheless it is possible to establish some empirical rules for the priority setting of industrial installations and for the measurement planning, once relevant emitters have been identified.

(i) The first step to select industrial sites with relevant impact normally is to look at emission inventories (per country and per facility) and to rank the facilities according to their annual emissions. The installations with the largest annual emissions clearly need closer consideration. Chapter 1 with the discussion of main sources gives some guidance which types of installations should be looked at.

A straightforward way to do so would be to define a certain threshold of annual emissions as relevant. This possibility seems to be simple at first glance. In reality, however, the additional air quality concentration load depends so heavily on local circumstances as the height of the outlet(s), topography, the distance from sensitive targets, the temperature of the effluents etc. that no general threshold can be defined. For example, large combustion plants fired with coal or oil generally have comparably high emissions of metals and metalloids due to their huge fluxes of flue gas. Therefore they will definitely contribute significantly to background levels in built up areas. However, because of their high stacks and efficient flue gas cleaning, they will generally not cause local hot spots of air pollution. This statement is confirmed by a recent evaluation of the cancer risk originating from power plants in the USA [73]. The maximum individual risk caused by all emitted carcinogens taken into account (including nickel and arsenic) was below 1×10^{-6} for 97 % of the installations and below 1×10^{-4} for all installations. It is therefore necessary to take into account further criteria mentioned below.

(ii) A second important criterion is the existence or possibility of a significant share of fugitive emissions for example from stock piles, ridge turrets or other openings in large production halls without flue gas cleaning, or from loading and unloading processes of heavy metal or metalloid rich materials. Also outlets with low emission heights (< 50 m) have to be considered.

It should be borne in mind that uncovered stockpiles, for example, do not correspond any longer to the techniques to be applied under the IPPC directive and the BREFS (compare chapter 1.5.2). The full enforcement of IPPC will thus reduce fugitive emissions. However, as long as they do exist, they have to be taken into account for the measurement planning.

There are two main reasons why fugitive emissions should be scrutinized carefully. Generally they stem from low emitting sources, therefore their emissions have low dilution factors and contribute more than proportional to ambient air concentrations in the near surroundings. This holds even more true for depositions often combined with coarse dust, which will have short residence times in the atmosphere and settle quickly near the source(s).

Secondly, fugitive emissions tend to be underestimated in emission inventories or are not included at all. Consequently, diffusion modelling will also underestimate the pollution burden.

A combination of criteria (i) and (ii), that is high annual emission combined with a significant share of fugitive emissions and/or emissions from low outlets, clearly makes the installation a candidate for closer inspection.

(iii) If available, the results of model calculations and/or indicative measurements should be used as indicators for the expected ambient air concentrations and/or depositions, and to use the modelled or measured concentration distribution for the appropriate placements of the sampling point(s). Again, great care should be taken to check whether fugitive emissions have been taken into account correctly. Measurements are necessary if the calculated ambient air concentrations including background levels for this area exceed the upper assessment threshold, and if protective interests as humans or agricultural areas can be exposed significantly (compare criterion (V)).

However, if the exceeding of upper assessment thresholds or limit values is already caused by high background levels without significant (> 50 %) additional burden by the factory, the area may be combined with other areas in exceedance to a larger zone, and no particular monitoring of this factory is necessary.

(iv) Further important criteria for relevant contributions from industrial installations are the results from indicative measurements, also from other media like soil, vegetation or other bioindicators. Elevated levels of metals and metalloids in the soil or in vegetables near facilities clearly point to relevant emissions into the air. Indicative measurements can be performed as spot check measurements with reduced time coverage and sample size (compare 3.2.3), and/or applying analytical methods with reduced accuracy. The source can clearly be regarded as relevant if

- metal and metalloid levels are above the upper assessment threshold and in addition;
- arsenic, cadmium or nickel concentrations are 50 % or more above the urban background levels. The proposed percentage of 50 % stems from the uncertainty of indicative measurements and takes additionally into account the interannual variability due to different meteorological conditions.

(v) A criterion of paramount importance is the exposure of protective interests in the surroundings of the installation. The position of residential quarters, of gardens, of playing grounds and, in the case of depositions, also of agricultural areas should be checked. If no health relevant long term exposure can occur near the factory or in areas where there is a risk of exceeding the limit values, measurements can be dispensed with.

Following the empirical rules mentioned above, one can reduce the number of the possible industrial hot spots to the relevant ones in order to arrive at a reasonable monitoring effort. Taking the example of nickel compounds, there are five major production sites and 22 major stainless steel production units in Europe. However, as also small facilities can be a significant source of local air pollution, both big and small plants have to be scrutinized during network design.

The number, position and size of areas with protective interests (e.g. residential areas) together with the area where upper assessment thresholds are exceeded and the spatial variation of the pollution burden are also decisive for the number and placement of monitoring stations after the identification of the relevant emitters. How distinct this spatial variation can be is shown in figure 3.2 for a medium sized town in Germany (Stolberg with about 60.000 inhabitants) with several industrial emitters of metals and metalloids. In 1989, the monitoring site about 600 m northwest of the main emitting plant had cadmium and arsenic levels twice as high as in the center of Stolberg (about 2 km from main source) and about one magnitude higher than the background in this area (third monitoring point) [7]. In 1990, the main emitting source changed to a cleaner technology (oxidation and reduction within one smelting reactor instead of the three steps sintering machine, stockpile and pit furnace)). It is interesting to notice how distinct the pollution levels could be reduced (compare monitoring results from 1989 and 1996). Recently, the pollution levels decreased even further (1997: arsenic and cadmium concentrations of 4.0 and 3.4 ng/m^3, respectively; 1998: 2.3 and 2.7 ng/m^3).

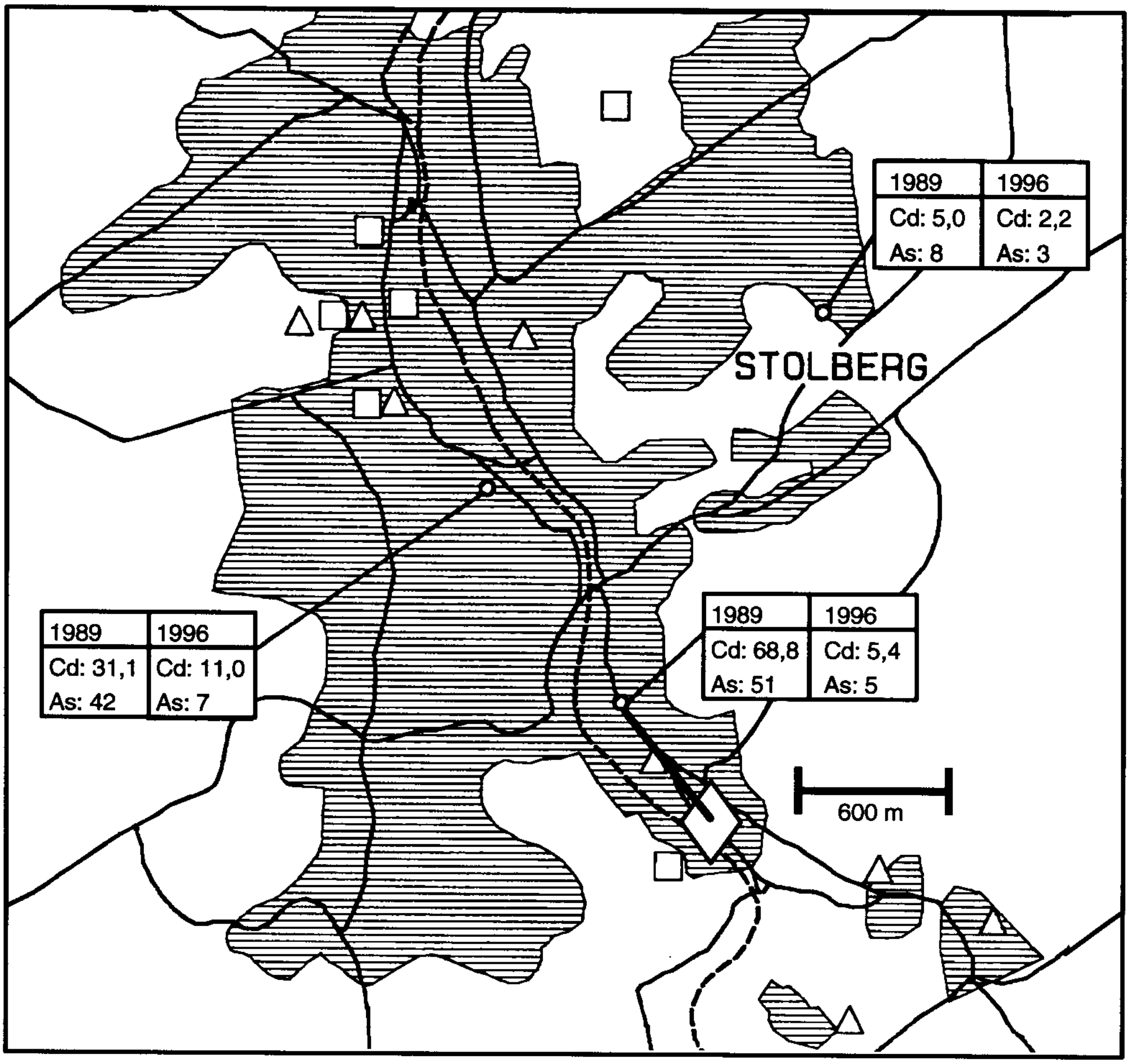


Figure 3.2: Annual averages [ng/m^3] (1989 and 1996) at three measurement sites (o) in Stolberg near metal producing and processing industry.

♦ : main emitter (lead foundry)
Δ: smaller emitters
☐: stock piles; build up areas are shaded

For an efficient measurement planning and the correct siting of monitoring station(s), the size and position of the areas with protective interests (e.g. residential areas) in relation to the emitter(s) as well as the approximate concentration field should be known beforehand. The approximate spatial distribution can be calculated by diffusion modelling and/or determined by indicative measurements (compare chapter 3.4). The indicative measurements (e.g. at random with reduced sample size and measurement periods less than a year) can be arranged in a regular grid (e.g. 500 x 500 m), the grid width determining the spatial resolution of the measurements. Figure 3.3 shows a recent example from a residential area situated north of a steel works, where nickel and cadmium compounds have been monitored for half a year with a frequency of 5 samples per month in a regular grid of 500 x 500 m [8].

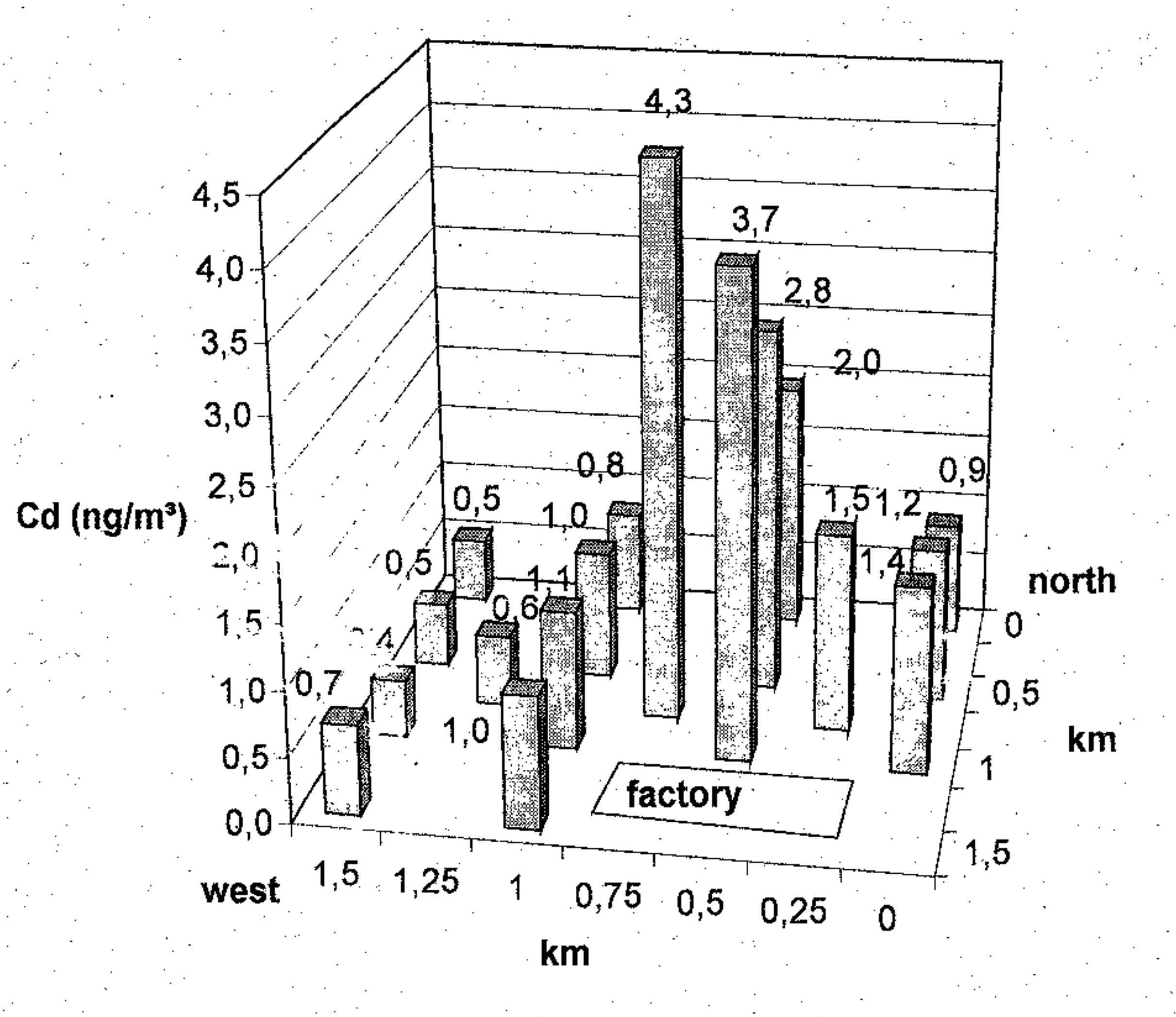


Figure 3.3: Measurements in a regular grid (500 x 500 m) in a residential area north of a steel works. Measurement period from October 1998 to March 1999. Measurement frequency 5 samples per month

If the spatial distribution of the pollution burden is known, monitoring site(s) for compliance checking can be chosen without much difficulty. Monitors should be installed at places where long term exposure of protective interests coincides with the highest pollution burden. Generally this will be the case at those parts of residential areas (for the protection of human health) which have the shortest distance from the industrial facility in the main wind direction. Again, small micro-environments and the direct influence of other minor sources should be avoided. The Working Group recommends that the monitoring site should be representative at least of an area of 250 m x 250 m. Consequently, sampling points should keep a minimum distance of 100 - 200 m from the fences of installation areas. It is recommended that a measuring station to check compliance in an industrial hot spot should be placed at a distance of 150 ± 50 m from the border of the installation, if protective goods can be exposed there.

If there is only one residential area adjacent to one side of the emitter, one monitoring station for compliance checking is sufficient, provided that the concentration field has been checked by diffusion modelling and/or indicative measurements. In the case of several residential areas situated in different directions in respect to the emitter or surrounding the plant, it may be necessary to install two monitoring stations. One station should be situated within the main wind direction, the other one in the residential area nearest to the plant. If nothing is known about the spatial distribution of the pollutant burden, the number of monitoring sites should be doubled.

This leads to the following recommendation for the monitoring of concentrations near industrial sites, if the pollution burden is above the UAT (compare chapter 3.2.4), and there is a significant added burden to the pollution (≥ 50 % of background levels) by the plant(s):

Case	Number of monitoring sites
one or several main emitter(s), one residential area, concentration field known	$N_0 = 1$
one or several main emitter(s), one residential area, concentration field unknown	$N_i = 2$
one or several relevant emitter(s), several residential areas, concentration field known	$N_0 = 1\text{-}2$
one or several relevant emitter(s), several residential areas, concentration field unknown	$N_i = 2\text{-}4$

This recommendation may cause high monitoring efforts in some Member States if many isolated smaller industrial facilities with pollution levels above the upper assessment threshold are scattered over the whole territory of the Member State. In this case it should be possible by derogation to group smaller industrial facilities of the same type and with similar flue gas cleaning together into one zone, even if they are not adjacent to each other; instead of placing them into different zones. This case is analogous to the possibility of grouping several traffic hot spots into one zone, proposed by the Working Group on assessment.

The network design for deposition measurements will be dealt with in chapter 3.1.2.

Rural background sites

Monitoring of this micro-environment is targeted at measuring pollution levels representative for large rural areas, which are not influenced by local emissions, but by long range transport. These levels can therefore be regarded as to represent the widespread burden on vegetation and other ecosystems in Europe. Consequently, annex VI of the first daughter directive [2] and the EMEP manual for sampling and chemical analysis [6] give criteria for the distance of monitoring sites from the nearest sources and for the spatial representativeness, which can be summarized as follows:

	1st daughter directive	EMEP manual
spatial representativeness	≥ 1.000 km²	> 2.500 km²
distance from		
- agglomerations, large pollution sources	> 20 km	50 km
- built up areas, other sources	> 5 km	
minor roads, small scale domestic heating		100 m

These criteria implicitly contain a definition of rural background areas and must be followed when setting up monitoring sites.

In the framework of EMEP, CCC (Coordinate Chemical Centre) is responsible for measurement data collection and handling. This section is mainly based on information and data received from CCC.

Metals have not been a part of EMEP’s monitoring programme before 1999. During the sixth phase of EMEP (since 1995), the co-operation concerning metals between EMEP and other international programs was, however, extended. As a first step the Steering Body of EMEP requested EMEP/CCC to collect already available data on metals among the participants. A number of stations have been reporting monitoring data on metals within the EMEP area in connection with various national and international programmes (HELCOM, AMAP, OSPARCOM, MEDPOL).

Concentration measurements of metals and metalloids from rural background and remote areas are collected by the EMEP network from approx. 20 sites in Europe. The EC-Member States Belgium, Denmark, Germany, Ireland, Finland and the United Kingdom have provided monitoring data [9]. In addition, wet or bulk deposition of metals and metalloids is measured at approx. 30 EMEP stations in Europe. The EC-Member States Denmark, France, Germany, United Kingdom, Ireland, Finland and Sweden are contributing [9]. The location of the EMEP monitoring stations having reported data on metals and POPs (Persistent Organic Pollutants) is presented in Figure 3.4.

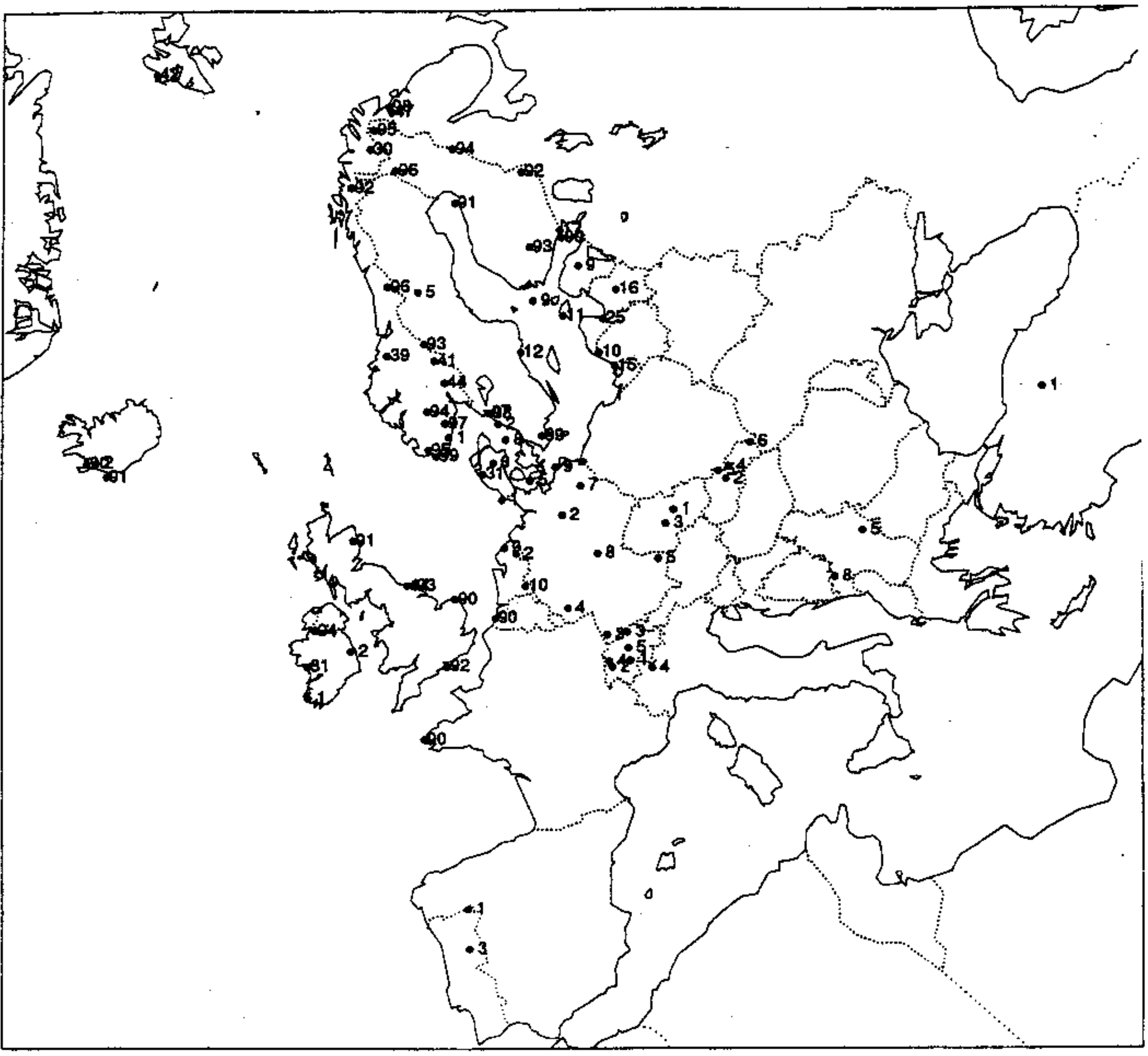


Figure 3.4: Location of monitoring stations which have reported data to the EMEP metal and POP data base [9]

The EMEP network in its present state is far from reaching spatial coverage for the European Union. There are considerable gaps particularly in Southern Europe, for concentration data also from Scandinavia [9].

In the framework of EMEP special attention is paid to the Cd monitoring and modelling, because only this metal is included in the present UN ECE protocol (compare chapter 1.5.2). The location of Cd monitoring sites, which data for 1996 and/or 1997 are included in the EMEP/CCC data base, is presented in the table of Annex C.

Information on the quality of the precipitation measurements is available from the HELCOM-EMEP-PARCOM-AMAP intercomparison test in metals in precipitation. The exercise was divided in an analytical and a field intercomparison part and included seven metals: Pb, Cd, Cu, Zn, As, Cr and Ni. The results from the analytical part of the intercomparison showed that a majority of the participating laboratories reported deviation values within 25 % of the theoretical values. The field intercomparison part of the exercise was carried out at the German EMEP station Deuselbach (DE04). The results have been published [59] (see also section 3.3.2).

As no particular eco limit values for the protection of ecosystems in rural and remote areas have been proposed (compare chapter 2), there is no need for compliance checking of eco limit values in those areas.

Instead of EC ambient air quality legislation for the input of metals and metalloids into remote ecosystems, the Working Group has recommended to follow a strategy of emission reductions and to cooperate closely with the UN ECE protocol on heavy metals and the EMEP monitoring network. In addition, it has to be borne in mind that rural and remote areas will also benefit from the improvement of air quality in the source regions, brought forward by the attainment of the proposed limit values for metals and metalloids, for particulates and also by complying with the IPPC directive. By abating the emissions of the main sources, long range transport will be reduced as well.

In order to assess any progress of this strategy in all Member States of the EC, it is absolutely necessary that the gaps in the monitoring network in remote areas will be closed. In addition, background data help to understand regional and transboundary transport processes and give some information on metal and metalloid levels hardly directly influenced by anthropogenic sources. Therefore the Working Group recommends to install 1 monitoring station for concentrations and wet or bulk depositions per 100.000 km². These background stations shall fulfil the siting criteria issued by EMEP [6] and should be used mutually for the EMEP network and for the purposes of the EC directive to provide background data for concentrations and depositions. Consequently, the following number Ni (based only on measurements) is recommended for rural areas:

Ni (rural) = A/100.000 (A = area of the country in square kilometers).

With full assessment, this figure can be reduced to the number of stations necessary for the EMEP network for signatories and 1 per EC Member State having not signed the UNECE protocol.

As no eco limit values have been proposed by the Working Group, it should be borne in mind that these numbers are recommendations rather than obligations for the Member States.

Microscale siting

The criteria for the microscale siting of measurements which were given by the Working Groups for other pollutants and particularly in annex VI No. II of the first daughter directive [2] apply for metals and metalloids as well. They are shortly summarized as follows:

- Metal and metalloid compounds should be sampled within an unrestricted air flow without any obstructions in the vicinity of the sampler (e.g. a minimum of 1,5 metres away from buildings, trees, etc.).

- Great care should be taken not to sample the exhausts or evaporative losses of measurement vans or from the outlet of stations, pumps, etc..

- The inlet sampling point should be between 1,5 m and 4 m above the ground. In the case of background measurements (urban, rural) higher positions up to ten metres may be considered.

- The sampler should be stable and mechanically safe.

- As the samples are to be analyzed for metallic compounds, the site should be checked for any localized potential source for contamination (e.g. paint brushing of steel constructions). Steps should be taken to avoid such contamination.

- For rural and remote stations, the siting criteria of EMEP [6] should be followed.

- Roadside sites should be positioned at the building line of residential buildings adjacent to busy streets. (Please note that roadside measurements are only optional for metals and metalloids.)

- In order to save costs, sampling (also grab sampling) can be collocated with measurement stations for other pollutants, especially for background measurements.

- The sampling sites should be fully documented according to the Guidance document of EEA and ERLAP.

In addition, interfering sources, security, safety against vandalism, access, electrical power and telephone, „visibility“ of the site - public profile, safety of public and operators, planning requirements, and others, should also be taken into account.

3.2.2 Monitoring Strategy For Deposition Measurements

Introduction

The most important micro-environment for compliance checking of the proposed deposition limit value for cadmium are residential areas with gardens or playgrounds for children and agricultural areas near industrial hot spots (compare chapter 1.3 and 3.2.1). In urban background locations without industrial impact, the deposition burden will normally be below the upper assessment threshold and often even below the lower assessment threshold (compare chapter 3.2.4). Consequently, the monitoring effort for this micro-environment can be kept on a low level.

This applies even more to rural and remote areas. For compliance checking, no monitoring is needed. However, deposition monitoring fulfilling the needs and requirements of the EMEP network is highly recommended, in order to establish a reliable European data base on heavy metal and metalloid deposition into ecosystems by long range transport, and for the validation of the models.

Industrial hot spots, experience of the Member States

In the Member States, three different strategies for monitoring of deposition near industrial hot spots are used at present, which will be shortly described.

Austria [69] has established a network of individual sampling points in urban areas and near industrial locations, where dust jars according to the Bergerhoff method [60] are exposed for one month. Annual means are calculated, and the national ambient air quality standard (compare chapter 1.5) must be met at each individual sampling point.

Belgium (Flanders) has developed a two stage approach for screening (indicative) investigations and for comprehensive monitoring [70]. In both cases, monitoring is restricted to a sector within the lee of the most frequently occurring wind directions, and to possible risk areas. As dustfall normally settles close to sources, all sampling points are within a maximum distance of 1 km from the source. For screening measurements, 4 jars are placed at distances of 100 m, 250 m, 500 m and 1.000 m from the border of the installation, respectively. For small installations (surface area of the plant < 0,04 km²), 2 jars at 250 m and 500 m distance are sufficient. NILU samplers (compare chapter 3.3.2) as described in a Belgian national standard [71] are exposed for 30 ± 2 days, and annual means are calculated from the results.

If the arithmetic mean of all sampling points is below the guide value (compare chapter 1.5), measurements can be stopped. If this mean lies between the guide and the limit value, the screening measurements will continue. If the results of at least one jar are above the limit value, comprehensive monitoring has to start.

In this case, the assessment area (the sector bordered by the main wind directions, the borders of the installation and a circle with a maximum distance of 1.000 m (compare figure 3.5) is divided into grids with meshes of 100 m, 250 m, 500 m and 1.000 m, parallel to the borders of the installation (compare figure 3.5). At each such point, a sampling jar (NILU sampler [70]) will be installed. Strictly speaking, this scheme applies to installations with surface sources or sources which emit lower than 30 m. For higher emitting sources, a somewhat more complicated monitoring regime must be followed.

If several companies are situated in each other's neighbourhood, the assessment areas may partly overlap. In this area only one common monitoring network needs to be installed.

From the yearly averages of all jars within the assessment area, an arithmetic average will be calculated, which will be compared with the limit and guide values. Because of the higher density of the network close to the source, this average will be a weighted one, with a stronger contribution of the sampling points close to the source (compare figure 3.5).

In Germany, dustfall measurements are performed in regular grids with grid widths of 1.000 m [72], 500 m or, if the deposition load is spatially very inhomogeneous, down to 250 m. At each intersection of the grid, a jar according to the Bergerhoff method [60] (compare section 3.3.2) will be exposed for 30 days. An annual average for each grid element will be calculated from the results of the four Bergerhoff samplers installed in the corners of the grid element. The result to be compared with the limit values thus refers to areas of 1 km², 0,25 km² or 0,0625 km², depending on the grid width. Sampling points situated on the area of the installation are not taken into account.

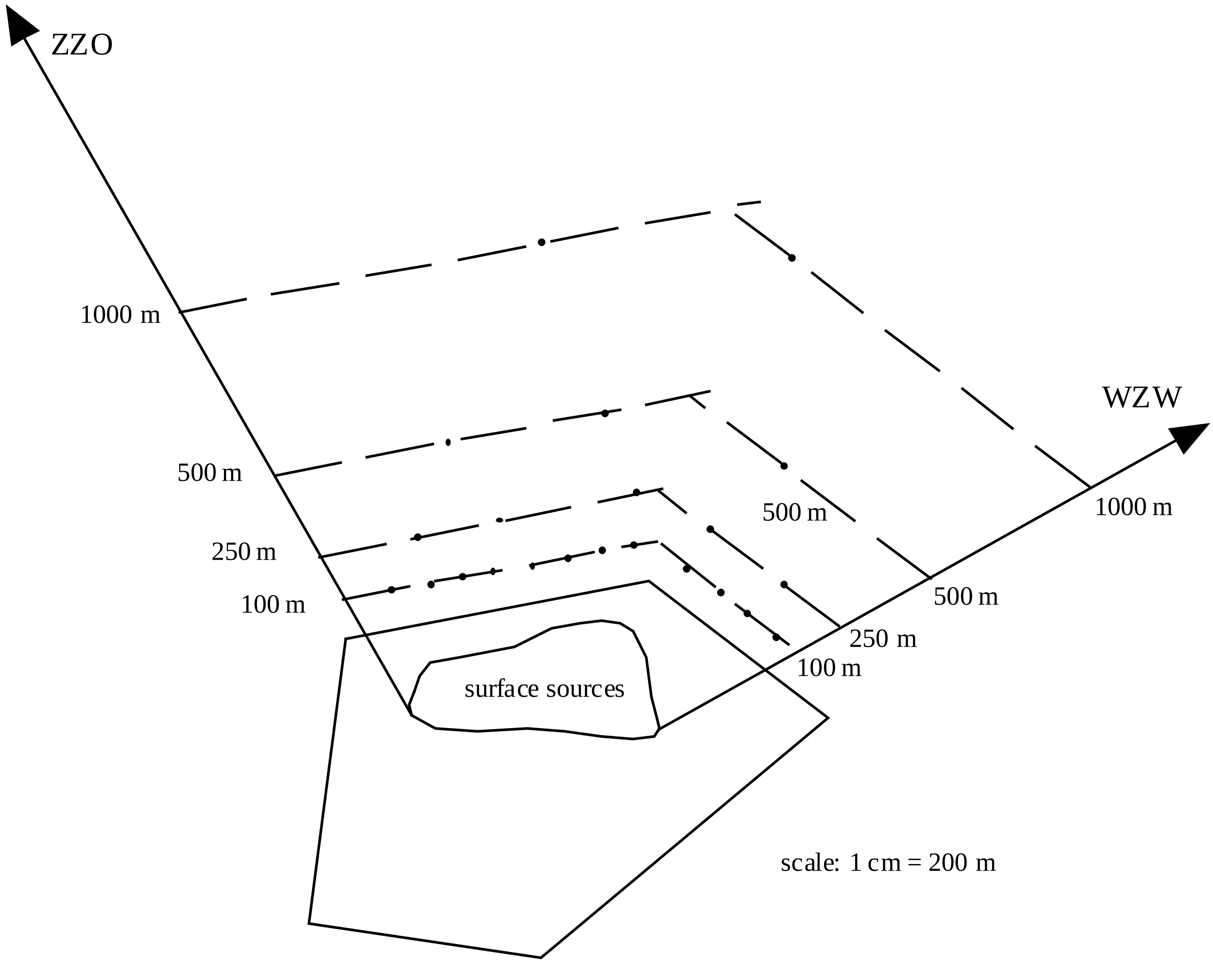


Figure 3.5: Monitoring network for dust deposition near sources in Belgium (Flanders) for sources with emission heights < 30 m

The grid must cover all areas potentially at risk up to a maximum distance of 30 times the height of stacks or outlets (height > 30 m), or an area which is 2 x 2 km² large for installations with emission heights < 30 m and surface areas of the plant < 0,04 km².

Proposal for a monitoring strategy near industrial hot spots

Measurements should start with indicative investigations, following the procedure applied in Belgium (Flanders). 4 jars shall be placed in the main wind direction at distances of 150 m ± 15, 250 m ± 25, 500 m ± 50 and 1.000 m ± 100 from the border of the installation, respectively. For small installations, 2 jars at 250 m and 500 m distance are sufficient. The samplers should be exposed for at least half a year and should be changed monthly. If the arithmetic mean of all samplers is below the upper assessment threshold (compare chapter 3.2.4), any further measurements can be dispensed with.

The proposed measurement planning for comprehensive deposition measurements near industrial hot spots (assessment based only on measurements) is outlined in figure 3.6. A regular grid of potential sampling points is laid over the area surrounding the installation up to a distance of 1.000 m from the factory borders in the main wind direction and of 250 m otherwise.

Up to a distance of 500 m from the factory borders, the grid width shall be 250 m, to take into account the spatial inhomogeneity of the pollution burden near the sources. For distances between 500 m and 1.000 m, the grid width shall be 500 m (main wind direction). Sampling points falling on the site of the installation are not taken into account (compare figure 3.6). The inception of the grid shall be the location of the plant.

Measurements have to be performed only for those grid elements which contain sensible targets which may be affected by cadmium deposition, as residential areas with gardens or playgrounds for children, and agricultural areas.

Annual arithmetic means are then calculated from the measurement results of the four samplers in the corners of each grid element to be assessed. The characteristic to be compared with the limit value thus corresponds to a deposition burden which is integrated over the area of the grid element. At least results from 3 sampling points per grid element should be available.

This integration procedure seems to be appropriate for deposition monitoring because of the following reasons:

- The uncertainty of deposition measurements is higher than that for concentration measurements (compare chapter 3.3.2). This uncertainty can efficiently be reduced by averaging the results of 4 (3) samplers.

- Deposition does not act on individual spots, but on surfaces carrying crops or on soil surfaces. A spatial integration takes this feature of deposition into account.

The exact location of the measurement points and the grid will depend on local conditions like the size of the factory area. Therefore, an individual measurement planning on the basis of the principles outlined here will be necessary.

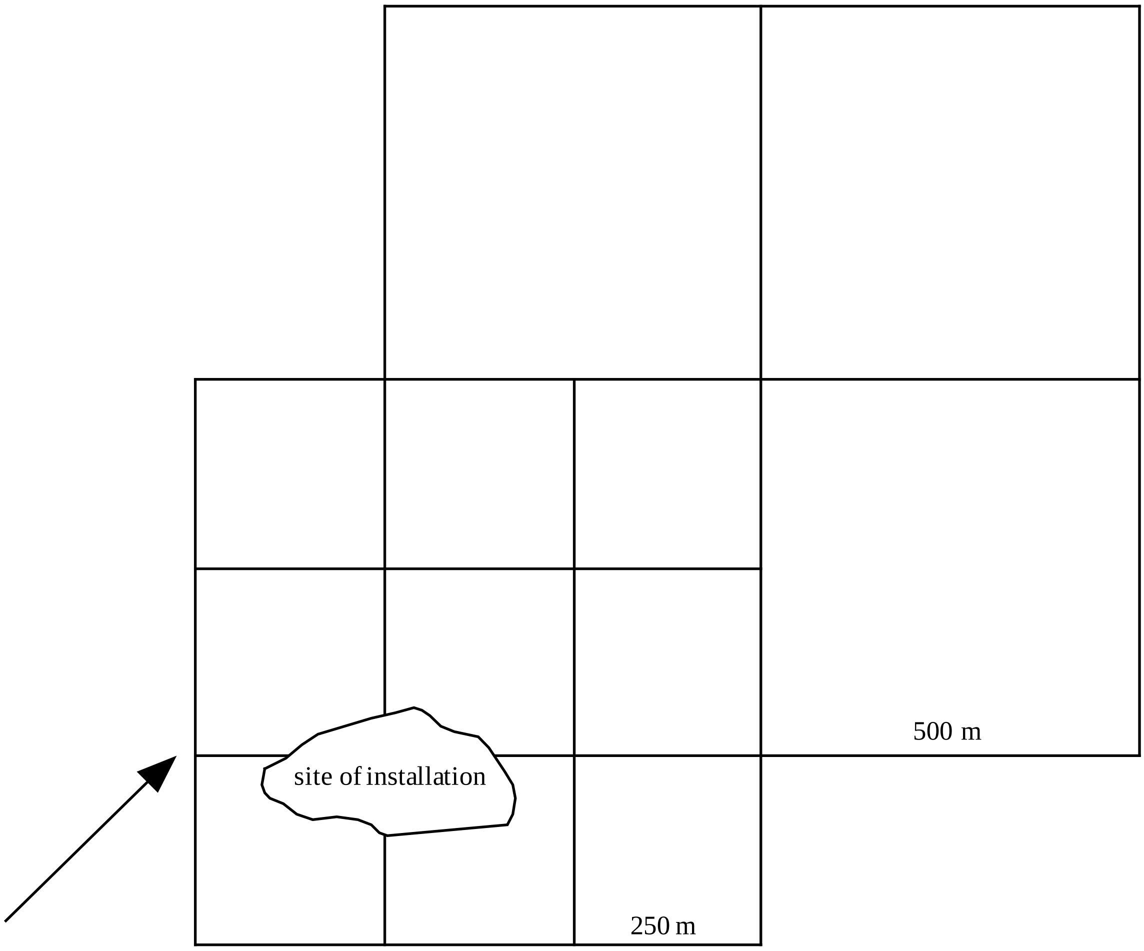


Figure 3.6: Proposal for a monitoring grid of depositions near industrial hot spots (assessment based on measurements only).
dot: potential measurement point
arrow: main wind direction

Deposition measurements by dust jars cannot separate dust originating from „fresh“ emissions of the plant from „old“ resuspended dust blown up again from any surfaces within that area. Experience has shown that resuspension can be considerable from even, paved areas such as roads or yards without vegetation, whereas resuspension plays only a minor role for overgrown areas (e.g. gardens, meadows, fields). Consequently, dust jars should be exposed at sites carpeted with vegetation, to minimize resuspension as far as possible.

<u>Monitoring strategy in urban areas</u>

If nothing is known about cadmium deposition in urban areas, preliminary measurements should be performed. One dust jar per urban background site for the measurement of cadmium, arsenic and nickel concentrations (compare table 3.2) should be exposed. The monitoring period should be at least one half year, with changes of the jar once in a month. If the Bergerhoff method or a comparable method is used, the monthly samples can be combined before analysis to reduce monitoring costs. If the measured depositions (yearly or half yearly averages) are below the lower assessment threshold (compare chapter 3.2.4) at the site, no further measurements are necessary. This will normally be the case, unless the site is influenced by industrial emissions. If the results range between the upper and lower assessment threshold, the monitoring regime for preliminary measurements should be continued at the site. If the upper assessment threshold is exceeded, deposition measurements should be performed in an area of 500 x 500 m^2, which includes the urban background site, exposing the dust jars at the corners of the square. The results are then calculated as an annual average from the exposed 4 dust jars.

3.2.3 Time Coverage

A complete resolution in time of a series of measurements can only be obtained by continuously or quasi-continuously operating samplers. For deposition measurements with sampling times of one month, quasi-continuous sampling does not cause excessive costs. 12 monthly samples per year will have to be analyzed. This figure can even be more reduced by combining the contents of several dust jars before analysis. On the other hand, there is always the risk of data loss by damage or contamination of the jars, especially when using glass jars in wintertime. Therefore a 100 % time coverage would not allow for the loss of a single sample. If allowance is made for the loss or contamination of one sample (corresponds to one month), a minimum time coverage of 90 % for deposition measurements is reasonable.

Concentration measurements are normally based on daily sampling, although with low volume samplers, longer sampling intervalls (e.g. one week) can be achieved. Quasi-continuous sampling of 365 daily means, hence a time coverage near 100 % is feasible, but the analysis of so many samples in the laboratory and the necessary logistics (daily change of samples, transport to the laboratory) are quite costly. The costs for logistics can be somewhat reduced by samplers which change and store loaded filters automatically (high volume samplers like Digitel can change and store up to 15 filters automatically). However, the high costs for analysis remain.

Because of high investment and operational costs, networks with continuously or quasi-continuously operating instruments tend to have few stations and consequently a poorer resolution in space. On the other hand, random sampling with reduced costs for operation and analysis is cheap enough to allow for more sampling points in a certain zone, thus giving a better resolution in space at the expense of an additional uncertainty in time resolution.

Especially for compounds like heavy metals and metalloids with effects from chronic exposure and hence an assessment on the basis of annual averages, at random sampling and analysis offers an obvious option to reduce monitoring costs, provided that the sample size is big enough to yield an acceptable overall accuracy.

The Working Group thinks that an expanded uncertainty of 10 % (on the 95 % confidence level, that is 2 times the standard deviation) compared with continuous measurements is acceptable for compliance checking. It should be borne in mind that this additional uncertainty refers to the reduced time resolution. Consequently, at random measurements for heavy metals and metalloids are considered equivalent to continuous measurements, provided that

- the sample size is big enough to yield an expanded uncertainty compared with continuous measurements of ≤ 10 % (95 % confidence level),

- the sampling dates be evenly spread during the measurement period (normally one year), which can be easily realised if they are chosen at random.

The necessary sample size N to keep the expanded uncertainty below 10 % was calculated by two independent methods. One method uses the resampling of stochastic samples from continuous or quasi-continuous time series of monitoring data, which then represent the population (sample size N_{max}). 12 data sets for cadmium compounds, 8 data sets for nickel compounds and 10 data sets for arsenic compounds from 4 EC Member States (Belgium, Italy, the Netherlands and Germany) were examined (compare tables 3.3 and annex C). The time series stem from urban background (U) and industrial (I) sites, in one case from a rural site (R). About one half of the data sets are not complete, but large enough for the resampling study. They were taken as population, though.

Resampling was performed by means of a computer program without replacement and without stratification [10, 11]. From each time series, a total of 100 stochastic „bootstrap“ samples of the considered size N were taken on the basis of daily means (24-values). For each bootstrap sample, the interesting statistic (arithmetic mean) was calculated. From the resulting bootstrap distribution of the mean value, the additional uncertainty due to stochastic sampling (standard deviation) was calculated in dependence of the sample size. It is thus possible to determine the necessary sample size (number of days N) which corresponds to an additional uncertainty of 5 % (= expanded uncertainty of 10 %). The results are presented in table 3.3 and the full data in annex.C, together with the results of the second method.

For indicative measurements, the tolerable uncertainty can be higher. Therefore the necessary sample sizes of daily means N to arrive at additional uncertainties of 10 % and 15 % are also presented in table 3.3.

Table 3.3: Sample sizes N corresponding to uncertainties (standard deviation) of 5 %, 10 % and 15 % calculated from different time series (compare text)

Pollutant:	Arsenic	uncertainty (standard dev.)	5 %	10 %	15 %
Site	type	year	N (days)	N (days)	N (days)
Hoboken (B)	I	1996	240	119	64
Hoboken (B)	I	1997	164	62	30
Essen (D)	I	1996	180	71	35
Essen (D)	I	1997	171	66	33
average:	**I**		**189**	**80**	**41**
Biest (NL)	U	1998	143	51	24
Bilthoven (NL)	U	1998	143	50	24
Vlaardingen (NL)	U	1998	182	73	36
Wolfsburg (D)	U	1996	302	198	126
Wolfsburg (D)	U	1997	288	177	108
average:	**U**		**212**	**110**	**64**
Kollumerwaard (NL)	R	1998	207	90	46

Pollutant:	Arsenic	uncertainty (standard dev.)	5 %	10 %	15 %
Site	type	year	N (days)	N (days)	N (days)
Hoboken (B)	I	1996	289	178	108
Hoboken (B)	I	1997	170	65	32
Essen (D)	I	1996	310	214	141
Essen (D)	I	1997	315	223	150
Terni (I)	I	1996	321	235	163
Terni (I)	I	1997	136	47	23
average:	**I**		**257**	**160**	**103**
Biest (NL)	U	1998	144	51	25
Bilthoven (NL)	U	1998	143	51	24
Vlaardingen (NL)	U	1998	185	75	37
Wolfsburg (D)	U	1996	196	82	42
Wolfsburg (D)	U	1997	198	84	43
average:	**U**		**173**	**69**	**34**
Kollumerwaard (NL)	R	1998	222	102	54

Pollutant:	Arsenic	uncertainty (standard dev.)	5 %	10 %	15 %
Site	type	year	N (days)	N (days)	N (days)
Hoboken (B)	I	1996	116	38	18
Hoboken (B)	I	1997	39	11	5
Essen (D)	I	1996	130	44	21
Essen (D)	I	1997	132	45	22
Terni (I)	I	1996	180	71	36
Terni (I)	I	1997	147	53	25
average:	**I**		**124**	**44**	**21**
Wolfsburg (D)	U	1996	114	37	17
Wolfsburg (D)	U	1997	173	67	33
average:	**U**		**144**	**52**	**25**

The second method uses a formula given by Bennett et al. [12] for the calculation of the variance var of the mean value <c>, calculated from a sample drawn out of a finite population of size N. The measured data (daily means) may be given as set $\{C_1, ..., C_n\}$ from a finite population (N = 365). If the population were infinite, the mean value $<C>_n$, the variance of the mean value $var(<C>_n)$ and the standard deviation (S) can be calculated by the well known formula (1) - (3):

$$(1) <c>_n = \sum_{i=1}^{n} c_i / n$$

$$(2) var(<c>_n) = s^2 / n$$

$$(3) s^2 = \sum_{i=1}^{n} [c_i - <c>_n]^2 / [n - 1]$$

However, in the case to be considered here the population of all daily means of a year is finite (N = 365 daily means). The variance in this case can be calculated according to Bennett et al. [12] simply as

$$(4) var(<c>_n) = s^2 / n - s^2 / N ,$$

which can be transformed into

$$(5) \quad var(<c>_n) = s^2 [1 - n / N] / n.$$

From this variance, the standard deviation $u\langle C\rangle_n$ of the mean value of sample size n can be easily obtained. If the standard deviation $u\langle C\rangle_n$ is devided by the mean value, the variation coefficient vpred (compare annex C, in percent) can be calculated.

The full data in annex C (one data sheet for each considered time series) demonstrate that the results obtained with the formula of Bennett [12] compare nicely to the resampling study. This can be taken either from the graphic presentations (thick line: resampling; dotted line: formula), showing the variation coefficient in dependence of the sample size, or from the tables (v(<C>): variation coefficient from resampling; vpred: variation coefficient calculated according to Bennett [12]).

Going back to the results presented in table 3.3, the necessary sample sizes N (daily means) to arrive at uncertainties of 5 %, 10 % and 15 % for all time series can be directly taken from that table.

The following conclusions can be drawn:

- The variations in the time series for nickel compounds are less pronounced than for cadmium and arsenic compounds. The strongest variations can be observed for cadmium compounds at industrial sites. Bearing in mind the manifold of nickel sources in urban areas, this result seems to be reasonable.

- Time series of cadmium compounds near industrial sites vary to such an extent that quasi-continuous monitoring is necessary for compliance checking to keep the additional uncertainty below 5 %. Time coverage must exceed 70 %.

- For urban background sites and also for the monitoring of nickel and arsenic compounds at industrial sites, it seems acceptable to reduce the necessary time coverage to 50 %, corresponding to a sampling frequency of every second day for compliance checking. This is a pragmatic proposal, bearing in mind that the additional uncertainty introduced by at random sampling may slightly exceed 5 % standard deviation in some cases for cadmium and arsenic. For nickel compounds, even a time coverage of 33 % (one day out of three days) would be acceptable.

- For indicative measurements, an additional uncertainty of 15 % (standard deviation) by random sampling seems appropriate. This corresponds to approximately 60 daily samples per year for arsenic and cadmium (not valid for industrial sites) and about 25 daily samples for nickel compounds. Again, to simplify things and make them more feasible, the Working Group proposes a minimum time coverage of 14 % (one daily sample a week at random, corresponding to 52 daily samples per year). The samples must be evenly distributed over the year. For indicative measurements of cadmium compounds at industrial sites, the time coverage has to be raised to 33 % (one daily sample out of 3 days at random, evenly distributed over the year).

- It has to be borne in mind that data sets from only four Member States could be included into the calculations. Hence it is questionable whether the results are really representative for all Member States. It is therefore recommended to base the analysis of necessary sample sizes on own data, if there are doubts that the figures derived here may not represent the situation in certain Member States. It has been stated already that longer sampling intervals (weekly or even monthly) can be applied for compliance checking, which may even improve the time coverage at lesser costs. The Working Group did not have time series with longer sampling intervals at their disposal, and consequently could not calculate minimum sample sizes for weekly or monthly samples. If the Member States want to make use of this option, they should take the minimum time coverages mentioned in table 3.4 as starting points, and analyze their proper time series determine the necessary sample sizes.

The proposals of the Working Group are summarized in table 3.4:

Table 3.4: Minimum time coverage and corresponding sample size

Case	Minimum time coverage	Corresponding minimum sample size (daily averages)
Cd, industrial sites, compliance checking	75 %	quasi-continuous
Cd, industrial sites, indicative measurements	33 %	122
As, Ni, Cd, urban background, compliance checking As, Ni, industrial sites, compliance checking	50 %	183
As, Ni, Cd, urban background, indicative measurements As, Ni, industrial sites, indicative measurements	14 %	52

3.2.4 Upper And Lower Assessment Thresholds

As outlined in the introduction to chapter 3, the upper and lower assessment thresholds (UAT and LAT) are important parameters defining the three assessment regimes. In those cases where pollution levels exceed the UAT, measurements are mandatory (Art. 6 of the Framework directive [1]). Between the UAT and LAT, measurements can be combined with modelling to assess the ambient air quality. The pollution level being below the LAT, model calculations and or objective estimations are sufficient for the assessment.

The previous Working Groups for the pollutants with already established position papers [4] have used the interannual variability Sy of time series as the basis for calculating the two thresholds: the UAT was defined as limit value minus twice the standard deviation of the interannual variability Sy, and the LAT as limit value minus three times the standard deviation. The rationale behind this approach is that assessment regimes with higher levels of uncertainties should be allowed only for zones where the limit values are definitely met and where variations of the pollution levels from year to year do not lead to breaches within a confidence interval of 95 %.

The annual averages from time series cannot be used directly for calculating Sy, because the annual variations may contain also a systematic trend of the data. This trend has to be removed first in order to arrive at the accidental scatter of the time series, from which the standard deviation of this scatter for individual years can be calculated.

The trends are removed by applying a linear regression model to the time series. The interannual variability is then defined as the standard deviation of all distances of individual years from the regression line.

Concentration data

Data sets from 4 stations in Germany and from 4 stations in the Netherlands were used for the analysis. Two German time series (Bottrop and Essen-Vogelheim) stem from industrial sites, two German data sets (Bonn and Dortmund) from urban background sites. The Dutch data originate from three urban background sites (Biest, Vlaadringen, Bilthoven) and one rural site (Kollumerwaard).

Unfortunately, no time series of continuously measured data were available in Germany, which were long and complete enough. Therefore, time series from at random monitoring (60 daily samples per year) had to be used. It has been shown in chapter 3.2.3 that this limited sample size is combined with an additional uncertainty of about 15 %, which will add to a certain extent to the interannual variability due to different meteorology or varing emissions. However, there is no simple way to remove this additional scatter from the data. Consequently, the interannual variations calculated below have to be regarded as upper limits. A minor factor that goes into the same direction is that time trends are not linear by necessity. Applying a linear model may thus overestimate the variability.

The results of the linear regressions of the time series (1990 until 1997 and 1988 until 1997, respectively) are presented in tables 3.5 - 3.9 for the different pollutants.

Table 3.5: Interannual variabilities from time series (1990-97) of four sites in Germany, nickel

Nickel site	trend/a; percent/a	Interannual variability Sy percent
Bonn	-1.9	18.5
Bottrop	-3.1	13.1
Dortmund	0.7	15.4
Essen	-0.7	10.3
average from 4 sites		14.3

Table 3.6: Interannual variabilities from time series (1990-97) of four sites in Germany, cadmium

Cadmium site	trend/a; percent/a	Interannual variability Sy percent
Bonn	-22.5	43.0
Bottrop	-6.8	15.8
Dortmund	-10.6	35.5
Essen	-11.7	11.9
average from 4 sites		26.6

Table 3.7: Interannual variabilities from time series (1990-97) of four sites in Germany, arsenic

Arsenic site	trend/a; percent/a	Interannual variability Sy percent
Bonn	-11.95	26.6
Bottrop	-7.31	7.6
Dortmund	-9.33	17.6
Essen	-7.70	18.6
average from 4 sites		17.6

Table 3.8: Interannual variabilities from time series (1988-97) of four sites in the Netherlands, arsenic

Arsenic site	trend/a; percent/a	Interannual variability Sy percent
Biest-Houtaker	-10.40	20.3
Vlaardingen-Floreslaan	-9.27	23.7
Bilthoven-Von Leeuwenh.	-9.97	23.5
Kollumerwaard-Hooge	-6.07	18.7
average from 4 sites		21.6

Table 3.9: Interannual variabilities from time series (1988-97) of four sites in the Netherlands, cadmium

Cadmium site	trend/a; percent/a	Interannual variability Sy percent
Biest-Houtaker	-6.57	16.4
Vlaardingen-Floreslaan	-5.37	13.3
Bilthoven-Von Leeuwenh.	-6.57	17.8
Kollumerwaard-Hooge	-7.58	12.9
average from 4 sites		15.1

The calculated interannual variabilities from the German and the Dutch stations correspond quite nicely to each other, so that they can be considered as representative at least for Western and Central Europe.

Deposition data

Data from Germany (4 time series) and Belgium (10 time series) were available. The results of the linear regressions of the 14 time series (1988 until 1998) from 10 industrial, 2 urban and 2 rural sampling site are presented in table 3.10.

Table 3.10: Interannual variabilities from time series (1988 - 1998) of 14 sites in Belgium and Germany, cadmium deposition

Cadmium deposition, site	Trend/a; percent/a	Interannual variability Sy percent
industrial, D (Bergerhoff)	9.8	19.2
industrial, B (NILU)	-7.9	26.9
industrial, B (NILU)	-10.7	19.4
industrial, B (NILU)	-7.2	15.1
industrial, B (NILU)	-7.8	29.6
industrial, B (NILU)	-3.0	26.0
industrial, B (NILU)	-10.1	34.8
industrial, B (NILU)	-15.3	52.8
industrial, B (NILU)	-1.8	47.7
industrial, B (NILU)	5.8	100.2
urban, D (Bergerhoff)	6.9	28.2
urban, D (Bergerhoff)	-2.8	18.6
average from 12 sites		34.9
rural, D (Bergerhoff)	6.4	32.2
rural, B (NILU)	15.1	167.7
average from 2 sites		116.1

It can be taken from the table that the calculated interannual variabilities are quite high and show considerable scatter. This may be due to the higher measurement uncertainties for deposition measurements (compare 3.3.2), especially at low depositions in rural areas. As only at industrial and urban sites there is any risk that the proposed limit value for cadmium deposition will not be met, UAT and LAT should be based on industrial and urban data stets only.

Bearing in mind that interannual variabilities are upper limits, the Working Group has agreed to propose the following percentages for the UAT and LAT (limit values - approx. 2 x Sy; limit values - approx. 3 x Sy, respect.)

Table 3.11: Proposed figures for the UAT and LAT calculated from interannual variabilities

Thresholds (percent of limit values)	Ni (concentration)	As (concentration)	Cd (concentration)	Cd (deposition)
UAT (limit-~ 2 x Sy)	70 %	60 %	60 %	40 %
LAT (limit-~ 3 x Sy)	50 %	40 %	40 %	20 %

A comparison with the percentages for the UAT and LAT laid down in the first daughter directive [2] and in the proposal for the second daughter directive [3] shows that the percentages proposed here are in the same range, except for deposition. However, the percentages are not necessarily equal, because they were individually calculated from time series for the compounds under consideration.

3.3 Measurement Methods

This section gives a general overview on methods of measurement of As, Cd and Ni in ambient air. It is not intended to be exhaustive nor to give full operational details. The information contained in this section has mainly been given by the members of the WG preparing this position paper and the CEN/TC 264/WG 14 “Reference Method for Determination of Pb, As, Cd, and Ni in Ambient Air”.

For the assessment of metals and metalloids in ambient air two different measurement approaches are commonly used: the determination of the concentration in ambient air (concentration measurements) and the collection of deposited metals and metalloids (deposition measurements).

3.3.1 Concentration Measurements

The determination of the concentration of metals in ambient air is normally divided into two major parts due to the low concentrations: the sampling step in the field and the analytical procedure in the laboratory.

3.3.1.1 Sampling

For the sampling of metals and metalloids the same type of sampling instruments, designed to collect airborne particles, are used. Such an instrument consists of a sample inlet, a collection medium, a pump and devices for measuring the volume or flow rate of the sampled air (critical orifice, volume meter or mass flow controller).

The **sampling inlet** and the **flow-rate** define the size range of the particles collected. The normal size ranges sampled are TSP, PM10 or other fractions of TSP. Recently, specific PM2.5

sampling heads have become available for commercial samplers. A detailed description of the performance and properties of the sampling inlet is given in reports of US and EC comparison programmes [13, 14, 15, 16] and the CEN Standard EN 12341 [17]. Standardisation of a measurement method for the PM2.5 fraction is underway at CEN level.

The position paper on Particles (1997) [18] gives a general overview on measurement and assessment of airborne particles.

The sampling devices used for metals in suspended dust may be roughly categorized by flow-rate into three classes:

- high volume samplers with about 30 or more m³/h (**HVS**)
- medium volume samplers with about 15 m³/h (**MVS**)
- and low volume samplers with less than 5 m³/h (**LVS**).

Table 3.12 gives an overview of commonly used sampling procedures ordered by flow rate. The flow rate depends on the head used and filter size, here the flow rate for TSP and PM10 heads are listed. (Attention: PM10 within these tables and text does not necessarily mean the same as PM10 tested in accordance with EN 12341).

Table 3.12: Sampling methods for particle bound metals and metalloids (Overview of commonly used methods in Europe)

Method	Description	Flow Rate (m³/h)		Filter Size (mm)	Typical Sampling Time
		TSP	PM10		
1. High volume sampler (HVS):					
NEN 2785, SFS 3863	US-EPA (Sierra-Andersen) Hi-Vol Sampler. Collects particles of aerodynamic diameters < 100 µm (TSP). Heads for PM10 or PM2.5 available	55-100	68	200x250	24 h
VDI 2463 Bl. 11	Digitel DHA-80. Filter changer for TSP. PM 10 Head available	40-60	30	150	24 h
2. Medium volume sampler (MVS):					
VDI 2463 Bl. 9	LIS/P Aerosol sampler. Sampling head has a laminar flow plate designed to make collection efficiency less sensitive to high wind speeds	15		120	24 h

Table 3.12 (cont.): Sampling methods for particle bound metals and metalloids (Overview of commonly used methods in Europe)

Method	Description	Flow Rate (m³/h)		Filter Size (mm)	Typical Sampling
		TSP	PM10		Time
3. Low volume sampler (LVS):					
VDI 2463 Bl. 7	Kleinfiltergerät (Small filter device). Sampling head fitted with a flow plate as in the LIS/P sampler. PM 10 Head available	2.6	2.3	50	24 h
EPA (RFPS-0789-073)	Graseby Andersen/GMW SA241 Dichotomous sampler: Two stage sampler with virtual impactor to collect PM10 and PM2.5. For both fraction: 2 µm teflon membrane filter		1	37	24 h
EPA (RFPS-0694-098)	Rupprecht and Patashnick Partisol Model 2000: Hub Unit and 0-3 Satellite Units. For PM10 and PM2.5. Manual sampling		1	47	24 h
EPA (RFPS-0498-118)	Rupprecht and Patashnick Partisol Plus Model 2025. For PM10 and PM2.5. Sequential air sampling		1	47	24 h
NILU	Two stage filter pack with two filters in series to collect PM10 and PM2.5 particles. For PM10: 8 µm Nucleopore membrane filter. For PM2.5: 2 µm teflon membrane filter with teflon backing		0.6	47	24 h
NILU	One stage filter pack sampler to collect PM10 particles. 2 µm teflon membrane filters with teflon backing		0.6	47	24 h
Pourbaix-Station	0,45 µm cellulose-nitrate membrane filter are used	0.6		50	24 h
M-Type sampler (UK)	Sampling head containing the filter (glass fibre or membrane filter), critical orifice for controlling flow and a dry gas meter		(0.3-0.9)	37	1d-1week
Harwell-Type sampler (UK)	Cellulose filter. M-Type and Harwell-Type are not strictly PM10 or TSP. They sample particle up to 8 µm at about 90 % collection efficiency at typical UK wind speeds		(0.3)	47	1 month

The typical **high volume sampler** as described by the **US-EPA** is commercially available with TSP and PM10 heads. This type of device was tested in the work for the European standard for sampling PM 10 (EN 12341). For sampling of total suspended particulate matter, flow rates between 55 and 100 m³/h are possible. The flow rate for sampling using a PM10-head is 68 m³/h. The construction of the TSP-head limits the sampling to particles of aerodynamic diameters below 100 µm. The filter is of rectangular shape and has a size of 200 mm x 250 mm. The high volume sampler, like most of the other devices, is commonly operating for 24 hours. National standards based on this technique are, for example, the Finnish **SFS 3863** and the Norwegian **NEN 2785**.

Another high volume sampler is the **Digitel DHA-80** which is described in the German guideline **VDI 2463 Part 11 [**19]. A special property of this sampler is the ability to change filters automatically at predefined times. Originally designed for monitoring TSP, in the meantime a PM 10 head has been developed and tested corresponding to EN 12341 [20]. Typical flow rate is 30 m³/h with the PM10 head; the filter diameter is 150 mm. The DHA-80 with the PM10 head was shown to be equivalent to the LVS-PM10 reference sampler (2.3 m³/h) - as described in EN 12341 - according to the test procedure of the EN12341 [21].

The so-called **LIS/P Aerosol sampler** is a medium volume sampler, the complete procedure is described in **VDI 2463 Part 9** [22]. It is normally operated at 15 m³/h. Glass, quartz fibre or membrane filters (with 120 mm diameter) are mounted in a sampling head with a laminar flow plate designed to make collection efficiency less sensitive to high wind speeds.

A low volume sampler is the so-called **Kleinfiltergerät** (small filter device), which is described in **VDI 2463 Part 7** [23]. Samples are taken at flow rates of 2.6 m³/h for TSP or 2.3 m³/h with the PM10-head onto a glass fibre, quartz fibre or membrane filter (with 50 mm diameter). The filter is placed in a sampling head fitted with a flow plate as in the LIS/P sampler. A modified Kleinfiltergerät (LVS-PM10 reference sampler (2.3 m³/h)) was successfully tested in the work for developing the new European Norm for PM10 (EN 12341).

A low volume sampling device is the **Sierra Andersen Dichotomous sampler**, being used for example in Norway. It is a two stage sampler which collects particles in the PM10 and PM2.5 size ranges at a flow rate of 1 m³/h. The filter system consists of two teflon membrane filters (37 mm diameter with 2 µm pore size).

The Rupprecht & Patashnik **Partisol Model 2000** Air Sampler with a PM10 head is also operated at a flow rate of 1 m³/h. It consists of a hub unit and 0 - 3 satellite units. Filter size is 47 mm. The Partisol Plus Model 2025 Sequential Air Sampler is fitted with a PM 2.5 head. The Partisol Model 2000 has been tested and corresponds to EN 12341:1997 [24]. Partisol samplers are used, for example, in France.

The **NILU two filter pack sampler**, the **M-type sampler** and the **Harwell type sampler** have a very low flow rate. The NILU two filter pack sampler consists of a two stage filter pack to collect particles in the PM10 and PM2.5 size ranges and is used at a flow rate of 0.6 m³/h. A Nucleopore membrane filter (47 mm, 8 µm pore size) is used for the PM10 fraction and a Teflon membrane filter (47 mm, 2 µm pore size) to sample the PM 2.5 fraction.

The British **M-Type sampler** has a TSP sampling head containing the 37 mm filter. Sampling rates of between 0.3 and 0.9 m³/h can be chosen to enable samples to be obtained over 1 day to – more typically - one week.

The **Harwell type sampler**, as used for example in UK, has a flow rate of ≈ 0,3 m³/h. It is not strictly TSP or PM10, at typical UK wind speeds it samples particles up to ≈ 8 µm, at ≈ 90% collection efficiency. A cellulose filter paper (47 mm) is used. Sampling period is one month.

As a rule the metals are sampled on a **daily basis** with the aim of calculating an annual mean. An exception is the one week respective one month sampling period in the United Kingdom where data for an annual mean shall be obtained.

The sampling inlet and the **flow-rate** define the size range of the particles collected. To assure that the correct size range of particles will be collected a particularly careful calibration of the flowrate going beyond the **calibration** "normal" for TSP measurements has to be carried out. Furthermore the information about the sampled volume of air is needed for the calculation of the concentrations. Therefore a thorough-going flow calibration is required to establish traceability to an SI traceable standard.

Due to the low concentrations of As, Cd and Ni in ambient air contamination of the sample has to be avoided or at least minimized. In this connection the preparation and transport of filters and especially the **filter material** are of greatest importance. Often the blank value of filter material is the limiting factor for the determination of a very low concentration. The suspended particulate matter is often collected on membrane filters made of cellulose nitrate with a pore size of 0.45 µm. Quartz microfibre, low metal background glass fibre filters and teflon filters are also used. In the two stage devices like the Dichotomous sampler and the NILU two stage sampler, fractions of dust are collected on teflon-filters. An overview of filter types and their properties is given in the following table 3.13, in tables 3.14 – 3.16 typical blank values are listed.

Table 3.13: Properties of filter types

Glass fibre filter	Borosilicate glass, therefore blank values in some cases unsatisfactory, but low flow resistance.
Quartz fibre filter	Quartz glass, lower blank values for the majority of elements in comparison with glass fibre filters, similar low flow resistance, but not so robust. Total digestion is easier compared with glass fibre filters. Relatively expensive.
Membrane filter	Cellulose acetate or cellulose nitrate, low blank values, but high flow resistance especially at high levels of humidity (due to condensation of water). Large filters are difficult to handle due to electrostatic charging.
Teflon Filter	Very low blank values. Teflon can not be digested under normal conditions. High flow resistance. Relatively expensive.

Table 3.14: Typical blank values of filter material - arsenic

Type of filter	Blank value [ng As/cm² filter area]	Detection limit [ng As/m³]
Glass fibre filter	40 – 60 (0.5)	5 – 15 (0.6)
Quartz fibre filter	0.5 - 5	0.1 – 1.5
Membrane filter	0.1 - 4	0.04 – 1.2
Teflon Filter	ca. 0.3	ca. 0.1

Values in () for special types

Table 3.15: Typical blank values of filter material - cadmium

Type of filter	Blank value [ng Cd/cm² filter area]	Detection limit [ng Cd/m³]
Glass fibre filter	0.1 – 0.6 (< 0.06)	0.06 – 1.0
Quartz fibre filter	0.07 – 0.3	0.02 – 0.3
Membrane filter	0.02 – 0.2	0.02 – 0.1
Teflon Filter	ca. 0.01	ca. 0.04

Values in () for special types

Table 3.16: Typical blank values of filter material - nickel

Type of filter	Blank value [ng Ni/cm² filter area]	Detection limit [ng Ni/m³]
Glass fibre filter	0.5 – 13	4 – 8
Quartz fibre filter	0.8 – 12	0.3 – 6
Membrane filter	1.4 – 10	0.3 – 4
Teflon filter	ca. 0.5	ca. 0.2

Remark: The detection limits are calculated based on 3 x standard deviation and a sample volume of 55 m³ air.

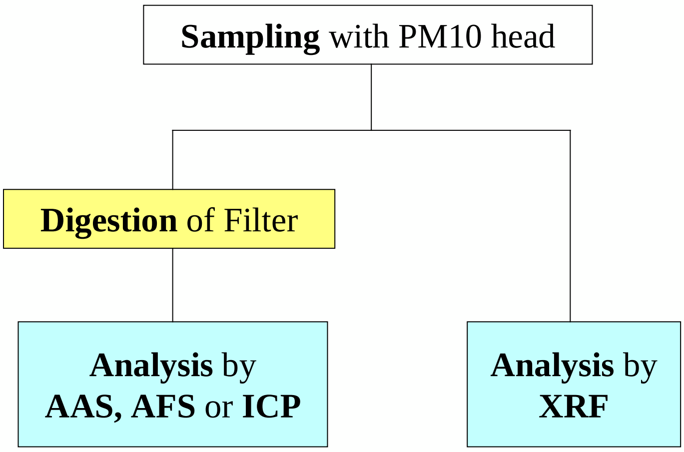
For quality assurance field filter blanks – that means filters which are handled in the same way as ”normal” filters but without sucking ambient air through them – and laboratory filter blanks have to be analyzed.

To complete this overview the new European standard – the **EN 12341** - concerning sampling of PM10 has to be mentioned. Within the standard a procedure is described to test PM 10 sampling devices against the **PM 10-reference sampler**, the so called **WRAC**. WRAC is an acronym and stands for **W**ide **R**ange **A**erosol **C**lassifier. The CEN TC264/WG 6 developing the test procedure for PM10 recognised that there are severe limitations to the use of the WRAC, even as a reference sampler, due to its impracticability. WG 6 therefore recommended that samplers that have been tested and shown to be equivalent to the WRAC, using the detailed field testing procedure (EN 12341), can be designated as ”equivalent reference samplers”. Therefore in the normative Annex B of EN 12341 two samplers in addition to the WRAC are listed as reference samplers: an LVS-PM10 reference sampler with a flow rate of 2.3 m³/h and an HVS-PM10 reference sampler with a flow rate of 68 m³/h. Both types were successfully tested by TC264/WG 6 and it could be demonstrated that they are in compliance with the WRAC.

3.3.1.2 Analysis

After sampling, the filter with the collected dust usually has to be digested by acid, if the analysis is done by atomic absorption spectrometry (AAS), by atomic fluorescence spectrometry (AFS), by inductively coupled plasma spectrometry (ICP-OES) or by inductively coupled plasma with mass spectrometry (ICP-MS). Alternatively, in the case of XRF (X-ray Fluorescence) and PIXE (Proton Induced X-ray Spectroscopy), the digestion step is not necessary, because a part of the filter can be directly irradiated with X-rays.

Diagram 3.7: Scheme of sampling, digestion and analysis



Digestion

The particle content of small filters (with about 50 mm diameter) can be digested in one piece, but for bigger filter sizes this is only possible with great amounts of digestion solution. Therefore bigger filters usually have to be partitioned into smaller pieces. In the latter case it is necessary to prove the homogeneity of collection efficiency over the surface of the complete filter area. Uniformity checks indicated an increased total aerosol mass deposit in the central zone of the filter [25, 26].

If a partitioning of filters is used, it is necessary to ensure that the subsamples are representative for the entire filter.

The applied digestion procedure depends strongly on the requirements of the analytical method used due to possible interference. Table 3.17 gives some examples of digestion methods. In general the closed vessel methods have the advantage of a reduced risk of loss. On the other hand for open vessel methods simpler instrumentation is needed. Vessels with an inner liner and cover made of Teflon or PFA and – for use under pressure – an outer high strength pressure vessel.

Table 3.17: Digestion methods

Method	Description / Remarks
Open vessels	As some of the interesting elements (especially As) form volatile compounds, care has to be taken that there are no losses during the digestion step in open vessels. - Acid mixture HNO_3 and HF, temperature 80°/130°C (VDI 2267 Part 1) [27] - Acid mixture HNO_3, $HclO_4$ and HF, temperature 90°/160°/220°C (VDI 2267 Part 1) - Acid mixture HNO_3 and HCl, temperature 100°C (ISO 9855) [28] - Acid mixture HNO_3 and H_2O_2, temperature 180°C (ISO 9855)
Closed vessels	- digestion with HNO_3/HF mixture, temperature up to 200 °C and pressure up to 20 MPa for up to 12 hours - digestion with HNO_3, temperature 180°C for 12 hours (pressure about 20 Mpa) (ISO 9855)
Closed vessels – Microwave digestion	- digestion with HNO_3/HF mixture, temperature 180°C

In table 3.18 an overview of the commonly used **analytical methods** for the determination of metals in ambient air is given. On the right are some appropriate international or national standards.

The detection limits obtained for measurement of ambient air are based on field and laboratory blanks. The detection limits vary depending of the filter types, the digestion procedure and the analytical technique.

Table 3.18: Commonly used analytical methods

Method	Digestion	Reference
Atomic Absorption Spectrometry (**AAS**) - **G**raphite **F**urnace-AAS - **H**ydride **G**eneration-AAS	yes	EPA, ISO 9855, ISO/CD 13812, NEN 2048, SFS 5008, VDI 2267 Part 1, 3, 6
Inductively Coupled Plasma (**ICP**) - ICP-**O**ptical **E**mission **S**pectrometry (OES) - ICP-**M**ass **S**pectrometry (MS)	yes	VDI 2267 Part 5
X-Ray Fluorescence (**XRF**) - **E**nergy **d**ispersive (Ed-) XRF - **W**avelength **d**ispersive (Wd-) XRF	no	NF X 43-027, VDI 2267 Part 2, 11, 12
Atomic Fluorescence Spectrometry (**AFS**) - **H**ydride **G**eneration-AFS	yes	

Analysis by Atomic Absorption Spectrometry (AAS)

This technique concerns the determination of the mass of elements, the atoms of which are capable of absorbing radiation within the optical spectrum range. This is achieved by the fact that each type of atom only absorbs radiation within a narrow spectral range of a few picometers and at a small number of wavelengths specific to the element concerned.

The purpose of GF-AAS is to transfer the sample solution to be measured into the gaseous phase and to atomize the analyte. The analyte atoms in the gaseous phase can only absorb radiation of specific wavelength usually emitted by a spectral lamp. The determination is done by measuring the absorbance, with correction for non-specific attenuation, at an element specific wavelength and – partly – with a modifier (Table 3.19).

Table 3.19: Absorption Wavelength and Modifiers for GF-AAS

	Wavelength	Modifier
As	193.7 nm	- $Mg(NO_3)_2$ and $NH_4H_2PO_4$ - $Mg(NO_3)_2$ and Pd
Cd	228.8 nm	- $Mg(NO_3)_2$ and $NH_4H_2PO_4$ - $Mg(NO_3)_2$ (only)
Ni	232.0 nm	no modifier necessary

With the listed wavelength spectral interference is largely excluded (spectral interference occurs due to the overlapping of absorption wavelength of various elements).

The main advantages of GF-AAS are analytical [29]; for example the very low detection limit. The main disadvantage is the mono-component analysis technique: Each metal must be measured separately, requiring the use of another light source for each element. A number of lamps are usually mounted in a carrousel, making the exchange somewhat simpler and more practical. Still, the same sample analysis for several specific metal parameters and contents is much more time-consuming than when the ICP-OES or ICP-MS technique is used.

Analysis of As as Hydride. The method is based on the AAS measurement of arsenic generated by the thermal decomposition of arsenic(III)hydride. Under the conditions of this method, only As(III) is quantitatively converted to the hydride. To avoid errors in determination, other oxidation states need to be converted to As(III) prior to determination. As(III) is reduced to gaseous arsenic(III)hydride (AsH_3) by reaction with sodium tetrahydroborate in a hydrochloric acid medium. Most organic materials interfere with the arsenic determination. Therefore they must be removed prior to the analysis by the digestion procedure. Annex A of document ISO 11989 gives details of the effect of potential interfering substances on the determination of arsenic.

For a detailed guideline about GF-AAS see ISO/CD 13812 [30].

Analysis by Inductively Coupled Plasma/Optical Emission Spectrometry (ICP-OES)

The basis of the method is the measurement of atomic emission by an optical spectroscopy technique. In optical emission spectrometry (OES) the atom or ion is excited thermally and the number of photons emitted during relaxation (transition to a lower energy level) is measured. The identification of the element takes place by means of the wavelength of the radiation (energy of photons), while the concentration is proportional to the intensity of the radiation (number of photons). As all the elements present are excited at the same time and therefore emit radiation simultaneously, it is possible to determine several elements at the same time.

Samples are nebulized and the aerosol thus produced is transported to the plasma torch where excitation occurs. Characteristic atomic- and ion-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP).

The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by detectors. The signals from the detectors are processed and controlled by a computer system. A background correction technique is used to compensate for variable background contributions to the determination of trace elements [31].

For the determination of metals, the ICP-OES technique has several key advantages, among which the very fast simultaneous analysis of different metals in one single test (multi-component analysis), offering a significant advantage from an economics point of view. According to the manufacturers, it also offers an assumed large linear range for almost all parameters, allowing – for instance – the formulation of calibration lines with a very limited number of concentrations of (mixed) standards with the two point calibration as a minimum. However, this is offset by several analytical disadvantages [29], the most important are the inferior detection limits and precision as compared to, for instance the GF-AAS technique.

For a detailed guideline on ICP-OES see ISO/CD 12235 [31].

Analysis by Inductively Coupled Plasma / Mass Spectrometry (ICP-MS)

This technique, in general, includes the following steps: The analyte solution is transferred into the pneumatic nebulizer producing an aerosol. A stream of argon carries the aerosol into the inductively coupled plasma formed by ionising and exciting the inert gas argon. Desolvation, atomisation and ionisation of the analyte take place in the plasma. Through a special interface the ions enter the vacuum part of the instrument, where they are separated on the basis of their mass-to-charge ratio by the mass spectrometer. The ions transmitted through the mass spectrometer are quantified by the detector (pulse counting method). Calibration with reference solutions, based on the linear relationship between concentration and measured pulse rate, allows quantitative analysis.

Table 3.20: Typical parameters for ICP-MS

Element	Mass	Internal standard
As	75	Sc
Cd	111	In
Ni	60	Sc

ICP-MS is a very sensitive and fast analytical technique. However, the dominating factors controlling the lowest detectable amount of metal are governed by the variability of the field and laboratory blank, which includes the influence of the filter material.

Analysis by X-Ray Fluorescence (XRF)

X-ray Fluorescence (XRF) is a fast, non-destructive technique to determine qualitative and quantitative elements. Multi-elements can be analyzed on the filter. The measurement time per element is very short, approximately 2 to 3 minutes. As there is no sample-treatment necessary, contamination during analysis is reduced.

The filter sample is placed in a sample holder and directly analyzed. Wavelength-dispersive-XRF uses an X-ray source to excite the atoms from solid samples. The XRF-analysis is performed with a X-ray-tube (Rh-type for As and Ni-analysis and Cr-type for Cd-analysis). The X-ray tube generates primary X-rays, which excite the atoms in the sample. The instrumental performance depends on the binding energy of the electrons in the atoms. The energy necessary to emit the electrons from the atom must be higher than the binding energy. The sensitivity of the element to be determined can be enlarged by optimizing the instrumental parameters (voltage (kV) and current (mA)). A primary filter, installed between the X-ray tube and the sample, eliminates the spectral interference from the X-ray tube. A collimator is located between the sample and the analysing crystal. It selects the X-rays emitted by the sample that will be allowed to pass the analyzing crystal. The collimator is a series of thin, high atomic number of parallel plates.

The analyzing crystal diffracts the emitted fluorescence radiation in different wavelengths. The X-rays, which follow Bragg's law ($\sin\theta = n\lambda/2d$), are diffracted by the analyzing crystal through the angle 2θ into a detector. Next to the 2d-value of the crystal, the resolution and the reflection also determine the choice of crystal. A universal crystal is LiF100. All elements from K (atomic number 19) can be determined. Less reflection but better resolution can be obtained with the LiF200 crystal. For the determination of lighter elements synthetic crystals with high 2d-values are used.

A spectral line of an element has a specific angle (analyzing crystal dependant). Under the angle position the intensity is measured, which is a measure for the concentration of the element. The intensity can be background corrected at the right and left side of the angle.

Detection of the diffracted x-rays is provided by a gas-flow proportional counter or the (NaI (Tl)-)scintillation detector; Both types convert each detected X-ray photon into a pulse of electrical charge. The magnitude of the charge pulse is proportional to the energy of the X-ray-photon and inversely proportional to the wavelength. Both detectors can be operated simultaneously in tandem. The scintillation detector counts the X-rays that pass through the proportional counter. The proportional counter is most effective for long wavelength X-rays (low energy). At shorter wavelengths the high efficiency of the scintillation detector becomes useful.

Table 3.21: Instrumental parameters for XRF

	X-ray tube	Line	X-crystal	Collimator	Detector	Tuber Filter	kV	mA	Angle (°2T)	BG1	BG2
As	Rh	KB	LiF200	300µm	Scint	Al (750µm)	60	50	30.428	YES	YES
Cd	Cr	LA	GE111	300µm	Flow	None	60	50	74.569	YES	YES
Ni	Rh	KA	LiF200	300µm	Duplex	Al (200µm)	60	50	48.653	YES	YES

For quantitative determination of different metals standards should be made with a comparable matrix as the samples. The standards should contain the elements, which to be determined. The standards are prepared through aerosol generation or with real samples. The calibration is carried out by comparison with an other technique, for example AAS or ICP [32]. The high stability of the x-ray-spectrometer offers the big advantage that calibration has a long lifetime. The minimal drift can be corrected with QC. The major disadvantage are the detection limits for As, Cd and Ni, which are above the corresponding values for GF-AAS or ICP-MS.

For a detailed description about X-ray spectrometry see [33] and [34].

Analysis by Proton Induced X-ray Spectroscopy (PIXE)

The principle of PIXE is similar to XRF in the sense that the elemental content in a sample is determined by measuring the characteristic X-ray from the atoms. The difference ist, that the atoms are excited by protons, coming from an ion accelerator, instead of X-rays. The advantage in using protons ist that the protons in most cases produce less background radiation. This enables the use of a simple energy dispersive X-ray detection system, which records the whole X-ray spectrum in one measurement. The response of the system is based in simple physical laws, which in principle make a "lifetime" calibration of the system possible.

With an automated PIXE system large volumes of particle filter samples can be analyzed without pre-treatment at a rate of 4 - 10 filters per hour. Detection limits around or below 1 ng/m³ are achieved for most heavy metals.

Analysis by Atomic Fluorescence Spectrometry (AFS)

Atomic fluorescence is the optical emission from gas-phase atoms that have been excited by absorption of electromagnetic radiation. The analysis of particulate matter requires that the analyte atoms are dissolved, vaporized, and atomized in a heat pipe, flame, or graphite furnace. A hollow-cathode lamp or laser provides the resonant excitation to promote the atoms to higher energy levels. The atomic fluorescence is dispersed and detected by monochromators and photomultiplier tubes, similar to atomic-emission spectroscopy instrumentation.

The atomic fluorescence spectrometry (AFS) technique is often used for the determination of As with the help of a hydride generation system. Within the hydride generation system the sample solutions are treated with sodium tetrahydroborate to generate the volatile covalent hydride of the analyte elements. The hydrides and excess hydrogen are swept out of the generation vessel into the furnace using a stream of inert gas (e.g. Argon). The hydrides are atomized and the resulting atoms are detected by atomic fluorescence.

The main advantage of fluorescence detection compared to absorption measurements is the greater sensitivity attainable because the fluorescence signal has a very low background level. The resonant excitation provides selective excitation of the analyte to avoid interference.

3.3.1.3 Species Specific Analysis Of As, Cd, And Ni Compounds In Ambient Air

It has already been pointed out in chapter 1.1 and 2 that the environmental mobility and behaviour, the biological availability as well as the toxicity of heavy metal and metalloids in the atmosphere depend on the specific compounds (species) which are present in ambient air and on physical properties as their size distribution (compare chapter 1.2). Different compounds of an element can vary to a great extent in their toxicology and carcinogenic potency. For example, nickel subsulfide is a strong carcinogen, whereas metallic nickel is not. These facts gave rise for the development of analytical methods to identify and quantitatively analyze specific species of the metals and metalloids in the environment.

Whereas a lot of progress has been achieved in the water phase (for literature surveys compare, for example, [35, 36, 37, 38]), attempts towards metal speciation in ambient air have been scarce. They have to cope, inter alia, with the following difficulties:

- Ambient aerosols are complex, inhomogeneous colloids. Metal compounds may be present in the gas, liquid (dissolved) or the solid phase. They can be enriched on the surface of aerosols or enclosed by other solid compounds.
- Concentrations are low (in the ng/m³ range), which frequently requires preconcentration and/or selective separation.

Consequently, several methods which are applicable in the water phase (homogeneous) or at dust from workplaces (higher concentrations) will not do for ambient air samples.

Basic types of speciation procedures for atmospheric samples can be roughly classified into three groups [39]:

- Direct analysis of particulate matter.
- Speciation of inorganic compounds after dissolution.
- The sequential or selective extraction.

The first approach (direct analysis) offers the possibility of determining specific compounds, but it is limited in sensitivity. It has therefore mainly been applied to dust samples from emissions or from working places. Frequently only surface concentrations can be determined and the discrimination between similar compounds is poor. Only crystalline materials can be analyzed. Because of the inclusion of a dissolution step, the latter two wet chemical techniques (dissolution/extraction) offer no direct determination of the compounds. However, they are more generally applicable. Some of the mentioned As, Cd and Ni compounds are insoluble in (mild) solvents, requiring very strong reagents to dissolve them. Consequently, they can be separated from more soluble species by sequential extraction or leaching.

In the following, the few species specific determinations of arsenic, cadmium and nickel compounds performed so far in ambient air will be summarized.

Speciation of arsenic

Arsenic hydride and some organic derivatives of arsenic as alkyl compounds are gaseous under environmental conditions, whereas oxides and sulphides are generally present in particulate matter. Thus the simultaneous detection of all arsenic compounds will have to include both phases under those conditions where a significant share of gaseous compounds could be present (for example near swamps or waste dumps). Consequently, some methods have been developed to sample and analyse gaseous species (see below). As under most conditions arsenic oxides are the predominant species, most work in ambient air has been concentrated on the separation of trivalent from pentavalent compounds.

The following table 3.22 summarizes the analytical methods published so far. Not all of them were tested and applied to real ambient air samples. Where this was the case, it is indicated in the third column of table 3.22, and the results were given already in chapter 1.1.

Table 3.22: Different approaches for the speciation of arsenic compounds in ambient air

Species	Sampling/separation, determination and comment	ambient air sample	Ref.
AsH_3	Adsorption on active carbon, detection by AAS, developed for working-place air	-	[40]
AsH_3/As_2O_3	Sample train of an impinger (NaOH) for As_2O_3 and silvered quartz trap for AsH_3, detection by gamma counting of ^{76}As	-	[41]
$AsCl_3/As_2O_3$	Cryogenic trap, detection by electrostatic accumulation furnace for electrothermal atomic spectometry	-	[42]
Arsenite/ arsenate	Size fractionated sampling by an impactor, reduction of the species by Zn-$NaBH_4$ technique, detection by hydride-generation AAS (results compare chapter 1.1)	City of Industry (Los Angeles, USA 1989)	[43]
Organo arsenates	Extraction procedure, detection by hydride-generation AAS, the stability of the organoarsenates in the aqueous extract was a significant problem	-	[44]
As(+3)/As(+5)	Reduction of sampled As(+3) with citric acid, detection by hydride-generation AAS (results compare chapter 1.1)	Darmstadt (Germany, 1986)	[45]
As(+3)/ As(+5)/DMA	Dilution of sampled As(+3)/As(+5) from glass fiber filters by an alkaline medium, DMA were sampled on silver plated pyrex beads, detection by DC-AES (results compare chapter 1.1)	Tampa Bay area (USA, 1975)	[46]
As(+3)/As(+5)	Sampling particulate matter on quartz fiber filters, extraction procedure with a mixture of H_2SO_4/HNO_3 1:2 (!) detection by hydride-generation AAS (results compare chapter 1.1)	City of Isfahan (Iran, 1999)	[47]

So far, no method for the selective sampling and extraction of really „all“ arsenic compounds has been applied to ambient air, although a comprehensive sampling train has recently been described [48]. Air is filtered through cellulose membrane to collect the particulate matter and is then bubbled through proper adsorbing solutions to retain the gaseous arsenic species exept arsine. This compound, if present, is retained in an oxidizing solution of permanganate as arsenate. For the analysis of the inorganic arsenic compounds, the filters are extracted with a $NaOH/Na_2CO_3$ solution. While As(0) remains indissolved on the filter, all other inorganic arsenic compounds are brought into solution. Metallic arsenic is determined after dissolution in HNO_3. As(+3) is determined by electrochemical methods, as well as As(V) after reduction by sodium disulphite in HCl (sum of As(+3) and As(+5)). For the determination of dimethyl- and monomethylarsine, the method can be modified by using filters impregnated with NaOH [48]. Unfortunately, the method has not been tested with ambient air samples.

Speciation of cadmium

No determination of cadmium species in ambient air have been published so far. Analytical methods available for the determination of cadmium compounds in other environmental media are compiled in the literature [49].

Speciation of nickel

Toxicological properties and the carcinogenic potency of inhalated nickel compounds strongly depend on the species involved (compare chapter 2). Therefore, methods for the speciation of nickel are of great importance for the correct assessment of effects.

The determination of nickel in air has been mainly restricted to the determination of the total content with conventional methods (compare chapter 3.3) or the determination of volatile compounds such as $Ni(CO)_4$ [50]. Nevertheless, nickel speciation has been applied to matrices such as dust occurring at work places [51, 52] or fly ash [53]. For ambient aerosols with a nickel concentration in the lower ng/m³ level, no universal analytical technique, capable of identifying and quantifying all nickel species, has been worked out so far.

The methods which appear particularly promising for the speciation of Ni are selective and/or sequential extraction. A compilation of such methods has been published [54], inter alia methods for the separation of oxidic nickel, sulphidic nickel and the determination of metallic nickel in the persence of nickel oxide. However, none of the described methods have been validated with ambient air samples.

Recently, a multistage extraction scheme for nickel speciation (compare Figure 3.8) originally proposed by Zatka et al. [52] and Kaiser [55] has been applied to ambient air samples collected near two different steel works [56] and one urban background site.

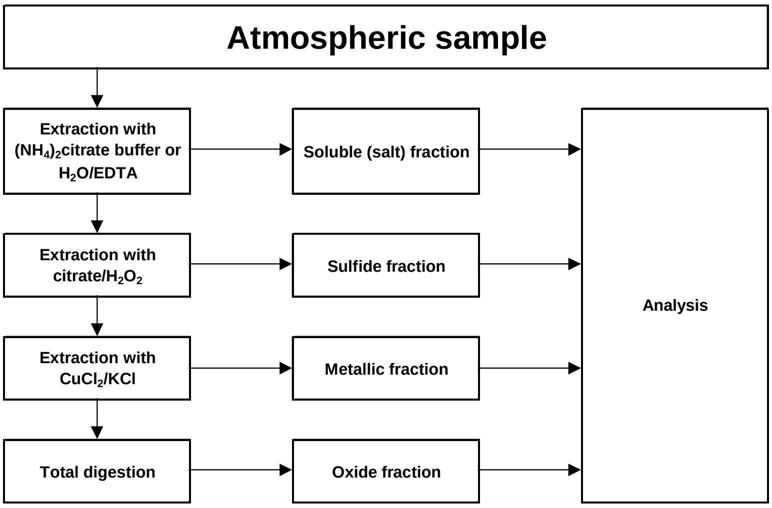


Figure 3.8: Multistage extraction scheme for nickel speciation [56]. Separation of soluble nickel, sulphidic nickel, metallic nickel and oxidic nickel

First, extraction for the separation of water-soluble and insoluble nickel species was carried out by means of a flow injection system with a 0,01 m EDTA solution in water, in order to determine in one step partly water soluble compounds (such as $NiCl_2$ or $NiSO_4$). The EDTA/water solution did not dissolve oxidic nickel, sulphidic nickel and metallic nickel [56]. The next steps laid down in figure 3.8 were applied to the residue to separate the different nickel species such as sulphidic nickel, metallic nickel and oxidic nickel. The results of this study are given in chapter 1.1.

To summarize, the following conclusions can be drawn:

- More research on the speciation of metal and metalloid compounds in ambient air is definitely needed.
- At present, the methods are still in the stage of research and development and not sufficiently validated and easy enough to handle for routine monitoring. Consequently, measurements to check compliance with the upcoming EC legislation have still to be based on the determination of total metal and metalloid contents in ambient aerosols.
- Nevertheless, the first results of species identification in ambient air samples give at least a rough idea of the most important compounds which have to be taken into account by the risk assessment.

3.3.2 Deposition Measurement Methods

As the components of settled dust (e.g. metals and metalloids) are analyzed by the same techniques already mentioned in chapter 3.3.1.2, the following section will be focussed on sampling methods.

Deposition can be defined as the mass of pollutants (in this case metal and metalloid compounds), which is transfered from the atmosphere to surfaces such as soil, vegetation, water or buildings within a given area (for example 1 m^2) in a given time (for example a day). On the one hand, deposition is a powerful mechanism to clean the atmosphere; on the other hand, deposited pollutants are transfered from the air into other media and may enter biogeological cycles and the food chain (compare chapter 2.5).

There are numerous atmospheric processes to deposit aerosols containing heavy metal compounds on surfaces. During dry periods, (dry deposition) particles are transported near the surfaces by turbulent diffusion and are then either impacted (coarser particles) or deposited by Brownian diffusion [57, 58] (fine particles < 0,1 µm). Dry deposition will thus depend on the particle size [59], on the wind speed, on thermal stability, on roughness, but also on the physical and chemical properties (surface resistances) of the surface to be considered [57, 58]. For vegetation, the degree of opening of the stomata is an additional parameter.

A very efficient form of deposition is the so called interception, that means, the removal of horizonally transported air bound pollutants by high obstacles (e.g. wood, buildings). Interception is one of the reasons of higher pollutant concentrations in the run off water from canopies compared with rainfall in open areas.

As dry deposition depends on so many parameters and properties of the acceptors, measurements of dry deposition and of deposition velocities are strictly valid only under the specific conditions of the measurements and can hardly be representative for a whole area with a variety of surface and meteorological conditions. Deposition monitoring including dry deposition must therefore rely on methods which simplify real world conditions by offering certain standardized surfaces as proxies, laid down by convention, or by biomonitoring of the vegetation at interest.

Other powerful deposition processes are the rain out (in-cloud scavenging) and wash out (below cloud scavenging) of pollutants, leading to wet deposition [57]. A special case of wet deposition is the transfer of pollutants to surfaces by fog or dew.

As a rule of thumb, it can be stated that wet deposition is the predominating removal process in rural and remote areas in Northern, Central and Western Europe [58]. Experiments in rural areas in Germany, for example, have shown that wet deposition accounts to up to 90 % of the total deposition of heavy metals in those areas [58, 59]. As wet deposition does not only depend on the pollutant concentrations in rain water, but also on the amount of rain, wet deposition can be quite high in mountaineous areas.

In urban areas and particularly near sources with a considerable share of particles in the coarse mode, dry deposition may outwheigh wet deposition considerably, as coarse particles have high deposition velocities and will settle close to sources. Dry deposition will probably also outwheigh wet deposition in dry areas in Southern Europe, but at present, there are no data available demonstrating this.

For the uptake of heavy metal and metalloid compounds by surfaces and for the evaluation of possible noxious effects, total deposition (bulk deposition, the sum of dry and wet deposition, interception and transfer by dew and fog) is what counts. Consequently, bulk deposition is the parameter to be monitored for compliance checking. The two different regimes mentioned above,

- near source areas with high pollutant concentrations and significant shares of coarse particles, leading to high deposition rates, or dry deposition as dominating process as in Southern Europe

- rural and remote areas in Northern, Central and Western Europe, where wet deposition is the dominating process,

have led to two different types of samplers for bulk deposition.

Monitoring in urban areas, near sources and in dry regions

In polluted areas, cylindrical deposit gauges with standardized dimensions made of glass, tupperware or plastics (polyethylene or polypropylene), as the Bergerhoff method [60], the American ASTM method [61] or the sampler described in the ISO draft proposal 4222.2 [62] are widely used. The material of the gauges must not interfere with subsequent analysis of the contents of metals and metalloids. Unknown materials and charges should be checked by the determination of blanks. Arsenic may, for example, be leached from certain glasses, and nickel may be an additive in some sort of plastic [66]. Details of the methods can be taken from table 3.23.

Table 3.23: Dimensions and properties of standardized cylindrical flat-bottomed vessels for bulk deposition

Method	Diameter of jar	Collecting area	Depth	Material	Sampling height
Bergerhoff (VDI 2119) [60]	8 - 11,5 cm	62 - 104 cm²	12 - 25 cm	glass, PE, PVDF, PP	150 cm
Iso draft proposal 4222.2 [62]	20 ± 0,2 cm	400 cm²	40 ± 1 cm		180 ± 20 cm

The deposit gauges are exposed for about 30 days by means of supports, being equipped with protective baskets for the gauges and with bird rings (optional) to reduce contamination by birds. Destilled water may be added prior to sampling [62]. Care must be taken that the volume of the gauges is big enough to sample the rain water during the whole sampling period without overflow.

After sampling, the deposit gauges are tightly sealed and transferred to the laboratory. Obviously extraneous matter such as leaves and insects are removed and the contents of the jars are carefully evaporated to dryness. The dry residue can then be weighted for the determination of the total dust precipitation. Subsequently, the dry residue is digested and analyzed for heavy metals and metalloids by the same methods already described in chapter 3.3.1.2 (e.g. by atomic absorption spectrometry (AAS), by inductively compled plasma spectrometry (ICP) or X-Ray Fluorescence (XRF)). A method using AAS has been described in a national standard [63].

The results of the measurements are normally expressed in microgrammes per unit area of the gauge and per unit of exposure time, for example per squaremeter and day (µg/m²d) for metal and metalloid depositions.

It must be borne in mind that cylindrical deposit gauges are measurement methods laid down by convention in order to monitor atmospheric deposits in a comparable way. Because of the manifold of parameters and surface properties influencing deposition (see above), the deposit gauges are no surrogates for any specific surface such as soil or vegetation. Measurements by different methods can differ by as much as 50 % [64], so that unified approaches as the choice of a reference method and a description of a testing procedure how to show equivalence are urgently needed. A Working Group has been established within CEN to work on a reference method.

On the other hand, comparative measurements using different types of deposit gauges have shown that the results of the measurements do not crucially depend on the dimensions of the vessel, which can therefore be modified within certain ranges [65].

The reproducibility (standard deviation) for the measurement of dust were determined to range from 17 to 33 mg/m²d for the Bergerhoff method [60] and 33 mg/m²d for the proposed ISO standard [62], corresponding roughly to 10 - 20 % for measurements in urban areas, depending on the pollution burden.

Standard deviations (including sampling and analysis) for cadmium measurements with the Bergerhoff method were 10 % for dual determinations in polluted areas and 30 % for urban areas [63]. The detection limit for cadmium was 0,1 µg/m²d. including blanks of the vessels [63] (threefold of blank determination scattering).

In a recent evaluation of the suitabilities of the Bergerhoff method for deposition measurements of 49 elements at three rural sites in Switzerland [66], it was found that the method was suitable, inter alia, for the determination of As, Ni and Cd depositions. Blanks of the methods for cadmium were low (2 % of median depositions), for nickel they were acceptable (15 % of median depositions). Relative standard deviations of single values in percent of the annual means ranged between 2 and 25 % for arsenic and nickel and between 3 and 29 % for cadmium [66].

An important advantage of the Bergerhoff method and other methods using cylindrical deposit gauges is the low price of the equipment. Analysis costs can be kept low by combining monthly samples before analysis, if only annual means of the deposition have to be determined.

In addition to the cylindrical deposit gauges, other methods using a Frisbee type disc as collection surface [67] or collection of the dust on adhesive films [68] have been described.

Monitoring in rural and remote areas

As deposition in rural and remote areas is mainly governed by wet deposition (possible exception: dry regions in Southern Europe), the monitoring devices for background measurements are designed to collect the rain as completely as possible. Samplers consist of funnels with various constructions and openings, which lead the rain into flasks, sometimes darkened to protect from algae and photodecomposition. During dry periods, aerosols containing heavy metal and metalloid compounds are deposited on the surface of the funnels and subsequently washed down into the storage bottle at the next rain event. Consequently, also these samplers measure bulk deposition, unless they are equipped with a cover steered by a rain sensor, which opens only during rain events (wet only samplers).

Recently, an international intercomparison exercise covering samplers from 15 European countries has been performed within the framework of HELCOM-EMEP-PARCOM-AMAP [59] for the determination of metals and metalloids, inter alia As, Cd and Ni, at a rural site in Germany. Figure 3.9 gives an impression of the variety of the samplers used and table 3.24 shows some details, inter alia dimensions, of the equipment [59].

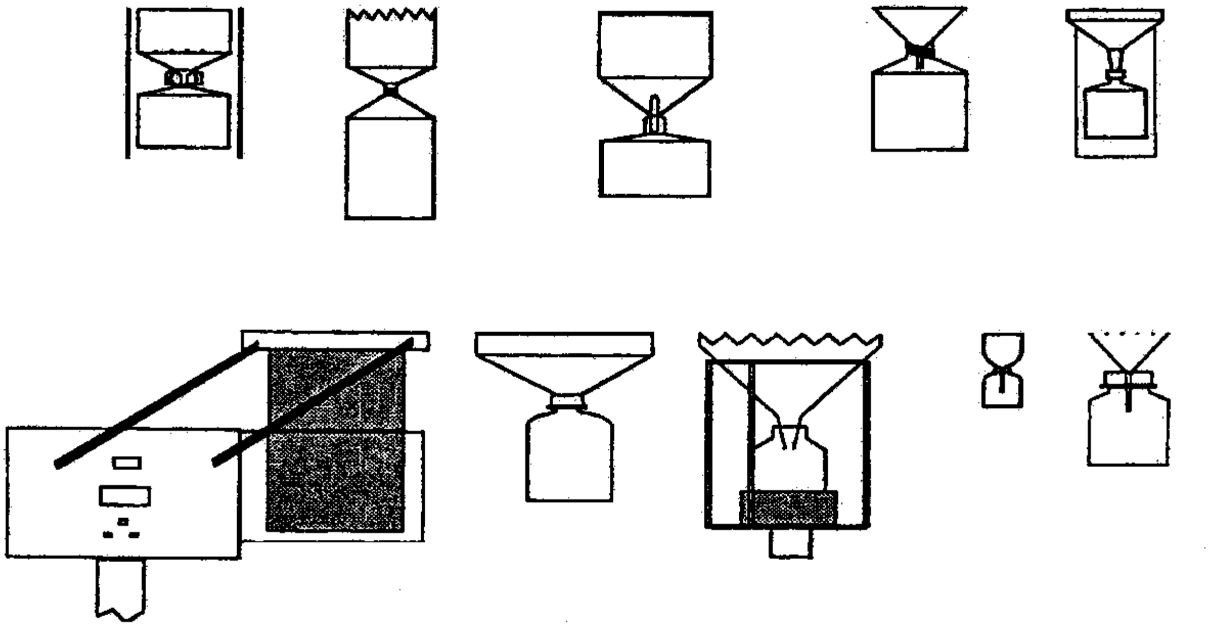


Figure 3.9: Principal construction of various deposition samplers used in Europe, which took part in an intercomparison exercise within the framework of HELCOM-EMEP-PARCOM-AMAP [59].
Upper part, from left to right: samplers from Austria, Czech Republic, NILU, France and Latvia.
Lower part, from left to reight: samplers from Poland, Italy, Slovakia, Sweden and United Kingdom.

Table 3.24: Dimensions and materials of various bulk deposition samplers used in Europe, which took part in the intercomparison exercise within the framework of HELCOM-EMEP-PARCOM-AMAP [59]

Type	Material of funnel	Diameter (funnel), cm	Collection surface, m²	Volume of collection flask, l	Sampling height, m	Intervals of funnel change
NILU/ Norway	PE	20	0.031	2.5	1.8	2 months
A.E.A. Tech-nology (UK)	PP	14	0.015	2.0	1.5	none
UBO (France)	PE	16	0.020	1.0	2.1	none
Italy		30.5	0.073		0.7	1 month
Austria	PP	17.4	0.024	0.5	1.5	none
MISU (Sweden)	LD PE	7.5	0.004	0.5	1.5	weekly

After sampling, the collected rainwater was analyzed by the participating laboratories by conventional methods such as ICP-AES, ICP-MS and AAS, respectively (compare chapter

3.3.1.2). Sometimes the filter was rinsed and changed in regular intervals, sometimes not (compare table 3.24).

As the measured metal and metalloid concentrations have to be transferred into depositions by multiplying them with the amount of rainwater collected, the deposition measurements depend on the correct measurement of rainfall. Taking the known period of exposure and collection surface, the results can then be reported as, for example, µg/(m² week).

One of the principal aims of the intercomparison exercise was to establish the overall uncertainty of the methods. Although an experimental protocol had been agreed upon prior to the experiments [59], the deviations between the participating samplers and laboratories were considerable. When weekly samples were compared, only 59 % of the samples showed deviations < 25 % from the reference value for cadmium, the corresponding percentages for arsenic and nickel being 50 % and 30 %, respectively. This result can slightly be improved by using means of two parallel operating samplers, but is much better when averages from weekly samples are calculated for longer exposure periods (in this case 11 weeks). Now, 69 % of the samples showed deviations < 25 % of the reference value for arsenic, the corresponding figures for cadmium and nickel being 73 % and 42 % [59]. Apparently, non systematic scatter of weekly samples is averaged out to a certain extent by averaging over longer intervals. The poorer results for nickel are probably due to a greater share of insoluble nickel compounds in the precipitation.

The intercomparison test gave rise to some important conclusions, how the reproducibility and accuracy of the measurements could be improved. Particularly, the shape of the samplers and the handling of the samples should be standardized (e.g. cleaning and rinsing of funnels), mean values of two parallel operating samplers should be used, and the results should be integrated over longer exposure periods (e.g. 3 - 6 months) [59]. In addition, the sampling height should not be lower than 1.5 m. Under these improved conditions, reliable depositions with standard deviations < 25 % of reference values can be measured even in remote areas with low concentrations and depositions.

In June 1999, CEN/TC 264 has charged an ad-hoc Working Group under the convenorship of Norway to work out a proposal for a reference method to measure the deposition of lead, cadmium, arsenic and nickel. Until this reference method will be established, the Working Group recommends to use either the Bergerhoff method or the NILU jar for deposition monitoring. However, there are indications that these two methods may not be equivalent. In a Belgian study, monitoring results with both methods for cadmium and lead were compared at two industrial monitoring sites, the ratios NILU/Bergerhoff being 1.97 and 1.68 for cadmium and 1.43 and 1.71 for lead, respectively [127]. This underlines the need for an internationally standardized reference method for deposition measurements.

3.3.3 Methods Currently Applied By The Member States, Norway And The U.S.A.

Measurements of metals in ambient air – especially arsenic, nickel and cadmium - are not carried out continuously over the whole territory of the EC. Only sporadic measurements are taken or occasional campaigns made in certain specific areas.

For the determination of metals the majority of the EC nations use measuring devices for sampling total suspended particulate matter. In more recent years some nations have started to collect the PM10 fraction. Table 3.25 gives an overview of the methods used by the Member States.

Table 3.25: Measurement Methods used in the Member States and Norway

Country	Type	Method (Device)	Remark	PM10	Analysis
Austria	HVS	Digitel DHA-80	Five daily samples per month.ca. 720 m^3 per nitrocellulose filter	since 1997	AAS or ICP
Belgium	LVS	own development	15 m^3/24 h. 0.45 µm cellulose nitrate filter		WD-XRF
Denmark	LVS	own development	58 m^3/24 h. Membrane filters, daily collection	Starting 2000	PIXE
Finland	HVS	SFS3863, SFS5008	Basis: US-EPA HVS. 24 h. Glass fibre filter	yes	AAS or ICP-MS
	LVS		Weekly collection, 50 l/min, membrane filter		ICP-MS
France	HVS	Digitel DHA-80	Daily sampling of PM10; 30 m^3/h; quartz fibre filter	since 1999	ICP-MS
	LVS	Partisol plus	Daily sampling of PM10; 1 m^3/h; Teflon filter	since 1999	AAS or ICP
Germany	HVS	VDI 2463 Sheet 11	Digitel DHA-80. 24 h. 60 m^3/h. filter changer for TSP (or PM10)	partially	AAS or ICP
	MVS	VDI 2463 Sheet 9	LIS/P aerosol sampler. 24 h, 15 m^3/h		AAS or ICP
	LVS	VDI 2463 Sheet 7	Kleinfiltergerät (Small filter device). 24 h. 2.4 m^3/h	partially	AAS or ICP
Italy	LVS		Daily sampling of TSP or PM10, membrane partially filter		AAS
Luxembourg	LVS		Daily sampling of TSP or PM10, membrane filter		XRF
Norway (At the time of writing, Norway is not a Member State of the EC)	HVS	NILU	Sierra Andersen HVS. 24 h. 1400 m^3/d. Quartz fibre or low ash paper filters	partially	ICP-MS
	MVS	NILU	Sierra Andersen Dichotomus Sampler. 24 h. 24 m^3/h	yes	ICP-MS
	LVS	NILU	Two Filter pack sampler. 14 m^3/24 h	yes	ICP-MS
		NILU	One stage Filter pack sampler. 14 m^3/h	yes	ICP-MS
Spain	HVS + LVS		HVS (35 m^3/h); MCV LVS (1 m^3/h) PM10 HVS Sierra Andersen 68 m^3/h PM10 LVS Partisol 2000 (1 m^3/h) PM10 LVS-3 (2,3 m^3/h)	partially	AAS
The Netherlands	HVS	NEN 2785	1500-2500 m^3 in 24 h		AAS
United Kingdom	LVS	M- or Harwell-Type Sampler	0.3 m^3/h, sample collected over one week or one month, cellulose filters		AAS, ICP, INAA

In **Austria** Digitel DHA-80 automatic sampling devices are mostly used. Five daily samples per month are taken with the aim of calculating an annual mean. The used nitro-cellulose filters are analyzed by ICP or AAS. Since 1999, all samples are taken with a PM10 inlet.

In **Belgium** the Flemish network ”heavy metals in ambient air” consists of 25 semi-automatic sampling stations. The metals are sampled continuously on a 24 hour basis. About 15 m³ air is sampled per day. The suspended particulate matter is collected on cellulose nitrate filters (0.45 µm, 50 mm diameter). Depending on the sampling location, Pb, Cd, Cu and Zn are determined with wavelength-dispersive XRF-spectrometry (WD-XRF). The sampling station is their own development. It has been tested in wind tunnels and has been compared in real outdoor conditions with PM10 samplers used in Great Britain and France. The Wallonia network consists of about 20 stations and uses the same methods. In the network of Brussels the same sampling technique is used, but the analysis is done by AAS.

In **Denmark** heavy metals have been measured in daily TSP samples continuously at rural sites since 1979 and at urban sites since 1982. TSP is collected with the Danish filter LVS sampler on 50 mm membrane filters. Analysis is performed with PIXE (Proton Induced X-ray Emission Spectroscopy).

In **Finland** heavy metals have been sampled at urban and industrial sites with high volume samplers (TSP and PM10) according to the Finnish standard SFS 3863 (determination of suspended particulate matter in the atmosphere, high volume method). The inlet aperture between the roof and shelter body samples particles of aerodynamic diameters < 100 µm (TSP), alternatively PM10 or PM2.5 can be sampled. The sampling time is the common 24 hours. At the Pallas Sodankylä GAW station aerosol samples are collected weekly on membrane filters (flow 50 l/min). The mass concentration of lead is often determined according to the Finnish standard SFS 5008 with the AAS-technique (based on Reference Method of Lead in Suspended Particulate Matter collected from Ambient Air (EPA, U.S. Code of Federal Regulations 40 CFR 50 Appendix G.7)).

In **France** a monitoring network for As, Cd, Ni and Pb started in May 1999 at six sites (urban and industrial). Two methods are checked:

- Low volume sampling of PM10 with Partisol Plus devices (1 m³/h) on teflon filters (2 µm). Digestion of metals is done with aqua regia according to ISO 9855. For analysis of Cd, Ni and Pb GF-AAS or ICP-OES techniques are used. As is determined by Hydride Generation Atomic Absorption (HG-AAS) or Fluorescence Spectrometry (HG-AFS). Analysis by X-ray fluorescence will also be checked.

- Sampling with a Digitel DHA 80 high volume sampler (30 m³/h) on quartz fibre filter (150 mm). Total digestion of particulate matter and filter by nitric and hydrofluoric acids. Determination of the concentration of As, Cd, Ni and Pb by ICP-MS.

In both cases the sampling is done daily with a sampling time of 24 hours.

In **Germany** the sampling equipment commonly used includes relatively high (40 m³/h), medium (15 m³/h) and low volume samplers (1-3 m³/h) as described in VDI 2463 (see table 3.12). The particles are collected over 24 hours onto a glass fibre / quartz fibre / membrane filter held in a sampling head fitted with a flow plate. The samples are analyzed by AAS or ICP-techniques after digestion of the filters in an oxidising acid mixture (according to VDI-Guideline 2267).

In the air pollution monitoring network of the German Federal Environmental Agency (Umweltbundesamt) TSP is collected on glassfibre filters at rural stations using Digitel DHA-80 instruments (VDI 2463 Part 11). The sampling frequency is daily. For analysis circular pieces (diameter 45 mm) are stamped out of the loaded filter.

In 1997 and 1998 PM10- and PM2.5-measurements were performed at different sites in North-Rhine-Westphalia and compared with respective TSP data [21]. The measurements was made with LVS-PM10 reference sampler (2.3 m^3/h) as described in EN 12341 and automatic filter changers Digitel DHA-80 (30 m^3/h). In the DHA-80 samples also As, Be, Cd, Ni, Pb and Zn were analysed.

Luxembourg: Suspended particulate matter in air is collected on cellulose nitrate membrane filters (with a pore size of 0.45 µm) and analyzed with X-ray fluorescence spectroscopy. The air is sampled at a rate of about 0.6 m^3/h. The procedure in Luxembourg is similar to the Belgian method.

In **Norway** NILU uses different types of samplers. Dust is collected with the Sierra Andersen high volume sampler, the Sierra Andersen Dichotomous sampler, the NILU two filter pack sampler or the NILU one filter sampler (data see Table 3.12). The analytical method is ICP-MS. They use filters consisting of quartz fibres or low ash paper filters. Digestion is made in closed Teflon bombs at 170-180°C for 8-12 h with conc. nitric acid. NB: At the time of writing, Norway is not a Member State of the EC.

In **Spain** high volume samplers (35 m^3/h) and low volume samplers (1 m^3/h) using glass fibre filters are utilized. Also, PM10 reference samplers according to EN 12341:1998 with quartz fibre filters are used. Depending on the laboratories, the filters are digested by an oxidizing mixture (HCl/HNO_3) and analyzed either by AAS according to the US EPA 40 Standard (CFR 50 Appendix G) or the Spanish standard UNE 77230:1998 equivalent to the ISO 9855:1993.

The Netherlands use a technique based on the US-EPA high volume sampler, which is described in the Dutch standard NEN 2785 [74]. Analysis is mostly done by AAS according to ISO 9855 for lead or NEN 2048 for cadmium. Field of application: Pb, Cd, Cu, Zn, As and Cr. Volume: 1500 – 2500 m^3 in 24 hours (70 – 100 m^3/h). Filter material is glass fibre (400-500 cm^2, capture capacity must be > 99 % for particles > 0.3 µm)). For As and Ni no standard for ambient air is given; standards for Workplace are available (NVN 2951 for As based on HAAS or HAFS and NVN 2945 for Ni based on GFAAS).

United Kingdom: Sampling of airborne particulate matter is undertaken with the UK ”M Type” sampler and the Harwell type sampler. Both types approximates to PM10. The flow rate is controlled to ≈ 0.3 m^3/h and material is collected over a one week period (M-Type sampler) on Millipore Aerosol Field Monitor filters (5.4 – 7.1 m^3 per day) or over a one month period on cellulose filter paper (Harwell type sampler, as used in RTE/N Sea networks). The filters are analyzed by AAS or ICP-Techniques or by Instrumental Neutron Activation Analysis (for some 30 metals) supported by ICP-MS and ICP-AES techniques for Cd and Ni.

AAS and ICP techniques are used in many Member States. XRF technology is mainly used in Belgium, Luxembourg and France.

So far national standards are only available for the measurement of metals and metalloids in ambient air. As they are to be harmonized, there is a great demand for an European standard for use as a reference method to measure As, Cd and Ni in ambient air.

The measurement methods used in the **United States of America** are described in the comprehensive EPA Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air [128]. For PM10 sampling, high volume samplers (Compendium Method IO-2.1) as well as low volume samplers (Dichotomous Andersen Sampler, Compendium Method IO-2.3) are applied. For the analysis of metals and metalloids, the whole variety of methods also used by the EC-Member States are described such as the Graphite Furnace Atomic Absorption (Method IO-3.2), X-Ray Fluorescence (Method IO-3.3), Inductively Coupled Argon Plasma Spectrometry (Method IO-3.4), Inductively Coupled Plasma/Mass Spectrometry (Method IO-3.5), Proton Induced X-ray Emission Spectroscopy (Method IO-3.6) and Neutron Activation Analysis (Method IO-3.7) [128].

3.3.4 Proposed Reference Method

Following the procedure adopted in previous EC Directives, it is proposed that a reference method shall be nominated. For monitoring compliance with the Directive limit values, Member States may then use the reference method or any other method which has been demonstrated as being equivalent to the reference method.

The reference method for concentration measurement shall be drafted by CEN /TC 264 WG 14. In 1996 WG 14 started its work in elaborating a reference method for the measurement of Pb, As, Cd and Ni which was based on minimum requirements: for each step of the measurement method (sampling, filter material, digestion and analysis) the minimum requirements which must be fulfilled are described. Examples of operation for different PM10 sampling methods (LVS, HVS) and analytical procedures (AAS, ICP) will be given in informative annexes. For this approach, a large extent of validation work would be necessary, because the performance characteristics of several methods will have to be worked out.

Due to limited monetary resources for validation work and in order to simplify the EN reference method the group preparing this position paper prefers a more ”classical” approach to define a reference method: to describe and validate one complete reference method. **Other methods can be used, if equivalency to the reference method has been demonstrated (either already within the standard (equivalence methods) or by the user)**. Such a classical approach is the basis of the following proposed reference method.

As described in chapter 3.3.1 the measurement method can be divided into two major parts: the sampling step and the following analytical procedure:

For **sampling** of As, Cd and Ni in the PM10 fraction of airborne particulate, it is sensible to use a reference method which is based on the EN 12341. For sampling of Pb in ambient air the daughter directive for SO_2, NO_x, particulate matter and lead specifies the PM10 method too, so a combined sampling of As, Cd, Ni and Pb will be possible.

Within the EN 12341 the Wide Range Aerosol Classifier (WRAC) is defined as the reference method for PM10. However, the CEN TC264/WG 6 developing the test procedure for PM10 recognized that there are severe limitations to the use of the WRAC, even as a reference sampler, due to its impracticability. WG 6 therefore recommended that samplers that have been tested and shown to be equivalent to the WRAC, using the detailed field testing procedure (EN 12341), can be designated as ”equivalent reference samplers”. Within the field tests done by WG 6 two sampling devices successfully met the criteria of an equivalent reference sampler for PM10: a high volume sampler (HVS) with PM10 head for a flow rate of 68 m^3/h and a low volume sampler (LVS) with PM10 head specified for a flow rate of 2.3 m^3/h. Both of these tested sampling devices for PM10 are suitable for the sampling stage of the reference method for As, Cd and Ni.

As discussed above, it is proposed that only one reference method should be nominated: the Working Group recommends the LVS-PM10 reference sampler as described in Annex B.1 (normative) in EN 12341 for the sampling stage. The LVS-PM10 has some practical advantages compared with the HVS-PM10 reference sampler (EN 12341 Annex B.2):

- It is possible to digest the total sample due to the small size of the filter (50 mm diameter). Therefore it is not necessary to prove the homogeneity of collection efficiency over the surface of the complete filter area.

- The change of a small filter of 50 mm or filter holder in the field is more practical than for a large sized filter of 250 x 200 mm, therefore possible contamination by handling is easier to avoid.

- Due to the lower flow rate and the smaller filter size the dimensions of the turbine (pump) and the housing are smaller. This allows easier installation and handling in networks and should reduce the costs of a complete sampling device.

Those sampling devices which have demonstrated equivalency to EN 12341 and which meet the minimum requirements for sampling metals and metalloids (e.g. material of sampling head should not contaminate the collected particles) may also be used by the Member States. These additional requirements for the sampler will be described within the standard under development by CEN/TC 264 WG 14.

The **filter** material should have a very low metal content and should retain 0.3 µm particles with a sampling efficiency better then 99.5 %.

The **digestion** procedure has to be complete, that means the collected particles should be totally dissolved by oxidizing acids. Otherwise – for example in the case of an incomplete digestion or extraction – the equivalency must be demonstrated.

For the **analytical procedure** the AAS-technique is proposed. With the AAS-technique the detection limits needed are achievable. A broad variety of AAS instruments are commercially available and the technique has been well introduced and accepted by the users. AAS is not necessarily the technique with the highest technological standard, but it is sufficient for the given task. Newer techniques, e.g. ICP-MS, are currently not so widely used as the AAS and the acquisition of such a new instrument is expensive. We assume that users of the ICP-techniques should have no significant problems in demonstrating the equivalence of their technique.

Furthermore the first daughter directive specifies the standard ISO 9855 as the reference method for the analysis of lead; this is based on an atomic absorption spectroscopy method. It is therefore an advantage to require only one instrument for the determination of the four metals and metalloids.

The **performance characteristics** of the reference method should be based on a sampling period of 24 hours. Then the method can be used for mandatory measurements and indicative measurements with differing numbers of samples per year to calculate an annual mean value. Further the comparison tests to demonstrate equivalency with another method is reasonable on a sampling period of 24 h.

For **quality assurance** a certified reference material shall be used.

3.4 Other Assessment Techniques

3.4.1 Modelling

The application of air quality models ranges from short-scale plume interaction and urban canyon effects, to intermediate scale-urban-rural interchange and finally to large-scale transport. That is, air quality modelling must address a wide range of temporal and spatial scales covering several orders of magnitude. The simulation of atmospheric dispersion and deposition of airborne particulate matter must take into account the interaction with corresponding meteorological phenomena occurring in these scales of time and space. Typical meteorological phenomena might be grouped according to their respective time and spatial scales as presented in figure 3.10. Additionally, in the upper part of the figure the classification of the horizontal scale according to Orlanski (1975) is given [75].

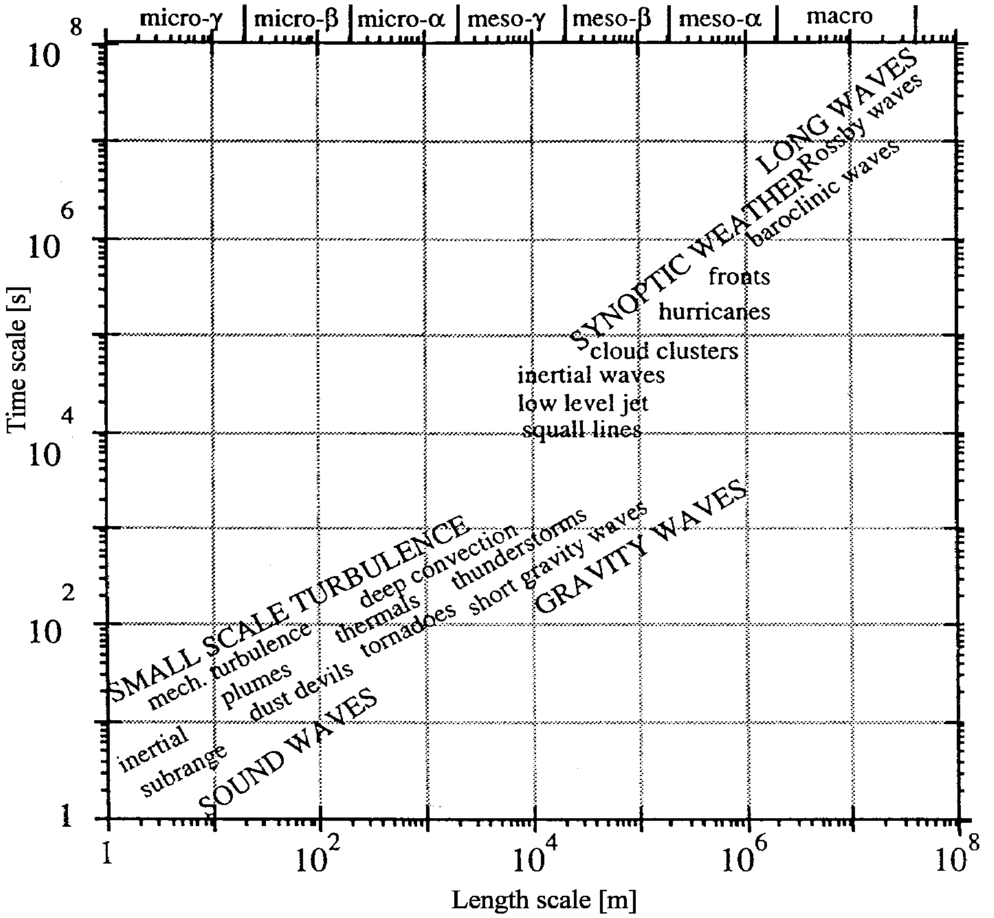


Figure 3.10: Scales of typical meteorological phenomena (from Dennis, 1996 [76], modified)

Depending upon the scope of an air quality model the underlying model theory, the numerical solution technique, the necessary input data and the output of these models may be different. According to the length scales which can be resolved air quality models usually are grouped into different classes:

- Microscale (β and α); consideration of local pollution around factories, power plants, and waste disposal sites as well as urban air pollution influenced by buildings and/or street canyons. Depending upon model sophistication flow structures in the range of some meters to about 1000 m may be taken into account.

- Mesoscale (γ and β); application beyond the range of microscale modelling. Depending upon model sophistication mesoscale phenomena induced by orography and temperature may be taken into account resolving flow structures in the range of about 1000 m to some 10 km.

- Mesoscale α and macroscale; application beyond the range of mesoscale (γ and β) modelling.

The modelling of transport and dispersion of airborne pollutants in the atmosphere has to take into account both, the structure of the atmospheric flow and the turbulence field. Depending on location, these 3-dimensional-fields may be influenced by large scale synoptic forcing, mesoscale effects including valley and slope winds, blocking and channelling effects of topography, and microscale effects, e.g. due to building structures or street canyons. Contemporary microscale and mesoscale modelling of transport and turbulent diffusion of airborne pollutants can be distinguished with respect to the degree of model sophistication.

The detailed structure of the atmospheric flow and turbulence fields may be approached from various levels of complexity. The most complex models solve the hydrodynamic (primitive) equations governing the air flow which take into account effects of thermal forcing, density variation and turbulent interaction. While these prognostic models are highly realistic they are burdensome in application and require high skill for their operation.

Simplification of the primitive equations based on the premise that the mechanisms making up the resultant wind field can be isolated and calculated separately is the basis of several classes of simplified physics models. A rather simple approach leads to mass consistent flow models which calculate topographically adapted non-divergent flow fields from measured wind data. Such diagnostic wind fields may serve together with corresponding turbulence data as an input for a subsequent atmospheric dispersion calculation of airborne pollution.

Atmospheric dispersion models are classified according to their level of complexity, too:

- Lagrangian particle models simulate the atmospheric dispersion by calculating trajectories of simulation particles which represent the airborne pollutant. The particles are subjected to the advective mean wind as well as to turbulent velocities which are determined via a Monte Carlo method. From the resulting spatial and time dependent distribution of the simulation particles the concentration distribution of the pollutant may be derived. Particle models may take into account directly many processes influencing the transport and the turbulent diffusion of airborne pollutants, e.g. sources may be arbitrarily shaped, deposition velocities and aerosol settling velocities due to sedimentation of particulate matter can be introduced directly.

- Eulerian dispersion models are solving the equation of conservation of an airborne pollutant on a fixed calculational grid, e.g. by a finite difference scheme, considering both, advection and turbulent diffusion. Eulerian dispersion models can be applied for non-stationary releases as well as for non-homogeneous wind and turbulence fields varying with time. With respect to particle models the performance of Eulerian models is slightly less, e.g. point, line, or area sources must be approximated by appropriate grid cells with a finite volume. Further problems may arise from the applied numerical solving scheme resulting into artificial diffusion.

- Gaussian puff models simulate the atmospheric dispersion by calculating trajectories of a number of puffs which represent the airborne pollutant. Similar to the simulation particles of the above Lagrangian particle models these puffs are moved according to the advective mean wind. Due to the turbulent diffusion the puffs spread out simultaneously. The parameters which characterize the dispersion situation were often derived empirically from field or wind tunnel experiments. From the resulting spatial and time dependent distribution of the puffs the concentration distribution of the pollutant can be determined. Gaussian puff models can be applied for non-stationary releases and horizontally non-homogeneous wind fields varying with time.

- Finally, the most simple approaches use analytical equations to calculate the atmospheric dispersion. Such analytical models are usually based on the simplified transport-diffusion equation, e.g. assuming a stationary and homogeneous flow field. The corresponding input parameters characterizing the dispersion situation were often the same as for Gaussian puff models. A typical example is the Gaussian plume model: Its application is easy and in combination with suitable dispersion parameters the attainable accuracy is fairly well. Thus analytical models are widely used within national regulations for the impact assessment of the dispersion of airborne pollutants.

In the following an overview will be given about suitable dispersion models currently applied in Europe for the determination of air pollution due to airborne arsenic, cadmium and nickel compounds. For each model

- the necessary input data will be specified,
- valuable notes for the application of the model will be given, including information about attainable accuracy with respect to long term averages as well as about model validation and evaluation,
- known advantages/disadvantages will be summarized,
- the documentation status will be referred.

The corresponding information about the microscale and mesoscale models was mainly supplied via an evaluation

- of databases, e.g. the Model Documentation System of the European Topic Centre on Air Quality (European Environment Agency) [77] or the Internet Handbook on Urban Climate (Internet-Handbuch der Stadtklimatologie) [78],
- of scientific publications, e.g. in conference reports from NATO-CCMS International Technical Meetings and International Conferences on Harmonisation within Atmospheric Dispersion Modelling for Regulatory Purposes as well as in comparative studies evaluating the performance of different microscale and mesoscale models, and
- of ad hoc-inquiries to model developers and users.

The following overview of air quality models was divided into three groups which follows the definition of the spatial scale in the above Model Documentation System of the European Topic Centre on Air Quality:

- Local scale models; comprising the simulation of phenomena and effects in the micro-scale and meso-γ-scale up to a spatial resolution of 30 km,
- Local-to-regional scale models; application to phenomena beyond the range of local scale modelling up to a spatial resolution of 300 km,
- Long range models; application to phenomena beyond the range of local-to-regional models.

In the following section 3.4.1.1 local scale and local-to-regional scale models will be considered whereas section 3.4.1.2 will deal with long range models.

3.4.1.1 Local Scale And Local-To-Regional Scale Modelling

For the determination of the local scale and local-to-regional scale ambient air pollution due to airborne cadmium, arsenic and nickel compounds a couple of microscale and mesoscale models may be applied. A variety of models with different model complexity is available to determine transport and dispersion of airborne material in the atmosphere up to source distances of about 20 km and more. They can be applied to calculate long term averages, i.e. over one year, of the airborne concentration and – partly – the deposition.

A variety of different microscale and mesoscale models has been screened and evaluated according to the application field of the model, model category, possible source configuration (including plume rise), parameterisation of turbulence, deposition, model limitations, input requirements (e.g. emission, meteorology, topography), output quantities, documentation status, validation and evaluation. Many of the investigated microscale models are mainly designed to calculate the dispersion of traffic induced emissions. Only a few ones permit dispersion calculations for airborne particulate matter. Ten models will be considered in more detail because they fulfil at least one of the following criteria:

1. Application in an EC-country for regulatory purposes, i.e. model is mandatory for the respective country,
2. Consideration of special aspects in atmospheric transport and deposition of airborne particulate matter,
3. Sufficient documentation status (preferably in English).

Table 3.26 presents these models together with their main characteristics. It must be expressed that this selection is not exclusive, this list could be expanded.

For each model the following information is given: model category, whether the model is applied for regulatory purpose in a country, the capability to treat dry and wet deposition, the applicable scale, some hints about the model validation and evaluation and, finally, a reference where additional information can be drawn from.

Table 3.26: Main characteristics of investigated local and local-to-regional scale models

Model name	Model Category	Applied for Regulatory purpose	Dry deposition	
			Deposition velocity	Settling velocity
ADMS-3/ ADMS-Urban	analytical; Gaussian puff	UK	yes	yes
AUSTAL-PC	Analytical; Gaussian plume	D	yes	correction of deposition velocity via particle diameter
HNS-ISAQA	analytical; Gaussian plume	H	yes	yes
HNS-COUNTRYWIDE	single layer trajectory box & Gaussian plume	H	yes	not explicitly designed for particulate matter
IFDM	analytical; Gaussian plume	B	yes	correction of deposition velocity
LASAT	Lagrangian particle simulation		yes	yes
ONM9440	analytical; Gaussian plume	A	yes	correction of deposition velocity
OPS	analytical; Gaussian plume & Lagrangian trajectory	NL	yes	not explicitly designed for particulate matter
KFZ.LAG/ STOER.LAG	Lagrangian particle simulation		yes	yes
WinMISKAM/ MISKAM	prognostic flow & Eulerian dispersion		yes	yes

Model name	Wet Deposition	Applicable scale: Local/ Local-to-regional	Model validation and evaluation	References can be drawn from
ADMS-3/ ADMS-Urban	yes	local/ local-to-regional	Prairie Grass; MVK	MDS/ETC
AUSTAL-PC	no	local; source distances > 100 m	via turbulence parameters from experiments at Jülich & Karlsruhe	IHUC
HNS-ISAQA	yes	local	Hungarian data, including aerosol measurements	MDS/ETC
HNS-COUNTRYWIDE	yes	local-to-regional	data from Hungarian air quality network	MDS/ETC
IFDM	yes	local	MVK; model intercomparison	MDS/ETC
LASAT	yes	local, including building effects/ local-to regional	Prairie Grass; Karlsruhe; Kopenhagen (MVK)	IHUC
ONM9440	no	local, adaptation for orography	Kincaid (MVK)	MDS/ETC
OPS	yes	local/ local-to-regional	MVK; model intercomparison	MDS/ETC
KFZ.LAG/ STOER.LAG	yes	local, including building effects/ local-to-regional	concentration predictions against reference datasets	MDS/ETC
WinMISKAM/ MISKAM	no	local, including building effects	Göttinger Strasse; model intercomparison	MDS/ETC IHUC

IHUC	Internet Handbook on Urban Climate (Internet-Handbuch der Stadtklimatologie [78]
MDS/ETC	Modell Documentation System of the European Topic Centre on Air Quality [77]
MVK	Modell Validation Kit [79]

The dispersion calculations of seven models are based on analytical equations for Gaussian plume, Gaussian puff or a combination of Gaussian plume with a box model approach. Three models are rather sophisticated; two of them (LASAT, KFZ/STOER.LAG) apply Lagrangian particle simulation techniques together with a suitable meteorological preprocessor supplying the required turbulence data and 3-dimensional diagnostic wind fields. WinMISKAM/MISKAM operates with a 3-dimensional prognostic flow model with a subsequent Eulerian dispersion model. These three models consider explicitly local scale characteristics, i.e. their flow fields take into account directly the influence of topography and buildings; arbitrarily shaped source geometry can be treated. However, it has to be mentioned again that Eulerian dispersion models must approximate the geometry of point, line, or area sources by appropriate grid cells with a finite volume.

All analytical models are applied in European countries for regulatory purposes. Most of them use schemes to parameterize turbulent diffusion, which seem to be specific for the respective country. Instead of these site specific turbulence parameterisations the models ADMS and OPS apply more generalized and hence site-independent approaches which are based on surface layer similarity and boundary layer scaling. Both particle simulation models apply these universal approaches in their meteorological preprocessors, too. The turbulent diffusion coefficients for the Eulerian dispersion model in WinMISKAM/MISKAM are calculated from universal approaches, too.

All models considered here are able to calculate the annual mean concentrations directly on the basis of either time series or joint frequency distributions of wind speed, wind direction and stability class as typically supplied by national weather services.

The models all calculate dry deposition. However, only a few explicitly apply aerosol particle settling velocities (ADMS, HNS-ISAQA, LASAT, KFZ/STOER.LAG, WinMISKAM/ MISKAM). AUSTAL-PC, IFDM and ONM9440 use aerosol particle size dependent velocities. HNS-COUNTRYWIDE and OPS are not explicitly designed for the application of the dispersion and deposition of airborne particulate matter. Wet deposition is considered only by ADMS, HNS-ISAQA, HNS-COUNTRYWIDE, IFDM, LASAT, OPS, KFZ/STOER.LAG.

A documentation of a microscale model is an important prerequisite for its successful application. The more sophisticated the model is the more essential is a well structured, detailed and user friendly documentation. The Model Documentation System of the European Topic Centre on Air Quality provides a ranking of the documentation status: A high grade documentation should therefore contain a complete scientific model description preferably published in a reviewed scientific journal, detailed user manuals, well documented results from model validation tests, a well-documented source code. The documentation state of the models considered here shows some differences: Scientific descriptions and user manuals are available in any case, their quality was not assessed extensively.

All models in table 3.26 were validated more or less extensively using different approaches. A very common validation tool is the Model Validation Kit (MVK) which was launched in 1991 as a European initiative for increased co-operation and standardisation of atmospheric dispersion models for regulatory purposes [79] The MVK is a collection of four experimental data sets (containing meteorological as well as tracer gas data from field experiments at Kincaid, Lillestrom, Kopenhagen and Indianapolis) accompanied by software for model evaluation.

Unfortunately the tracer experiments from the MVK deal only with neutral gas. Local scale tracer experiments with airborne particulate matter are not available. Nevertheless, ADMS and IFDM were validated with the MVK (see Tab. 3.26). Other models were validated on the basis of single datasets from the MVK, i.e. the Kincaid or Kopenhagen data which are characterised by emission heights larger than 100 m. Other reference datasets which were applied within the frame of model validation are the tracer experiments carried out at O’Neill, Nebraska (Prairie Grass, near surface emissions) [80] and at the Karlsruhe research Centre (release heights 60 m, 100 m, 160 m, 195 m) [81,82] The local scale model HNS-ISAQA was validated against data from power plants (one year data) as well as from a cement plant (6 months, dust load deposition) in Hungary [83] whereas the corresponding local-to-regional scale model HNS-COUNTRYWIDE was validated against air and precipitation data from the Hungarian air quality network [84].

Within the frame of a comparison and assessment of currently available microscale flow and dispersion models which has been carried out in the Project ”Europäisches Forschungszentrum für Maßnahmen zur Luftreinhaltung” a couple of local scale models was evaluated [84]. MISKAM from table 3.26 has participated in this model intercomparison together with some other microscale models available from different institutions, e.g. ABC [78], ASMUS [78] or DASIM [78]. These three models determine the flow around buildings taking into account turbulent wakes in front of and behind obstacles. Generally the subsequent dispersion calculation can deal with depositing material. Up to now, these models are not explicitly designed to be applied for airborne particulate matter.

In one part of the model intercomparison the ability of the models to calculate annual means and percentiles was tested. For the model intercomparison data from an urban climate field experiment ”Göttinger Strasse, Hannover” were used, mainly because of their completeness. The differences between the results of most of the models were not pronounced enough, to single out any one of them as the best. The error margin of MISKAM was comparatively low. However, in order to put this result on a broader statistical basis the corresponding microscale flow and dispersion models still have to be tested with other appropriate datasets.

Another possibility to check the validity of models is to intercompare them for predefined conditions with the results either of well known analytical solutions (e.g. from simple hydrodynamic flow or dispersion conditions) or of other well known and broadly accepted models. Such extended model verification tests have been carried out and documented for the Lagrangian particle simulation model LASAT.

The only model for which no specific validation is documented is AUSTAL-PC (based on the Guideline ”Technische Anleitung zur Reinhaltung der Luft – TA Luft (1986)”) which is used in Germany for the environmental impact assessment of additional long term exposure from air polluting sources. However, the dispersion parameters implemented in this guideline are based on extensive field experiments carried out in the flat terrain surrounding the research centres of Jülich and Karlsruhe (typical for high roughness length). They represent the best overall fit to the dispersion experiments for all dispersion categories and source distances larger than 100 m. Therefore it is appropriate to use the Gaussian model of the TA Luft to assess long term average concentration data for source distances larger than 100 m up to some 10 km in nearly flat terrain which is not disturbed by buildings.

For the above micro- and mesoscale models the attainable accuracy in terms of annual mean values of concentration and deposition of airborne particulate matter is difficult to specify. The corresponding model uncertainty comprises the following components [85]:

- input data errors; i.e. source term data must be well known with respect to e.g. source strength and particle size distribution, meteorological input data – e.g. in terms of a joint frequency distribution of wind speed, wind direction, stability class, and precipitation – must be representative for the model domain,

- stochastic or turbulent fluctuations; e.g. if the annual mean values of concentration and deposition are calculated with a joint frequency distribution of meteorological data derived from observations from one year then it must be guaranteed that this year is really statistical representative. However, this becomes less important if an uniform meteorological data base which will be derived from the years 1997 to 1999 will be applied for all models of concern,

- limitations from model physics or model physics errors; depending upon the approximations implemented a model has application limits, e.g. the classical Gaussian plume model cannot take into account the vertical shear of wind direction, explicitly, or - as another example - Eulerian dispersion models provide airborne concentrations as averages through the grid cells of the calculational grid which are difficult to be compared with point measurements,

- lack of knowledge and lack of data; e.g. suitable long term validation data from field experiments dealing with the atmospheric dispersion and deposition of aerosols - if possible in built-up areas - are not available.

The experience with non-depositing airborne pollutants shows that in nearly flat terrain the ratio of predicted to observed annually averaged air concentrations covers the range of about 0.5 to 2 if Gaussian plume models are applied [85,86]. Recent studies [87] related to the determination of yearly averages and percentiles of traffic induced pollutant concentrations in built-up areas show that prognostic models, e.g. WinMISKAM, as well as diagnostic models, e.g. ABC, DASIM, or LASAT, can reproduce measured averages and percentiles with an accuracy of about ±20-30%. However, essential prerequisites are reliable emission inventories and the proper modelling of other input parameters, e.g. meteorology, as well as the reliability of the observed annual mean concentrations which serve as a reference. It can be stated that the statistical representativeness of all these data seems to be more crucial than the ability of the models to describe complex flow features [87,88] This assessment of the attainable accuracy has to be restricted if atmospheric dispersion and deposition of particulate matter is considered: Additional uncertainties will reveal, but cannot be specified properly due to the lack of suitable measurements. These uncertainties depend on the physical properties of the aerosol (e.g. particle size distribution, particle shape) and its interaction with surfaces, e.g. deposition fluxes due to deposition velocity, settling velocity, and wet deposition processes as well as removal processes when deposited material is whirled up and becomes airborne again. From this it is expected that the attainable accuracy of model calculations will decrease significantly if applied to particulate matter.

From the overview presented here it can be concluded that a couple of models is available for both, local and local-to-regional scale modelling of long term airborne concentration and deposition of aerosols containing cadmium, arsenic, and nickel compounds. The corresponding characteristics and application fields of the models can be drawn from table 3.26. Simpler models are based on Gaussian type approach; they can be used in the local-to-regional scale if the boundary conditions are simple with respect to the source configuration, the meteorological data base, and the terrain structure. Their handling is easy and the requirements with regard to the input data are low. - However, if terrain effects, the influence of buildings, or street canyons become important more sophisticated models should be applied. Among the models which were considered here ADMS, LASAT, and KFZ/STOER.LAG are able to calculate the atmospheric transport and turbulent diffusion in the local scale and in the local-to-regional scale up to source distances of some 10 km and more (WinMISKAM up to source distances of some 100 m). These models take into account airborne emissions from arbitrarily shaped sources as well as the influence of structured terrain and buildings on the resulting flow and concentration fields. A successful application of such sophisticated models requires a high amount of skilfulness and experience of the user. The more sophisticated a model is the more skilled must be the user of the model. This additionally necessitates the availability of an extensive, complete and user friendly documentation of the model, including scientific description, user manuals, documentation of model validation and evaluation, detailed source code.

The validation status of all models, the simple and complex ones, is not satisfactory. This is mainly due to the fact of lacking validation datasets especially dealing with the atmospheric dispersion and deposition of particulate matter. This makes furthermore the specification of the attainable accuracy a difficult task.

3.4.1.2 Modelling Of The Long-Range Transport Of As, Cd And Ni

Concentrations and depositions of heavy metals measured in remote areas indicate that a significant part of heavy metals emitted into the atmosphere can be transported far away (1000 km and more) from the sources. To simulate such a transport different long-range transport heavy metals models have been developed for Europe for the last two decades. These models have been compiled and discussed in the background document (Petersen, 1996 [89]) prepared for the joint EMEP-WMO Workshop in Moscow in 1996. A modified summary of the long-range transport models for heavy metals, presented originally by Petersen (1996) is given in table 3.27. Compared to the original, the modified summary table includes only those models which take into account As, Cd and Ni. In addition, new models developed after 1996 are also included in table 3.27.

All models listed in table 3.27 belong to one of the four following categories: Lagrangian-Trajectory, Lagrangian-particle, Climatological and Eulerian.

Table 3.27: Summary of European long-range transport models for As, Cd and Ni

Model		
Name	Type	
		Institution
NILU-EMEP	Lagrangian one-layer trajectory model modified for heavy metals	NILU (Norwegian Institute for Air Research) Kjeller, Norway
TREND	Statistical Approach of a Gaussian plume model and a trajectory model	RIVM (National Institute of Public Health and Environmental Protection) Bilthoven, The Netherlands
OPS (Operational Priority Substances)	More operational version of TREND	TNO (Netherlands organization for applied scientific research) Delft, The Netherlands
EUROTREND		
HHLRT (Hamburg Long Range Transport Model)	Three-dimensional stochastic model	Meteorological Institute, University of Hamburg, Germany

Model					Refe-rences
Name	Application				
	Input		Output		
	Meteorological	Calculated substances	Receptor area	Time scale	
NILU-EMEP	6-hourly from the Norwegian Numerical Weather Prediction Model	**As**, **Cd**, V, Mn, Pb, Sb, Se	Birkenes, Southern Norway	Daily averages	[93]
TREND	Long-term averages from the Dutch Meteorological Office	**As, Cd, Ni**, Sb, Cr, Cu, Pb, Zn	North Sea	Annual averages	[94]
OPS	Long-term averages from the Dutch Meteorological Office	**Cd, Ni,** Cr, Cu, Pb, Hg, Zn	North Sea, Dutch Wadden Sea	Annual averages	[95]
EURO-TREND			River Rhine drainage basin		[96]
HHLRT	6-hourly analysis from the European Centre for Medium-Range Weather Forecasts (ECMWF)	**Cd,** Pb	North Sea	Monthly averages	[97]

Table 3.27 (cont.): Summary of European long-range transport models for As, Cd and Ni

Model		
Name	Type	
		Institution
GKSS-EMEP	Lagrangian one-layer trajectory model, sulfur model modified for inert particle associated substances	GKSS (Research Centre Geesthacht) Germany
TRACE	Improved climatological-type model	IIASA (International Institute for Applied Systems Analysis) Laxemburg, Austria
HMET (one layer)	Eulerian one-layer model in the EMEP grid system	The IBM Bergen Environmental Sciences & Solutions Centre, Bergen, Norway
HMET (two layers)	Eulerian two-layer model in the EMEP grid system	DNMI (Norwegian Meteorological Institute) Oslo, Norway

Model					References
Name	Application				
	Input		Output		
	Meteorological	Calculated substances	Receptor area	Time scale	
GKSS-EMEP	6-hourly from the Norwegian Numerical Weather Prediction Model and from European monitoring network	**As, Cd,** Zn, Pb	North Sea Baltic Sea	Monthly/annual averages	[98]
TRACE	Improved climatological input	**As, Cd,** Zn, Pb	Europe	Annual averages	[99]
HMET (one layer)	6-hourly from the Norwegian Numerical Weather Prediction Model and from European monitoring network	**As, Cd,** Zn, Pb	Europe	Monthly/annual averages	[100, 101]
HMET (two layers)		**As, Cd,** Zn, Pb, Cu, Hg			[102]

Table 3.27 (cont.): Summary of European long-range transport models for As, Cd and Ni

Model		
Name	Type	
		Institution
ASIMD (Asymmetric Advection)	Eulerian three-dimensional model in the EMEP grid system	MSC-E (Meteorological Synthesizing Centre - East) of EMEP, Moscow, Russia
LPMOD (Large Particle Model)	Eulerian three-dimensional model in the EMEP grid system	MSC-E (Meteorological Synthesizing Centre - East) of EMEP, Moscow, Russia
EMAP (Eulerian Model for Air Pollution)	Three-dimensional Eulerian model	National Institute of Meteorology and Hydrology, Sofia, Bulgaria

Model					References
Name	Application				
	Input		Output		
	Meteorological	Calculated substances	Receptor area	Time scale	
ASIMD (Asymmetric Advection)	6-hourly from the Russian Numerical Weather Prediction Model	**Cd,** Pb, Hg	Europe	Monthly/annual averages	[103, 104]
LPMOD (Large Particle Model)	6-hourly from the Russian Numerical Weather Prediction Model	**Cd,** Pb	Europe	Monthly/annual averages	[103, 90]
EMAP (Eulerian Model for Air Pollution)		**Cd,** Pb	Bulgaria	Monthly/annual averages	[105]

Lagrangian-Trajectory group is represented by the NILU-EMEP and GKSS-EMEP models in Table 3.27. Both models are one-dimensional and describe transport of pollutants in the well-mixed layer. Since backward trajectories are used both models are receptor oriented and can easily be used for multiple emission sources. The advantages of this approach are: simplicity, fast computations, available long-term meteorological input data, good temporal resolution of meteorological input data, complete elimination of the numerical diffusion. Weak points are the following: diurnal variation of the mixing height is not taken into account, transport of heavy metals above the mixing layer is not included, mass of pollutants is not fully conserved, especially non-linear chemical reactions cannot be parameterized. In addition a significant part of the pollutants, once transported above the mixing height is not taken into account in further simulation of the transport in these models.

Lagrangian-particle category, in table 3.27, includes one model - HHLRT. This is an advanced fully three-dimensional approach. Advantages of this model are: full vertical resolution of the atmosphere, accurate parameterization of the horizontal and vertical advection, easy and accurate parameterization of the horizontal and vertical diffusion. Main disadvantages are: long computation and large computer memory required, limited set of meteorological input data available for the computations. Also, it is rather difficult to include more complicated chemical reactions in this model.

There are three models in the climatological category in table 3.27: TRACE, TREND and OPS. These models are simple and fast in operational applications especially in long-term simulations. The main weakness of this category is the same as for the Lagrangian-Trajectory group, and in addition: simplified meteorological input data with poor temporal resolution which do not take into account the periods with the intensive transport, only a limited number of physical processes can be included in the statistical description.

Eulerian category in Table 3.27 includes HMET, ASIMOD and LPMOD. The latest version of the HMET model has two dynamic horizontal layers, lower below mixing height and upper above the mixing height. Vertical structure of ASIMOD and LPMOD includes 4-6 layers, depending on the version but orography is not taken into account in these models. The main advantage of the Eulerian models is a possibility of detailed description of physical and chemical processes including non-linear chemical reactions. On the other hand, numerical diffusion can be a problem and a major disadvantage in applications of these models.

Under the frame of EMEP modelling of heavy metal (HM) long-range transport started in 1995. 3D model ASIMD has been developed in MSC-E to simulate long-range transport of HM, in particular of Cd [90].

The latest version of the MSC-E model is described in [106]. It includes basic processes and mechanisms of pollutant transport and scavenging from the atmosphere, i.e. emission, advective transport, turbulent diffusion, dry and wet deposition. It is an Eulerian model operating within geographical scope of the EMEP region (135×111 cells) with spatial resolution 50×50 km and time step 20 min. The model deals with five atmospheric layers along the vertical with thicknesses of 100, 300, 700, 1000 and 1800 m. The present version of this model takes into account pollutant transport by large-scale vertical fluxes up to four-km height. The model is capable of calculating fields of concentrations, depositions and budget (country-by-country) matrices. Seasonal dependence of washout ratio was introduced. The model includes natural emissions of heavy metals as well as influx from the background outside the model domain.

All models listed in Table 3.27 deal with Cd, many with As, but only two, TREND and OPS, simulate atmospheric transport and deposition of Ni. In general, comparison of model results and observations indicates approximately a “factor of two” agreement for As and Cd, for air concentrations and concentrations in precipitation. Model results for Cd are closer to observations than model results for As. For Ni, there is a lack of validation data which are sufficient for the territory of Europe.

EMEP activity in a field of modelling of HM transboundary transport and deposition

MSC-E is a leading EMEP center in the field of HM transport modelling. MSC-E provides European countries with fields of concentration and depositions of HMs and assessments of country-to-country transport on annual basis. Results for cadmium transport in 1996 presented below were adopted from the report by Ryaboshapko et al., [106].

Concentration and deposition patterns

Cadmium surface air concentration field is demonstrated in figure 3.11. The south-west part of Poland, the Czech Republic, the central part of Great Britain, Spain and Bulgaria can be referred to regions with high air concentrations of cadmium. Mean annual concentrations in these regions can be higher than 2 ng/m^3. Relatively “clean” countries are for instance, France, Germany and Austria. Here concentrations range from 0.15 to 0.5 ng/m^3. Countries of Northern Europe can be referred to the most clean European regions. In these countries concentrations do not exceed 0.15 ng/m^3.

The map of cadmium deposition intensities is given in figure 3.12. The deposition field configuration actually corresponds to the field of air concentration - maximum deposition intensities are observed in Poland, Great Britain, Spain and countries of south-eastern Europe, minimum values - in the north of the EMEP region. In the most polluted regions deposition values can exceed 0.5 kg/km^2/yr and in the most clean ones they do not exceed 0.05 kg/km^2/yr.

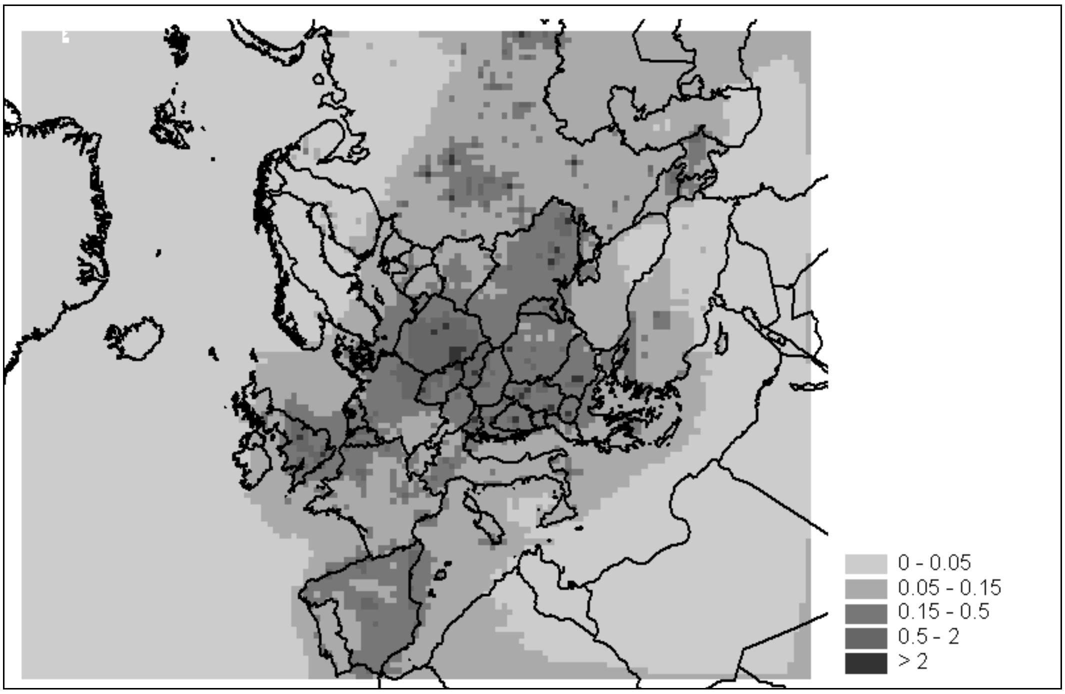


Figure 3.11: The field of mean annual surface air concentrations of cadmium, ng/m³

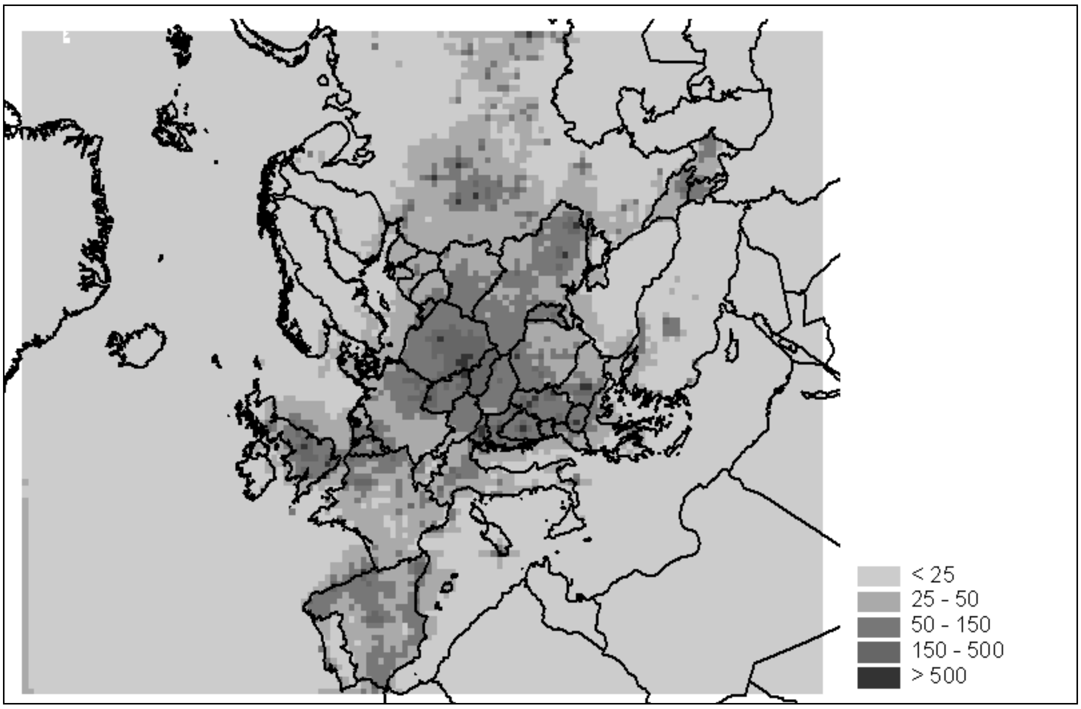


Figure 3.12: Field of total (dry and wet) deposition of cadmium, g/km^{2}y

Comparison with measurements

Values of cadmium concentrations measured and calculated are presented in figures 3.13 and 3.14 (see list of EMEP HM and POP monitoring sites in Appendix C and map of their locations in fig. 3.4). As it follows from the figures for the majority of stations the agreement of measured and calculated concentrations in air is rather good (within the first tens of percent). Averaged over all the measurement sites calculated and measured values are equal to 0.32 and 0.37 ng/m^3 correspondingly, correlation coefficient is equal to 0.89. For concentrations in precipitation on the whole measurement data are somewhat higher than calculated ones. Averaged over all the measurement sites calculated and measured values are equal to 0.042 and 0.092 µg/l correspondingly, correlation coefficient is equal to 0.72.

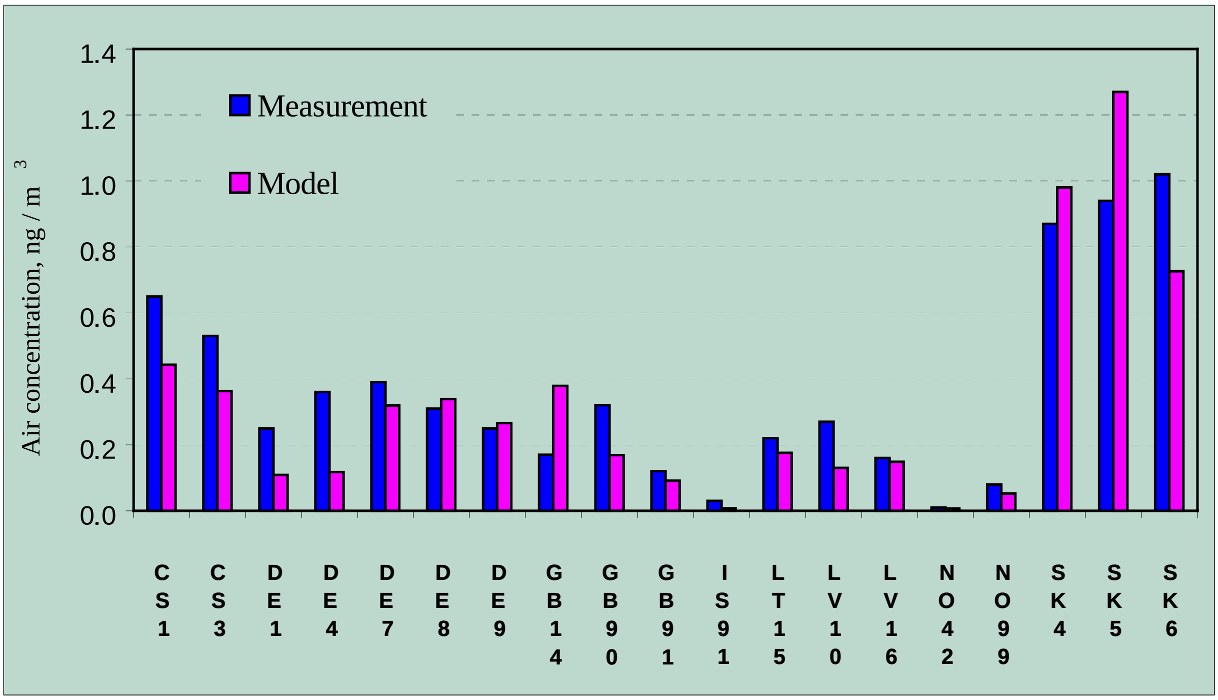


Figure 3.13: Comparison of calculated and measured mean annual air concentration values of cadmium for individual monitoring stations in 1996 (ng/m^3)

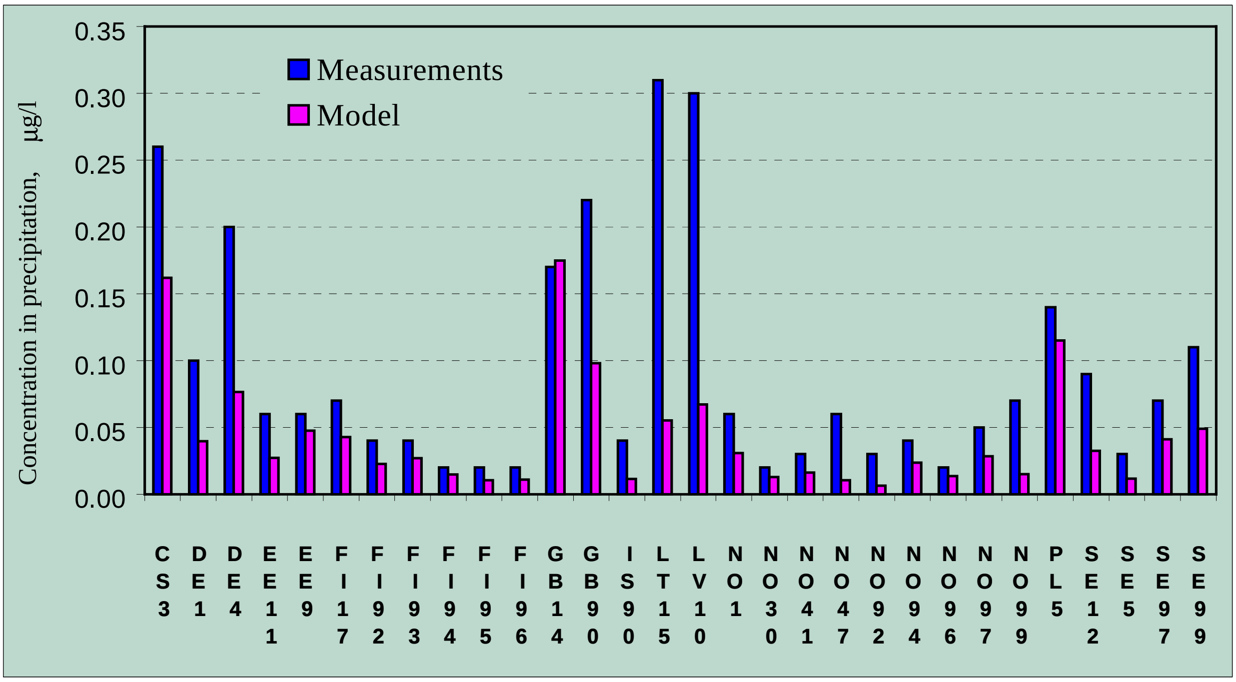


Figure 3.14: **Comparison of calculated and measured mean annual concentrations in precipitation of cadmium for individual monitoring stations in 1996 (µg/l)**

Estimates of EC countries pollution resulted from long-range Cd transport

Substantial anthropogenic emissions in individual countries and relatively long life-time of cadmium pose prerequisites for raising the problem of transboundary transport. For each country-receiver deposition on it is determined by its own emission sources, sources of other European countries and natural and globally distributed sources. Contributions of different countries to depositions on the country under consideration can be quite different and dependent on many factors: emission level, distance from emission sources and meteorological conditions.

In the table 3.28 for each EC country the following modelling results are presented: input of three major country-emitters; input of own, natural and global sources. It follows from table 3.28 that for considerable number of EC countries the main source of cadmium pollution is transboundary transport. The contribution of natural and globally distributed sources is insignificant. At the same time the contribution of depositions of cadmium from own sources can be quite significant for some countries.

Table 3.28: Major countries-sources and their contribution to depositions of cadmium to EC countries-receivers in % (adopted from MSC-E report [106])

Country	Major countries-sources (input in %)			Contribution own source	Input of natural and global anthropogenic sources, %
Austria	Slovakia - 15	Slovenia - 14	Czech. Rep. - 11	21	7
Belgium	France - 37	UK - 6	Germany - 5	41	3
Denmark	Poland - 22	UK - 12	Germany - 12	26	5
Finland	Russia - 12	Poland - 11	UK - 5	33	17
France	Spain - 16	UK - 6	Belgium - 3	57	7
Germany	Czech. Rep. - 16	Poland - 11	France - 8	45	5
Greece	Bulgaria - 13	Yugoslavia - 10	Macedonia - 7	38	8
Ireland	UK - 40	France - 4	Spain - 4	18	20
Italy	Spain - 5	France - 5	Slovenia - 4	62	9
Luxembourg	France - 75	Germany - 7	UK - 2	8	2
Netherlands	Belgium - 22	France - 14	UK - 13	24	6
Portugal	Spain - 32	UK - 2	France - 1	37	27
Spain	France - 2	UK - 1	Portugal - 1	89	7
Sweden	Poland - 23	UK - 10	Germany - 7	3	18
UK	France - 3	Poland - 2	Germany - 1	86	3

Intercomparison studies

The MSC-E model took part in some intercomparison experiments. During macroscale experiment ETEX [91] the transport scheme of the model demonstrated good agreement of modelled and measured data. The MSC-E model together with TREND, GKSS, and EMAP models participated in the intercomparison study of Cd models. The purpose of the study was to indicate the consistency of the results obtained by different models. Modelled wet deposition, concentrations in precipitation and in air derived on the basis of emission and meteorology for 1990 were compared between each other and measurements. The comparison showed that the results of four listed models are similar enough and model-versus-measurement discrepancies are mainly within a factor of 2 [92].

3.4.2 Biomonitoring

Introduction

Measurements of ambient air concentrations or depositions only point to a principally possible effect, but not to the real occurrence of this effect. Thus, aside from measurements of ambient air quality, additional important information has to be gained by monitoring possible air pollution effects systematically on the living environment by means of cost effective bioindicators, serving as surrogate for a whole category of environmental compartments e.g. man, animal, vegetation etc. Bioindicators are defined as follows: "Bioindicators are organisms or communities of organisms reacting to pollutants by functional changes or by accumulation of the pollutant" [107]. Procedures using bioindicators offer therefore obvious advantages:

- Synergistic effects caused by several air pollutants can be revealed.
- Studies of biological matter offer retrospective data. For example, needle analyses provide retrospective data on the past 1 to 3 years (separately for each year). As a rule, the information supplied covers the growing season. With the help of biological methods spots of severe pollution can easily be identified source related.
- The accumulation of persistent pollutants such as metal and metalloid compounds in bioindicators allows to assess the hazards to human and animals caused by the intake of polluted food and fodder plants.

Although the results of biological detection methods provide valid information on the airborne pollutants in concern and their impact on the living environment and are useful means to detect and identify sources, they can not be used to measure ambient air concentrations, since the reaction of a bioindicator is the result of the effective dose, given by a stochastic exposure scenario over a certain time. Therefore these methods are no suitable tool for compliance monitoring. However, the use of biomonitors offers complementary, additional information on effects, which cannot be gained otherwise.

After this more general introduction, we will focus on the use of biomonitors for metal and metalloid compounds.

Biomonitors for the assessment of metal and metalloid compounds

As oral uptake and ingestion of contaminated food is one of the major uptake routes for arsenic, cadmium and nickel compounds (compare chapter 2.2.2), the analysis of the accumulation of such compounds in plants is the method of choice for biomonitoring metals and metalloids. Both active and passive biomonitoring has been widely used.

Passive biomonitoring stands for sampling plants at their natural growth site. This method requires to take representative samples in order to reduce the influences of confounding factors such as soil, physiological condition and genetics [108].

Moss monitoring has been extensively used since the seventies [109] to study the airborne intake and burden of metals and metalloids into the environment. Mosses are not equipped with stomata and rhizoms and accumulate directly via their large surface area. Hence, interactions with soils or the atmosphere can be excluded.

Herpin et al. [110] investigated the burden of various heavy metals in certain mosses throughout Germany. The results agree with the known locations of heavily polluted areas such as the Ruhr area, Saarland, large parts of eastern Germany. Aside from identifying the polluted areas, the results also reflect the influence of various emission sources. The repeated investigations (Sievers and Herpin, [111]) yielded changes in the heavy metal burden found in the mosses, primarily in eastern Germany. Clear decreases in the heavy metal concentrations were detected.

Another recent example is the study of temporal and spatial trends of metal contents (inter alia Cd and As) of Bavarian mosses (Hypnum Cupressiforme) [112].

The Scandinavian countries have launched in 1985 a monitoring program for the heavy metal content in mosses. This program has formed the basis of comprehensive moss monitoring in the framework of EMEP, where several other European countries participate. The EMEP program aims at assessing the regional burden of heavy metals, at identifying problem areas, and at establishing baseline data for the evaluation of trends. For example, results for atmospheric metal deposition in France using five common mosses as bioindicators have recently been published [113].

Other passive biomonitors which have been applied for metals are fruiting bodies of wild edible mushrooms [114] or lichens [115].

Active biomonitoring uses specific plant species cultivated under standardized conditions and exposed according to a specific method and protocol (time of exposure, hight, sampling proceedure of plant parts etc.). In order to have a high reproducibility, methods require a high measure of standardisation (propagation conditions, selected varieties, developmental stages and growth conditions of plants). Standardised exposure methods offer the possibility to monitor air pollution effects/accumulation over selected time intervalls in a given area or araound certain sources. Parallel exposure in remote areas allows the determination of background concentrations in order to determine the baseline values of pollutants in bioindicators.

All this ensures a high reproducibility of the obtained results; moreover, deviations due to the procedure are kept at a minimum. Standardisation of the biological detection methods makes the results obtained in different regions comparable. The temporal and spatial variations become apparent.

Mosses can be also used as active biomonitors by exposing for example Sphagnen sp. or Hypnum sp. during four to six weeks in nets made from nylon with subsequent analysis for heavy metals in the laboratory.

The most well-known example of active biomonitors is the standardized grass culture [116]. The standardized grass culture (Lolium multiflorum ssp. Italicium) is exposed during the growing season at selected sites for periods of 14 days. After the 14 days exposure period the grown grass is cut and processed for analytical proceedures and a new vessel exposed at the exposure site. If air pollution concentrations are low, several grass cultures are exposed parallel at the same site. Analytical results can be pooled and average seasonal or monthly means be generated. Individual results which do not fit in with the rest are considered separately. When exposed in a grid like monitoring network, a space and time evaluation will render local hot spots. Results further more allow risk evaluations for grazing animals when compared with limit values. If such limits are being exceeded, further studies of the vegetation become necessary and precautionary measures need to be addressed.

The standardized grass culture has widely been applied in polluted regions in Germany [117] and Belgium [118], for example in the vicinity of a non-ferrous metal smelter at Hoboken. Here, a study has been conducted since 1980 with cultures of perennial ray grass (Lolium perenne). Two systems have been used:

- Permanent cultures (grass is grown in containers and exposed from April until November. Every 28 days the regrowth of the grass is harvested and analyzed).

- Alternating cultures (every fortnight a new container is exposed for 14 days. After exposure the grass is clipped and analyzed).

Near Hoboken, the grass was analyzed for cadmium, copper, lead, arsenic and mercury.

Another bioindicator belonging to the accumulating indicators is green cabbage (*Brassica oleracea* var. acephala). The green cabbage method [119] serves as a surrogate for garden grown vegetables and provides information on the accumulation of hazardous pollutants over a given time and location and thus allows risk estimations for foodstuff taken up orally. Due to the waxy and curly surface of the leaves, the area of accumulation is comparatively large and the waxy surface reacts lipophilic, an important feature for the accumulation of organic substances.

Green cabbage plants can either be planted directly in garden soil or are exposed on selected sites in containers using uncontaminated soil over a period of 90 to 100 days. *Brassica oleracea* var. acephala is a winter-hardy plant offering the unique advantage of an exposure during winter months, where pollution concentrations are frequently higher in comparison to the growing season.

Besides green cabbage other vegetables like spinach and lettuce have been widely used as active bioindicators in the vicinity of polluting sources in Germany [120] and Belgium [118]. The Belgian data have been used to derive tolerable cadmium and lead deposition thresholds for various vegetables (compare chapter 2.5).

To sum up, accumulation of metals in plants caused by ambient air pollution can be easily determined by active or passive bioindicator monitoring methods and the subsequent chemical analysis of plant material. The results obtained can be used for risk evaluations for man and animal by comparing results with limit values for food and fodder plants. Consequently, the use of bioindicators is recommended as additional tool in order to assess.

- the input of metals and metalloids into crops and fodder plants near sources (hot spot analysis),
- the widespread accumulation of metals and metalloids within eco-systems,
- the success of air pollution abatement measures for given sources and technologies.

3.5 Quality Assurance

Uncertainties in a measurement system are of two different types, namely systematic and random uncertainties. The systematic uncertainty is introduced as a result of a basic fault in the system, which may be difficult to identify and therefore, to control or to reduce. In statistical terms, systematic uncertainties do not follow a normal or other well-defined distribution and replication of the measurements will not reduce them to tolerable levels. A leak in the sampling system or the use of the wrong calibration curve will lead to systematic uncertainties. Conversely, random uncertainties are those which comply with well known distributions and they can be reduced by close control of the measurements process and meticulous attention to detail. Replicate measurements will reduce this type of uncertainty.

The overall uncertainty is made up of the random uncertainties in sampling, calibration factors, flowrate and time measurements. In the evaluation of the method an attempt should be made to examine every component of the system and the procedure which could affect the result. Where possible every source of systematic and random uncertainty should be listed and its effect on the overall standard error of the method stated. Also the uncertainty due to the imperfect spatial representativeness of the sampling point(s) should be addressed.

The areas, which are likely to give rise to the greatest uncertainties, need to be described and QA-QC procedures should be available to check that components are operating correctly. Special attention is given to those areas, which are likely to give rise to significant errors [123].

Objectives
Quality assurance is a system of procedures that ensures that :

- Measurements are precise and accurate.
- Results are comparable and traceable.
- Data are representative of ambient conditions.
- Optimal use is made of resources.

The major constituents of a quality assurance system are:

- Network design : number of stations, siting criteria.
- Measurement technique : sampling, analytical and calibration procedure.
- Equipment evaluation and selection : validation of methods, test of instrument performances.
- Routine site operation : comparison tests in field conditions, maintenance, management and training.

QA-QC Procedures:
QA/QC procedures are described in the WHO UNEP GEMS/AIR Methodology Review Handbook Series, UNEP/WHO (1994a) and UNEP/WHO (1994b) [126].
In general the recommendations given for sampling PM10 should be followed.

Quality control (QC) is the procedure, which is necessary to ensure that measurements carried out, will meet the required standard of accuracy and precision [123].The aim of a quality control procedure is to specify tests to ensure that samplers and analytical instruments are operating correctly by a) eliminating so far as is possible, systematic uncertainties, b) reducing random uncertainties to a minimum.

In order to achieve the overall aims of the quality control procedure, a quality control statement should be prepared for each measuring station, listing:

- The method in use, i.e. type of instrument, type of filter paper etc;
- Calibration procedures and schedule including frequency of blank measurements;
- Maintenance procedures and schedule;
- Sampling and reading requirements;
- Reporting procedures;
- A report on parallel measurements with the Reference Method.

Examinations and performance tests should be carried out to ensure that the sampling system meets the basic requirements of the Directive Reference Method and that each system is operating satisfactorily without leaks. Each analytical instrument should be checked periodically for characteristic performances.

Quality assurance (QA). Quality Assurance is the procedure, which will ensure that the quality control procedures achieve their objectives. Quality assurance is an integral part of any monitoring programme. It is necessary to ensure that the objectives of the programme are being met and that all the results from the different networks are comparable [123]. The EPA manual on Quality Assurance Procedures describes quality assurance as the quality control on the quality control [125].

The intercomparability of different types of measuring systems is important and it is necessary to make sure that all types of equipment within the network give results, which are comparable with the reference method. Intercomparison test procedures need to be described together with data evaluation and acceptance procedures.

Essentially quality assurance is necessary to ensure that all the component parts of particular network are operating in such a way that the requirements of the directive are met and that all the results which are obtained comply with the Reference Method requirements.

A quality assurance programme needs to:

- Identify the characteristics which are most important in determining the accuracy of the final result;
- Define the acceptance limits, particularly in the case of the most important parameters;
- Set the frequency of testing of main characteristics;
- Identify the methods which should be used in the test procedures;
- Set reporting procedures;
- Lay down procedures to be followed in the case of non-compliance;
- Define the management structure for the network.

Accreditation of laboratories

Currently QA/QC programmes only exist in a few monitoring networks of the EC Member States and with a variable degree of efficiency. Particular comparison tests are required to assure the quality of the measurements and capability of the laboratories.

Different standardized QA/QC systems have been developed in recent years such as the Good Laboratory Practice (OECD), the ISO 9000 and the EN 45000 laboratory accreditation procedures. The EN 45001 procedure was developed by CEN in collaboration with the Commission and is best adapted for testing laboratories in the field of air pollution measurements. Nowadays the ISO 17025 has been produced as the result of extensively experience of the implementation of ISO/IEC Guide 25 : 1990 and EN450001:1989 both which it now replaces. It contains all of the requirements that testing and calibration laboratories have to meet if they wish to demonstrate that they operate a quality system, are technically competent and are able to generate technically valid results [122].

Accredited laboratories ensure to meet management and technical requirements as:

- Qualified and experienced personal.
- Adapted infrastructure and measurement environment.
- Calibrated instruments.
- Apropriated methods for preparation and storage.
- Technical and scientific methods.
- Validated test results.
- Accurate registration and reporting proceedings.
- An adequate quality system which is alert for corrective and preventive actions.
- Validation of the measurement methods and standardization at CEN or ISO level.
- Certification of equipment: test of instrument performances (the development of a standardised CEN-test procedure is therefore urgently needed). The EN 12341 is an example of a test procedure.
- Organisation of intercomparison at EC level; organisation by the Commission of EC wide Intercomparison exercises (round robin tests, inter-laboratory exercises, spot checks in the monitoring network) to ensure comparability of the measurements at international level.
- Publication by the Commission of guidance documents, organisation of training and workshops.

The quality system in the networks must have clear and detailed operational manuals and guide books on:

- site operation;
- quality assurance/quality control on samplers and analytical equipment;
- data handling;
- training, workshops, information exchange/technology transfer.

Laboratories asking for accreditation are audited by national or an international accreditation organisation. The audit mainly concerns aspects such as laboratory installation and equipment, qualification and training of personnel, proper quality control, technical audit and traceability of the measurements.

The Group recommends that laboratories involved in monitoring and analysis should be accredited in accordance with the procedures of EN 45001 and future procedures as ISO/TEC 17025 [122].

Other recommendations:

1. A compliance test programme should be carried out for each type of sampling and measurement system, when the reference method or an already tested equivalence method is not being used.
2. Quality control procedures should be organized.
3. The quality control procedure should be applied to all sites within a network.
4. A quality assurance procedure should be set up for each network to ensure that the quality control procedures being carried out within the network are effective.
5. The quality assurance procedure should include practical checks of the performance of samplers and analytical instruments both within laboratories and between laboratories. The central laboratory can achieve this by carrying out random checks on the volume sampled and by circulating certified reference material or by intercomparison tests.
6. Parallel measurements using the reference and candidate methods should be carried out and the data evaluated as follows:
   - Carry out a linear regression analysis of the data obtained from the candidate and reference systems
   - Acceptance of a particular candidate system should be based on the correlation coefficient obtained from linear regression analysis of the results from the candidate system and the reference method system and on the level of agreement between the results from the two systems.
7. A test method how to demonstrate equivalence of measurement methods with the reference method is clearly needed and should be described either at CEN level or as guidance document by the EC.

3.5.1 Data Quality Objectives

Data treatment

The arsenic, cadmium and nickel mass concentrations are calculated by dividing the filter mass loading by the pertinent total flow during the sampling time. The arsenic, cadmium and nickel concentrations shall be expressed under real pressure and temperature conditions with respect to the ambient air conditions in the environment.

Data evaluation and uncertainty assessment

When the measurements have been carried out, the relevant statistical quantities (annual average) for which limit values are defined, are to be estimated. Particularly for short measuring periods, this introduces major uncertainties. To our knowledge, no generally accepted methodology is available; we introduce here some important aspects only.

When estimating these concentration statistics from the measurements, the following aspects should be considered:

- Meteorological variability,
- Empirical relations for various emission situations,
- Correction for uncertainty of measurements.

Van der Wiel et al. (1988) discuss the impact of measurement uncertainty on concentration statistics [124]. The variations related to measuring imprecision introduce upward shifts in the percentiles, which become increasingly important for higher percentiles. The reliability of this procedure is dependent on the size of the data basis; as, in some cases with rarely occurring high concentrations, as for example around point sources, the correction may result in even larger errors. More evaluation is needed [124].

- Uncertainty of individual measurements

The uncertainty of measurements in field conditions depends on:

- The performances of the measurement system (sampling, calibration, analysis);
- The expertise of the laboratory responsible for the measurements or, in practice, the quality system implemented by the laboratory;
- The spatial representativeness of the selected measurement locations.

Standard testing procedures should be established to determine the uncertainty of the measurements by a given instrument in laboratory and field conditions, in particular for type approval of the instrumentation. It is however far more difficult to estimate the measurement uncertainty in routine field conditions. This estimation can only be performed experimentally by submitting the measurement system to quality control in field conditions over a longer period of time (typically 3 months).

Concerning the spatial representativeness of the measurement location, a wrong location will undoubtedly lead to an underestimation of the true concentration, as the measurement strategy is aimed at the measurement of the highest concentrations. In practice however, it will be impossible to estimate the extent of the associated uncertainty. It is therefore proposed not to consider this element in the uncertainty estimation, but to require a detailed report on the siting criteria.

The regular organisation of quality controls during the measurement period constitutes therefore the only way to contain the uncertainty of the measurements within the established limits and to document the quality of the determinations.

Depending on the assessment method that is to be implemented, data quality objectives must be established in order to comply with the monitoring objectives. They will be defined in terms of required precision and uncertainty, minimum time coverage and minimum data capture. The precision and uncertainty are expressed as maximum uncertainty on the basis of the results of the arsenic, cadmium and nickel compounds.

Required precision and uncertainty (expressed as maximum uncertainty):

- Mandatory measurements at fixed sites (24 h samples): 25 % for cadmium (target value for individual measurements), 40 % for arsenic and nickel
- Indicative measurements: 50 % (target value for individual measurements)
- Modelling: 50 % (for yearly averages)
- Objective estimation: 100 %

Minimum time coverage of the measurements has been considered in chapter 3.2.3:

- Mandatory measurements at fixed sites: 75 % for cadmium at industrial sites, 50 % for cadmium at urban background sites and for arsenic and nickel at all sites.
- Indicative sampling: 14 % (once per week or 8 weeks evenly distributed over the year, or at random throughout the year) for arsenic, nickel at all sites and cadmium at urban background sites, 33 % for cadmium at industrial sites.

Minimum data capture:

- Mandatory measurements: 90 % (breakdown allowed for 36 days per year)
- Indicative measurements: 90 % (breakdown allowed during 10% of the time)

The proposals of the Working Group are summarized in table 3.5.1:

Table 3.5.1: Data Quality Objectives

Case	Technique	Time coverage	Uncertainty
Areas above x% of the limit value	Fixed measurements; Supplementary modelling recommended	50 % 75 % (Cd at industr. sites)	25 % (Cd) 40 % (As, Ni)
Between x% and y% of the limit value	Indicative measurements and Modelling	33 % 14 %	*50 %
Below y% of the limit value	Objective estimations and Modelling	---	*100 %

**Data-objectives according the Pb position paper [121].*

3.5.2 Maintenance And Calibration

The importance of proper maintenance procedures cannot be overemphasized. It is only through proper instrument support that equipment can be relied upon to operate satisfactorily and for extended periods in the field. Maintenance schedules for the replacement of consumable parts, diagnostic checks and equipment overhaul should in all cases follow manufacturers recommendations.

Proper calibration of equipment is essential for obtaining accurate and reproducible air quality data. The following points relate specifically to particulate samplers [18]. It is impossible to calibrate a particulate sampler by passing through ambient particulate mixtures into the inlet and comparing to a measured value. Thus, QA/QC procedures focus on flow rate measurements and intercomparability. Flow rate audits should be conducted 2-4 times per year.

The mass-measurement process also needs to be checked. QA/QC procedures need to be established for the laboratory analysis of filters. The method should be validated according to ISO8466.

3.6 Reporting Of The Results

The directive on ambient air quality assessment and management (framework directive [1]) ranks the adequate information of the public within its main objectives (article 1). Consequently, the first daughter directive [2] contains in article 8 detailed requirements for public information [2], which apply in principle also to other air pollutants such as metal and metalloid compounds. However, there are some important differences to be taken into account. Whereas the first daughter directive has limit values with short time scales (hours to daily means) and even alert thresholds which make up-to-date information a necessity, the proposed limit values in this document refer to annual means. In addition, there will often be considerable time delays between sampling and analysis, which has to be performed off line in the laboratory. An up-to-date information on a daily basis will therefore be neither necessary nor possible. In principle, annual reporting of the annual means to the public and appropriate organisations should be sufficient, combined with an indication of any exceedances and an assessment in relation to the limit values and information on the health effects of the pollutant inquestion. This report should also contain the background levels which are reported to the EMEP network. However, to inform the public and relevant organisations comprehensively on possible hazards of long term exposure to arsenic, cadmium and nickel compounds, and to rise public awareness, it is recommended by the Working Group to issue short reports on a three monthly basis by the Member States. These reports should publish rolling annual averages, including the most recent data available, and compare them with the limit values. Where appropriate, the reports should be published on a routine basis by means of electronic media.

3.7 Summary Of Key Points, Chapter 3

Chapter 3 deals with assessment methods such as mandatory measurements including network design, indicative monitoring and modelling, and sets up requirements and data quality objectives for these techniques.

The chapter starts with tailoring the general assessment requirements of the framework directive to the specific requirements for arsenic, nickel and cadmium compounds. From the results presented in the preceding chapters it can be concluded that (i) the assessment of long term effects (annual means) is sufficient, (ii) that deposition of cadmium should be measured, (iii) that the important micro-environments to be monitored are the urban background and residential and agricultural areas near industrial hot spots.

Network design and the number of monitoring stations for compliance checking in urban background areas by and large correspond to the requirements laid down in the first daughter directive. As there is no specific need to monitor traffic exposed sites, the number of fixed monitoring stations can be reduced (for example from 10 to 8 stations in agglomerations or zones with more than 6 million inhabitants).

For the identification of the relevant industrial hot spots, criteria are given which should be taken into account when setting up monitoring networks. Inter alia, high annual emissions combined with significant shares of fugitive emissions or emissions from low outlets, the results from indicative measurements or modelling, and the exposure of protected interests should be taken into account. Monitors should be placed where long term exposure coincides with the highest pollution burden. Very small micro-environments should be avoided, and it is proposed that the monitoring site should at least be representative for an area of 250 x 250 m². The same criteria for microscale siting as in the first daughter directive are applicable.

Although monitoring of rural and remote sites is not mandatory, as no eco-limits have been proposed, it is recommended to install one background station per 100.000 km² (concentration and deposition). The siting criteria of EMEP should be followed for this station, and the results should mutually be used for the EMEP network and the purposes of this directive.

The most relevant micro-environment for monitoring cadmium deposition are residential and agricultural areas near industrial hot spots. A measurement strategy is outlined in chapter 3 for this case, whereas monitoring in urban background areas can be kept on a low level. It is proposed that deposition limit values should not apply to a single spot, but to small areas of 250 x 250 and 500 x 500 m², respectively.

By two independent statistical methods, the sample size necessary to meet the requirements for mandatory measurements (expanded uncertainty ≤ 10 %) has been calculated using quasi-continuous time series of daily means from 4 Member States (Belgium, Italy, the Netherlands, Germany). Minimum time coverages for random measurements are 75 % (cadmium, industrial sites), 50 % (arsenic, nickel (all sites) and cadmium, urban background), and 14 % for indicative measurements.

Upper and lower assessment thresholds were derived analyzing the interannual variability from 8 time series. For the upper assessment threshold, values of 60 % (arsenic and cadmium concentrations) and 70 % (nickel concentrations) were found, the corresponding percentages for the lower assessment threshold being 40 % and 50 %.

The measurement methods (sampling, digestion and analysis) which are currently applied by the Member States for the monitoring of metal and metalloid compounds in ambient air are described, including a short characterization of their advantages and disadvantages (concentrations and deposition). Some of those methods have been standardized on a national level. For sampling, high-medium- and low volume samplers are used, either with TSP or PM10 sampling head.

Analytical procedures involve atomic absorption spectrometry, inductively coupled plasma spectrometry, atomic fluorescence spectrometry, and X-ray fluorescence. These methods routinely monitor the total content of heavy metals and metalloids in the aerosol.

Methods for species specific analysis are still in the stage of research and development and cannot be recommended for routine monitoring. As(III) has been separated from As(V), and some nickel compounds have been analyzed by selective and sequential extraction. No methods have been applied for cadmium in ambient air so far. The Working Group recommends to launch additional research programs for species specific measurement methods.

Several types of cylindrical deposit gauges are available to measure the bulk deposition of cadmium, and several types of samplers for wet deposition. Standard deviations of about 25 % or better can be achieved according to intercomparison tests.

CEN TC 264/WG14 is currently establishing a reference method for the determination of lead, cadmium, arsenic and nickel in ambient air. Until this standard will be available, the Working Group proposes to use as provisional reference method a sampler for PM10 as described in EN 12341, a filter with a very low metal content, a complete digestion of the particles, and the atomic absorption spectrometry for analysis. This method will be described, among other methods, in the upcoming CEN standard, and allows for the determination of lead together with the other elements. Any other method which can be demonstrated to be equivalent can be used by the Member States. The data shall be expressed under real pressure and temperature conditions.

Chapter 3 gives guidance for the quality assurance of the data. The required uncertainty for mandatory measurements is proposed to be 25 % for cadmium, 40 % for arsenic and nickel, and 50 % for indicative measurements and modelling. The minimum data capture should be 90 %.

Annual reporting of the data is sufficient, but to inform the public comprehensively, three monthly reports on a routine basis are recommended. Where appropriate, electronic media should be used.

For the various scales to be considered (microscale, mesoscale and long range transport), the corresponding dispersion models currently applied in Europe are shortly characterized, together with known advantages and disadvantages. For gaseous compounds, prognostic and diagnostic models can reach under ideal conditions an uncertainty of ± 20 - 30 % for annual averages, under condition that reliable emission inventories and meteorological input data are used. For long range models, typical uncertainties range around a factor of 2. However, for particulate matter and their components, additional uncertainties as particle size distributions, interaction with surfaces, deposition fluxes or resuspension will deteriorate this attainable uncertainty considerably. In addition, only some models take into account wet deposition. For the calculation of long range transport (1000 km and above), different long range transport models for heavy metals have been developed and some of them are applied in the framework of EMEP. The advantages and disadvantages of the models are discussed.

3.8 Literature To Chapter 3

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ANNEX A

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ANNEX B

Table 1: Annual emissions of heavy metals in the 15 Member States per source category in 1990 (t/a)

Branch	SNAP 90	As	Cd	Ni
Total	*0*	*575*	*203*	*4860*
Stationary combustion	**01+02+03**	**492**	**58.3**	**2860**
Publ. power, cogeneration & district heating	**10000**	**277**	**19.4**	**1760**
Public power etc. brown coal	01bc	20.2	3.42	24
Public power etc. hard coal	01hc	130	4.42	94.4
Public power etc. fuel oils	01fo	117	10.2	1560
Public power etc other fuels	01of	9.73	1.06	3.05
Comm. instit. & residential combustion	**20000**	**37.8**	**10.1**	**130**
Commercial etc. brown coal	02bc	2.0	0.483	15.5
Commercial etc.hard coal	02hc	23.4	1.39	38.4
Commercial etc. fuel oils	02fo	9.46	2.35	73
Commercial etc. other fuels	02of	2.82	5.91	1.94
Industrial combustion	**30000**	**177**	**28.7**	**973**
Industrial combustion brown coal	03bc	65.6	8.95	80.7
Industrial combustion hard coal	03hc	52.3	1.58	69.7
Industrial combustion fuel oils	03fo	50.6	12	805
Industrial combustion other fuels	03of	8.72	6.07	14.8
Production processes	**40000**	**77.3**	**78.4**	**202**
Petroleum industries	40100	-	-	1.0
Iron & steel industry	40200	35.1	39.5	143
Coke production	40201	1.68	2.89	3.79
Blast furnace	40202	16.4	1.13	18.5
Pig iron	40203	0.17	0.512	0.283
Open hearth furnace	40205	-	2	-
Basic oxygen furnace	40206	1.64	2.18	5.33
Electric arc furnace	40207	10.9	25.9	87.5
Rolling	40208	-	-	-
Sinter plants	40209	4.01	4.66	26.8
Foundries	0402xx	0.28	0.18	0.51

Table 1 (cont.): Annual emissions of heavy metals in the 15 Member States per source category in 1990 (t/a)

Branch	SNAP 90	As	Cd	Ni
Non-ferrous metal industry	40300	**31.5**	**34.2**	**13.3**
Al industry	40301	0.303	0.412	12.5
Cu industry	0403cu	6.85	1.77	0.122
Ni industry	0403ni	-	-	-
Other non-ferrous industry	0403ot	-	-	-
Pb industry	0403pb	9.34	7.55	-
Zn industry	0403zn	-	19.1	-
NPK fertilizers	40407		0.738	0.066
Chloro-alkali industry	40413	-	-	-
Organic chemical industry	40500	-	-	-
Halogenated HC production	40524	-	-	-
Pesticide production	40525	-	-	-
Paper pulp (Kraft process)	40602	-	-	-
Paper and pulp industry	04060x	-	-	-
Road paving with asphalt	40611	-	-	-
Cement industry	40612	3.83	1.79	19.9
Glass industry	40613	6.96	0.548	10.4
Battery manufacturing	40615		0.001	
Synthetic grit blasting	0406xx	-	-	-
Extraction & distribution of fossil fuels	**50000**	**0.541**	**0.012**	**0.734**
Solvent use	**60000**	**-**	**0.332**	**-**
Paint use	60100	-	-	-
Industrial degreasing	60201	-	-	-
Dry cleaning	60202	-	-	-
Other solvent use	0603&4	-	0.332	-
Wood preservation	60406	-	-	-
Road transport	**70000**	**-**	**36.6**	**285**
Road transport combustion	0701-5	-	33.6	270
Road transport non-combustion	0706/7	-	2.75	9.06
Other mobile sources & machinery	**80000**	**1.653**	**7.9**	**1480**
Other transport combustion	08comb	1.65	7.9	1480
Other transport non-combustion	0802nc	-	-	-

Table 1 (cont.): Annual emissions of heavy metals in the 15 Member States per source category in 1990 (t/a)

Branch	SNAP 90	As	Cd	Ni
Waste treatment & disposal	**90000**	**2.56**	**16.1**	**27.3**
Waste incineration	90200	2.56	16.1	27.3
Landfill	90400	-	-	-
Cremation	90900	-	0.01	-
Hg thermometers and vapour lamps	09xxxx	-	-	-
Agriculture	**10000**	**0.05**	**5.21**	-
Pesticide use	10600	-	-	-
Nature	**11000**	-	-	-
Electrical equipment	**eel**	-	-	-

Table 2: Cd emissions in Europe according to UN/ECE report [t/a]

Country	UN/ECE reported official emission data (April 1999)							
	1990	1991	1992	1993	1994	1995	1996	1997off
Austria	3.09					1.79		
Belgium	9.52	3	4	1	4.4	6.38	4.62	5.62
Denmark					1.16	1.12	1.09	0.87
Finland	6.1	2.5	2.2	3.0	2.7	2.5	1	0.6
France	15.4	15.8	15.2	14.7	14.3	13.3	13.1	
Germany	30					11		
Greece							3	
Ireland								0.9*
Italy	53.79				29.90			
Luxembourg					0.532	0.382	0.368	
Netherlands	2.38	2.33	2.33	1.84	1.68	1.51	1.83	1.82
Portugal								2.4
Spain	36.7							
Sweden	2		1.3		0.7	0.8		
United Kingdom	25.4	24.9	25.7	25.5	24.2	15	14.5	15.1

* Expert estimates of J. Pacyna (see MSC-E report, [62, chapter 1]

Table 3: Annual emissions of Cd in Austria [t/a]

Sector	Cd [t/a]
Combustion in energy and transformation industries	0.39
Non-industrial combustion plants	0.76
Combustion in manufacturing industry	0.25
Production processes	0.22
Road transport	0.08
Other mobile sources and machinery	< 0.01
Waste treatment and disposal	0.04
Agriculture	0.05
Other sources and sinks	< 0.01
Total	1.79

Table 4: Annual emissions of heavy metals in Denmark in 1997 [t/a] (According to SNAP 97)

Source Sectors	As	Cd	Ni
Combustion in energy and transformation industry	0.435	0.316	8.782
Non-industrial combustion plants	0.127	0.229	2.685
Combustion in manufacturing industry	0.267	0.215	9.397
Production processes	0	0.060	0.228
Road transport	0	0.033	0.235
Other mobile sources and machinery	0.032	0.012	0.965
Total	0.861	0.866	22.29

Table 5: Annual emissions of heavy metals in Finland in 1997 [t/a]

Branch	As	Cd	Ni
Energy production	0.911	0.349	9.391
Industry (fuels)	1.604	0.423	9.918
Industry (processes)	9.750	0.337	8.795
Mobile sources	n.a.	n.a.	n.a.
Waste management	0.002	0.002	0.001
Total	12.27	1.11	28.11

Table 6: Annual emissions of heavy metals in Flanders in 1997 [t/a]

Branch	As	Cd	Ni
Electricity production	0.172	0.007	0.303
Steel	0	0.285	1.583
Non-ferro	1.291	1.658	0.321
Production of glass material	0	0.317	0.051
Refinery	0.016	0	26.168
Incineration industrial waste	0.013	0.003	0
Incineration waste	0	0	0.014
Chemical industry	0	0	1.106
Traffic	0	0.052	0.365
Machinery; electrotechn. industry	0	0	0.119
Total	1.492	2.322	30.03

Table 7: Annual emissions of heavy metals in France in 1996 [t/a]

Branch	As	Cd	Ni
Combustion in energy and transformation industries	1.5	0.2	107.9
Non-industrial combustion plants	0.1	2	11.2
Combustion in manufacturing industry	16.3	3.7	97
Production processes	1.3	2.1	9.4
Road transport	0	0.4	2.7
Other mobile sources and machinery	0	0	0.8
Waste treatment and disposal	0.5	4.7	2.9
Total	19.7	13.1	231.9

Table 8: Annual emissions of heavy metals in Germany per source category in 1995 (t/a)

Branch	SNAP 90	As	Cd	Ni
Total	*0*	*33*	*11*	*159*
Stationary combustion	**01+02+03**	**21.0**	**3.0**	**139.5**
Publ. power, cogeneration & district heating	**10000**	**10.4**	**1.72**	**46.6**
Public power etc. brown coal	01bc	6.3	0.99	7.7
Public power etc. hard coal	01hc	3.7	0.4	3.4
Public power etc. fuel oils	01fo	0.4	0.03	34.7
Public power etc. other fuels	01of	0.1	0.3	0.8
Comm. instit. & residential combustion	**20000**	**2.4**	**0.5**	**14.0**
Commercial etc. brown coal	02bc	1.1		8.2
Commercial etc. hard coal	02hc	1.3		2.4
Commercial etc. fuel oils	02fo	-		3.4
Commercial etc. other fuels	02of	-		-
Industrial combustion	**30000**	**8.2**	**0.78**	**78.9**
Industrial combustion brown coal	03bc	5.1	0.71	6.2
Industrial combustion hard coal	03hc	2.3	-	3.2
Industrial combustion fuel oils	03fo	0.8	0.07	69.5
Industrial combustion other fuels	03of	-	-	-
Production processes	**40000**	**12.6**	**7.754**	**20.2**
Petroleum industries	40100	-	-	-
Iron & steel industry	40200	2.9	5.11	15.3
Coke production	40201	0.1	0.26	0.35
Blast furnace	40202	1.7	0.14	4.2
Pig iron	40203	-	-	-
Open hearth furnace	40205	-	-	-
Basic oxygen furnace	40206	0.07	0.56	1.5
Electric arc furnace	40207	0.35	2.93	3.8
Rolling	40208	-	-	-
Sinter plants	40209	0.6	1.1	5.3
Foundries	0402xx	0.08	0.12	0.15

Table 8 (cont.): Annual emissions of heavy metals in Germany per source category in 1995 (t/a **)**

Branch	SNAP 90	As	Cd	Ni
Non-ferrous metal industry	40300	**5**	**2.3**	**-**
Al industry	40301			-
Cu industry	0403cu			-
Ni industry	0403ni			-
Other non-ferrous industry	0403ot			-
Pb industry	0403pb			-
Zn industry	0403zn			-
NPK fertilisers	40407	-	-	-
Chloro-alkali industry	40413	-	-	-
Organic chemical industry	40500	-	-	-
Halogenated HC production	40524	-	-	-
Pesticide production	40525	-	-	-
Paper pulp (Kraft process)	40602	-	-	-
Paper and pulp industry	04060x	-	-	-
Road paving with asphalt	40611	-	-	-
Cement industry	40612	0.3	0.164	2.5
Glass industry	40613	4.4	0.18	2.4
Battery manufacturing	40615		-	
Synthetic grit blasting	0406xx	-	-	-
Extraction & distribution of fossil fuels	**50000**	**-**	**-**	**-**
Solvent use	**60000**	-	**-**	-
Paint use	60100	-	-	-
Industrial degreasing	60201	-	-	-
Dry cleaning	60202	-	-	-
Other solvent use	0603&4	-	-	-
Wood preservation	60406	-	-	-
Road transport	**70000**	-	**n. a.**	**n. a.**
Road transport combustion	0701-5	-	-	n. a.
Road transport non-combustion	0706/7	-	n. a.	n. a.
Other mobile sources & machinery	**80000**	**n. a.**	**n. a.**	**n. a.**
Other transport combustion	08comb	n. a.	n. a.	n. a.
Other transport non-combustion	0802nc	-	-	-

Table 8 (cont.): Annual emissions of heavy metals in Germany per source category in 1995 (t/a **)**

Branch	SNAP 90	As	Cd	Ni
Waste treatment & disposal	**90000**	**-**	**n. a.**	**-**
Waste incineration	90200	-		-
Landfill	90400	-	-	-
Cremation	90900	-	n. a.	-
Hg thermometers and vapour lamps	09xxxx	-	-	-
Agriculture	**10000**	**n. a.**	-	-
Pesticide use	10600	-	-	-
Nature	**11000**	-	-	-
Electrical equipment	**eel**	-	-	-

Table 9: Annual emissions of heavy metals in Italy in 1994 [t/a]

Branch	As	Cd	Ni
Combustion in energy and transformation industries	2.9	2.7	304.4
Non-industrial combustion plants	0.5	1	25.6
Combustion in manufacturing industry	32.6	22.1	129.2
Production processes	1	2.7	2.4
Road transport	0	0.3	2.2
Other mobil sources and machinery	1	0.4	67.8
Waste treatment and disposal	0.2	0.7	8.4
Total	38.1	29.9	540

Table 10: Annual emissions of heavy metals in Luxemburg in 1997 [t/a]]

Branch	As	Cd	Ni
Public power, cogeneration & district heating	0	0.004	0.005
Comm. instit. & residential combustion plants	0.016	0.023	0.238
Industrial combustion plants and processes with combustion	0.897	0.248	1.133
Non combustion processes	0.066	0.022	0.144
Road transport	0	0.004	0.028
Other transport	0.007	0	0.003
Waste treatment & disposal	0.004	0	0
Total	0.99	0.301	1.551

Table 11: Annual emissions of heavy metals in The Netherlands in 1997 by source category according to the CORINAIR-97 definitions [t/a]

Source Category	As	Cd	Ni
Combustion in energy and transformation industries			
Public power	0.00873	0.00303	0.503
Petroleum refining plants	0.131	0.128	72.6
Coal mining, oil/gas extraction, pipeline compressors	0.0000067	0.0000067	0.00374
Non-industrial combustion plants			
Commercial and institutional plants (1)	0.00246	0.00211	1.17
Residential plants	0.015	0.001	0.362
Plants in agruculture, forestry and aquaculture	0.00424	0.000807	0.403
Combustion in manufacturing industry			
Comb. in boilers, gas turbines and stationary engines	0.0153	0.00532	3.41
Processes with contact	0.0205	0.0465	0.0071
Production processes			
Processes in iron and steel industries and collierries	0.551	1.04	1.21
Processes in non-ferrous metal industries	0.239	0.195	0.444
Processes in inorganic chemical industries	0	0.232	0.205
Processes in organic chemical industr. (bulk production)	0	0.00199	0.000944
Processes in wood, paper pulp, food, drink and other industries	0.000764	0.000185	0.216
Extraction and distribution of fossil fuels and geothermal energy			
Liquid fuel distribution (except gasoline distribution)	0.0000017	0.0000018	0.000976
Solvent and other product use			
Chemical products manufacturing or processing	0	0.0109	0.0074

Table 11 (cont.): Annual emissions of heavy metals in The Netherlands in 1997 by source category according to the CORINAIR-97 definitions [t/a]

Source Category	As	Cd	Ni
Road transport			
Passenger cars (r)	0.0971	0.0154	0.0782
Light duty vehicles < 3,5 t (r)	0.0114	0.00181	0.0108
Heavy duty vehicles > 3,5 t and buses (r)	0.00878	0.00138	0.0264
Mopeds and motorcycles < 50 cm³	0.000436	0.0000693	0.00036
Motorcycles > 50 cm³	0.000821	0.000131	0.00092
Automobile type and brake water	0.0186	0.0307	1.22
Other mobile sources and machinery			
Railways	0	0	0.000296
Inland waterways	0	0	0.0111
Maritime activites	0.0107	0.00431	8.24
Agriculture	0	0	0.00382
Other off-road	0	0	0.00263
Waste treatment and disposal			
Waste incineration	0.0659	0.106	0.0719
Other waste treatment	0.0000292	0.0000775	0.0164

Table 12: Annual emissions of heavy metals in Sweden in 1995 [t/a]

Branch	As	Cd	Ni
Mining	0.09	0.02	0.45
Glass industry	0.02	0.01	0
Cement industry	0	0.001	0
Refineries	0	0.03	0.82
Iron and steel	0	0.13	8.00
Non-ferrous metals	0.78	0.17	0.01
Casting	0	0	0.11
Engineering industry	0	0.005	0.02
Waste incineration	0	0.008	0
District heating	0.19	0.06	6.60
Combustion of that industry	0.13	0.15	13.00
Dwellings	0.09	0.18	3.30
Total	1.30	0.76	32.31

Table 13: Annual Emissions of heavy metals in the United Kingdom in 1996

	As	Cd	Ni
Comb in Energy Prod & Trans	7	4.7	128
Comb in Comm/Inst/Res/Agri			
Domestic	12	0.4	16
Other	2.7	0.1	35
Combustion in Industry			
Treated Wood	9	-	-
Iron & Steel	0.7	0.5	7
Other Combustion in Industry	13	0.4	92
Non-Ferrous Metals	3.2	7.0	0
Cement	0.1	0.2	1
Glass Production	0.8	0.3	5
Production Processes			
Processes in Industry	0.0	0.3	2
Iron & Steel	1.8	1.9	4
Extr./Distrib. of Fossil Fuels	0.0	0.0	0
Road Transport	0.0	0.5	0
Other Transp. & Mach.	0.0	0.0	0
Waste Treatment & Disp.	0.3	2.6	1
Total	50.5	18.9	291

ANNEX C

Table 14: Monitoring sites included in the EMEP data base on Cd for 1996, 1997

Country	Station	Station name	Location		Height above
	Codes		Lat.	Long.	sea level (m)
Czech Rep.	CS1	Svratouch	40°44’N	16°02’E	737
	CS3	Kosetice	49°35’N	15°05’E	633
Denmark	DK31	Ulborg	56°17’N	8°26’E	10
Estonia	EE9	Lahemaa	59°3’N	25°54’E	32
	EE11	Vilsandi	58°23’N	21°49’E	6
Finland	FI9	Uto	59°47’N	21°23’E	7
	FI17	Virolahti II	60°31’N	27°41’E	4
	FI53	Hailuoto	65°00’N	24°41’E	4
	FI92	Hietajarvi	63°10’N	30°43’E	173
	FI93	Kotinen	61°14’N	25°04’E	158
	FI94	Pesosjarvi	66°18’N	29°30’E	257
	FI95	Yuoskojarvi	69°44’N	26°57’E	147
	FI96	Pallas	67°58’N	24°7’E	566
Germany	DE1	Westerland	54°55’N	8°18’E	12
	DE2	Langenbrugge	52°48’N	10°45’E	74
	DE3	Schauinsland	47°55’N	7°54’E	1205
	DE4	Deuselbach	49°46’N	7°03’E	480
	DE5	Brotjacklriegel	48°49’N	13°13’E	1016
	DE7	Neuglobsow	53°09’N	13°02’E	62
	DE8	Schmucke	50°39’N	10°46’E	937
	DE9	Zingst	54°26’N	12°44’E	1
Iceland	IS2	Irafoss	64°05’N	21°01’W	61
	IS90	Reykjavik	64°08’N	21°54’W	61
	IS91	Sturhofdi	63°24’N	20°17’W	118
Ireland	IE1	Valentia Observatory	51°56’N	10°15’W	9
	IE2	Turlough Hill	53°02’N	6°24’W	420
Latvia	LV10	Rucava	56°13’N	21°13’E	18
	LV16	Zoseni	57°08’N	25°55’E	183
Lithuania	LT15	Preila	55°21’N	21°04’E	5

Table 14 (cont.): Monitoring sites included in the EMEP data base on Cd for 1996, 1997

Country	Station Codes	Station name	Location		Height above sea level (m)
			Lat.	Long.	
Norway	NO1	Birkenes	58°23’N	8°15’E	190
	NO30	Jergul	69°24’N	24°36’E	255
	NO39	KÍrvatn	62°47’N	8°53’E	210
	NO41	Osen	61°15’N	11°47’E	440
	NO42	Zeppelinfjell	78°54’N	11°53’E	474
	NO44	Nordmoen	60°16’N	11°06’E	440
	NO47	Svanvik	69°27’N	30°02’E	474
	NO92	Overbygd	69°03’N	19°22’E	90
	NO93	Valdalen	62°05’N	12°10’E	800
	NO94	Mosvatn	59°50’N	8°20’E	940
Norway	NO95	Ualand	58°31’N	6°23’E	220
	NO96	Namsvatn	64°59’N	13°35’E	500
	NO97	Solhomfjell	58°56’N	8°48’E	260
	NO99	Lista	58°06’N	6°34’E	13
Poland	PL4	Leba	54°45’N	17°32’E	157
	PL5	Diabla Gora	54°09’N	22°04’E	157
Portugal	PT1	Braganca	41°49’N	6°46’W	691
	PT3	V. d. Castelo	40°25’N	7°33’W	16
Slovakia	SK2	Chopok	48°56’N	19°35’E	2008
	SK4	Stara Lesna	49°09’N	20°17’E	808
	SK5	Liesek	49°22’N	19°41’E	892
	SK6	Starina	49°03’N	22°16’E	345
	SE5	Bredkalen	63°51’N	15°20’E	404
	SE11	Vavihill	56°01’N	13°09’E	172
	SE12	Aspvreten	58°48’N	17°23’E	20
	SE51	Arup	55°45’N	13°40’E	157
	SE97	GÍrdsjon	58°03’N	12°01’E	113
Turkey	TR1	Cubuk II	40°30’N	33°00’E	1169
United Kingdom	GB14	High Muffles	54°20’N	0°48’W	260
	GB90	East Ruston	52°48’N	1°28’E	5
	GB91	Banchory	57°05’N	2°32’E	120
Yugoslavia	YU5	Kamenicki vis	43°24’N	21°57’E	813
	YU8	Zabljak	43°09’N	19°08’E	1450

The sites codes used are the new EMEP codes introduced in 1992. Stations without standard EMEP codes have been coded with country ISO code and number from 90 and higher. Most of the presented stations carry out measurements of As and Ni as well.

ANNEX D

Resampling of mean values and calculation of variation coefficients of mean values from 30 time series of some member states.

(For the definition of units and symbols compare text of chapter 3.2.3.)

Pollutant:	Arsenic	**vpred =**	**0,05**	**0,10**	**0,15**
Site	**type**	**year**	**N (days)**	**N (days)**	**N (days)**
Hoboken (B)	I	1996	240	119	64
Hoboken (B)	I	1997	164	62	30
Essen (D)	I	1996	180	71	35
Essen (D)	I	1997	171	66	33
average:	**I**		**189**	**80**	**41**
Biest (NL)	U	1998	143	51	24
Bilthoven (NL)	U	1998	143	50	24
Vlaardingen (NL)	U	1998	182	73	36
Wolfsburg (D)	U	1996	302	198	126
Wolfsburg (D)	U	1997	288	177	108
average:	**U**		**212**	**110**	**64**
Kollumerwaard (NL)	R	1998	207	90	46

Pollutant:	Cadmium	**vpred =**	**0,05**	**0,10**	**0,15**
Site	**type**	**year**	**N (days)**	**N (days)**	**N (days)**
Hoboken (B)	I	1996	289	178	108
Hoboken (B)	I	1997	170	65	32
Essen (D)	I	1996	310	214	141
Essen (D)	I	1997	315	223	150
Terni (I)	I	1996	321	235	163
Terni (I)	I	1997	136	47	23
average:	**I**		**257**	**160**	**103**
Biest (NL)	U	1998	144	51	25
Bilthoven (NL)	U	1998	143	51	24
Vlaardingen (NL)	U	1998	185	75	37
Wolfsburg (D)	U	1996	196	82	42
Wolfsburg (D)	U	1997	198	84	43
average:	**U**		**173**	**69**	**34**
Kollumerwaard (NL)	R	1998	222	102	54

Pollutant:	Nickel	**vpred =**	**0,05**	**0,10**	**0,15**
Site	**type**	**year**	**N (days)**	**N (days)**	**N (days)**
Hoboken (B)	I	1996	116	38	18
Hoboken (B)	I	1997	39	11	5
Essen (D)	I	1996	130	44	21
Essen (D)	I	1997	132	45	22
Terni (I)	I	1996	180	71	36
Terni (I)	I	1997	147	53	25
average:	**I**		**124**	**44**	**21**
Wolfsburg (D)	U	1996	114	37	17
Wolfsburg (D)	U	1997	173	67	33
average:	**U**		**144**	**52**	**25**

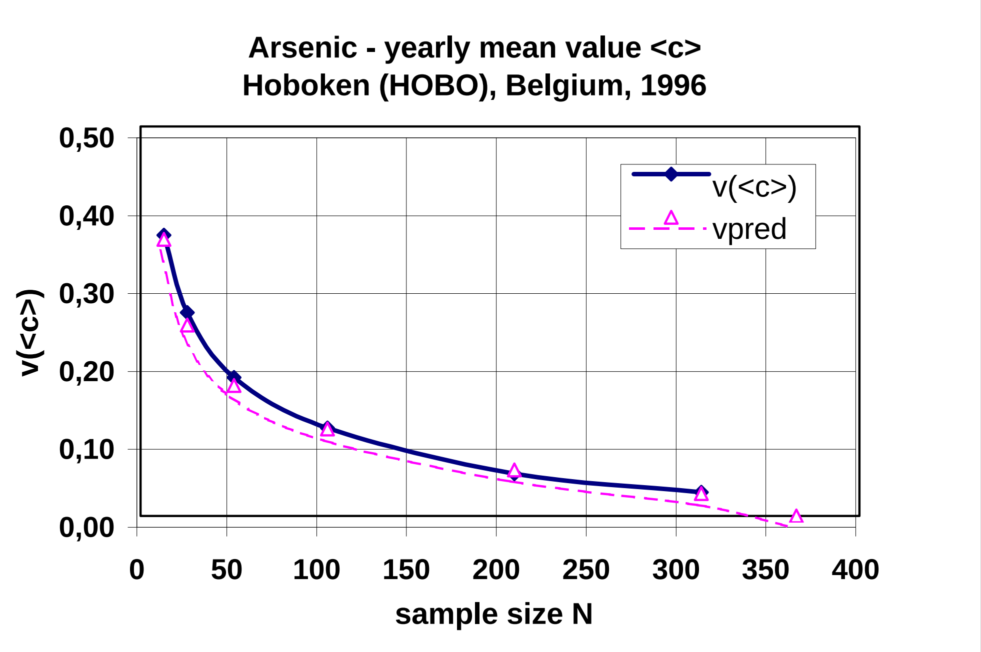
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Hoboken, Belgium**	**units:**	**ng/m³**
poll:	**Arsenic**	**data:**	**1996**

N	<c>	u(<c>)	v(<c>)	vpred
13	1,8	0,66	0,36	0,36
26	1,9	0,48	0,26	0,25
52	1,8	0,33	0,18	0,17
104	1,8	0,20	0,11	0,11
208	1,8	0,10	0,05	0,06
312	1,8	0,06	0,03	0,03
365	1,8			0,00
Nmax:	362		s =	2,4



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	240
0,10	119
0,15	64

Resampling of mean values

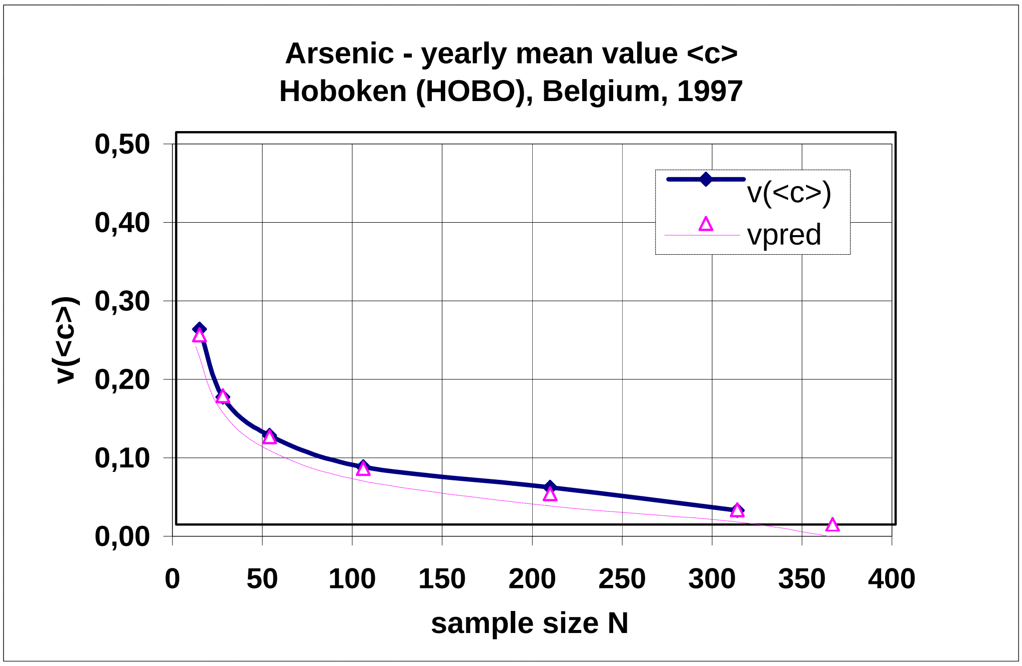
(100 samples of size N without replacement)

N: **sample size** **Nmax:** **maximum sample size available**
<c>: **mean value** **vpred:** **s * SQRT(1/N - 1/365) / <c>**
u(<c>): **standard deviation of the mean value <c>**
v(<c>): **u(<c>) / <c>**

site: **Hoboken, Belgium** **units:** **ng/m³**
poll: **Arsenic** **data:** **1997**

N	<c>	u(<c>)	v(<c>)	vpred
13	3,8	0,95	0,25	0,24
26	3,9	0,64	0,16	0,16
52	3,9	0,44	0,11	0,11
104	4,0	0,29	0,07	0,07
208	3,9	0,19	0,05	0,04
312	3,9	0,07	0,02	0,02
365	3,9			0,00

Nmax: 365 s = 3,4



N = 1 / [(vpred*<c>/s)^2 + 1/365]

vpred	N
0,05	240
0,10	119
0,15	64

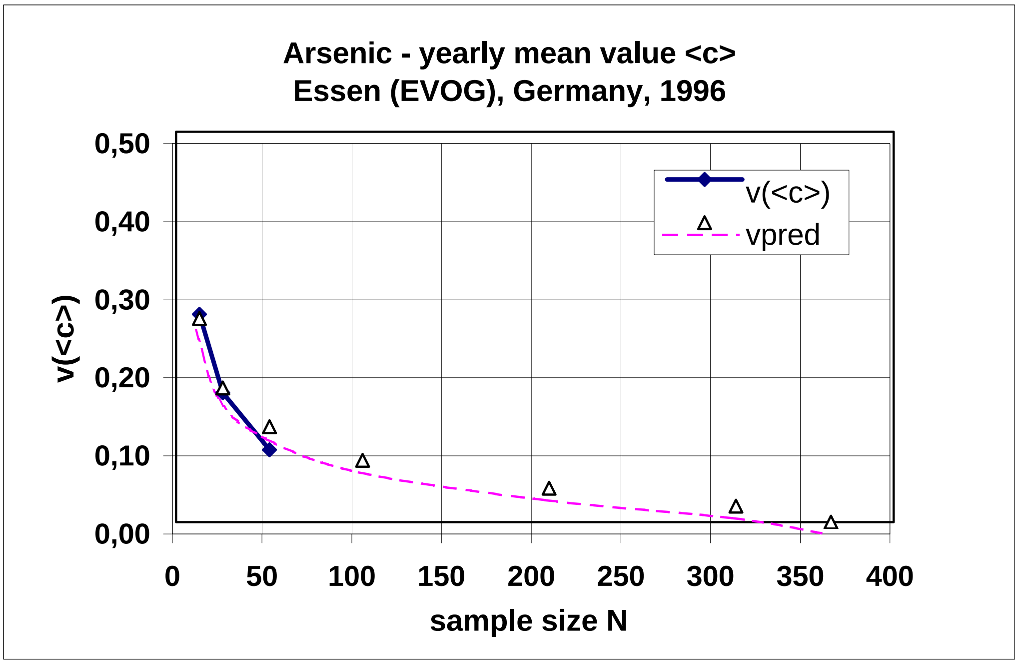
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Essen, Vogelheim, Germany**	**units:**	**ng/m³**
poll:	**Arsenic**	**data:**	**1996**

N	<c>	u(<c>)	v(<c>)	vpred
13	3,1	0,83	0,27	0,26
26	3,3	0,55	0,17	0,17
52	3,2	0,29	0,09	0,12
104	3,2			0,08
208	3,2			0,04
312	3,2			0,02
365	3,2			0,00
Nmax:	100		s =	3



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	180
0,10	71
0,15	35

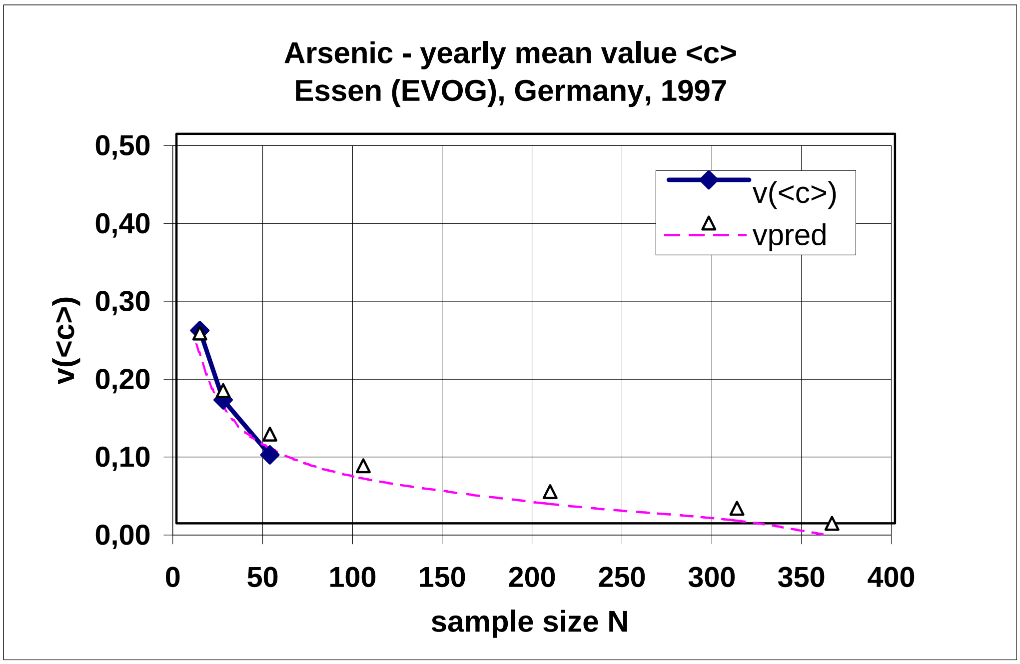
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Essen, Vogelheim, Germany**	**units:**	**ng/m³**
poll:	**Arsenic**	**data:**	**1997**

N	<c>	u(<c>)	v(<c>)	vpred
13	2,1	0,53	0,25	0,24
26	2,1	0,33	0,16	0,17
52	2,1	0,19	0,09	0,11
104	2,1			0,07
208	2,1			0,04
312	2,1			0,02
365	2,1			0,00
Nmax:	94		s =	1,9



N = 1 / [(vpred*<c>/s)^2 + 1/365]

vpred	N
0,05	171
0,10	66
0,15	33

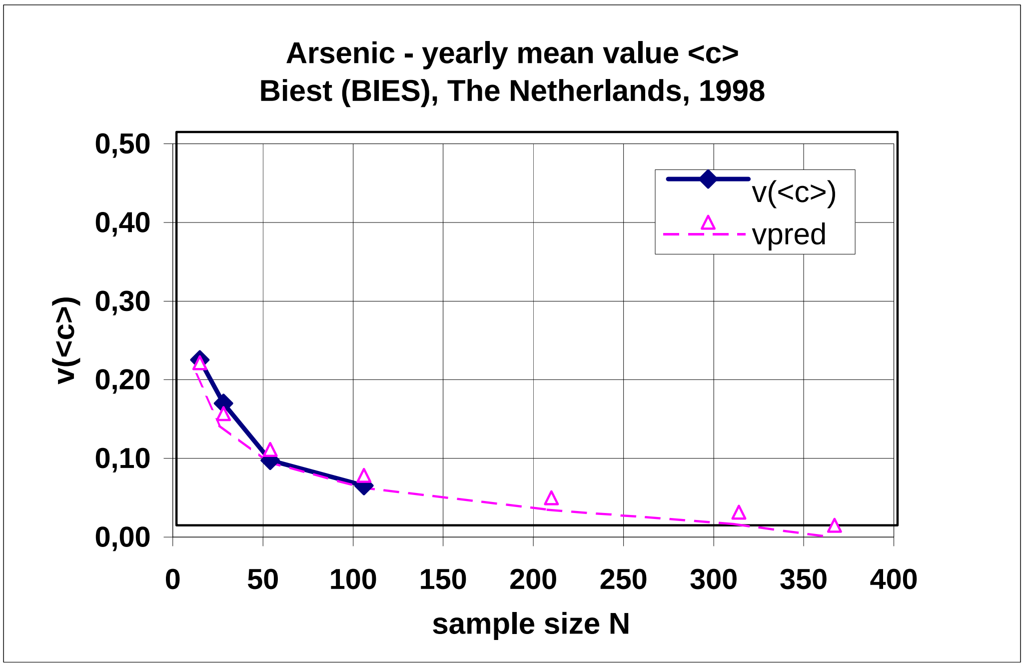
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Biest, The Netherlands**	**units:**	**ng/m³**
poll:	**Arsenic**	**data:**	**1998**

N	<c>	u(<c>)	v(<c>)	vpred
13	1,1	0,23	0,21	0,21
26	1,1	0,17	0,16	0,14
52	1,1	0,09	0,08	0,10
104	1,1	0,05	0,05	0,06
208	1,1			0,03
312	1,1			0,02
365	1,1			0,00
Nmax:	163		s =	0,82



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	143
0,10	51
0,15	24

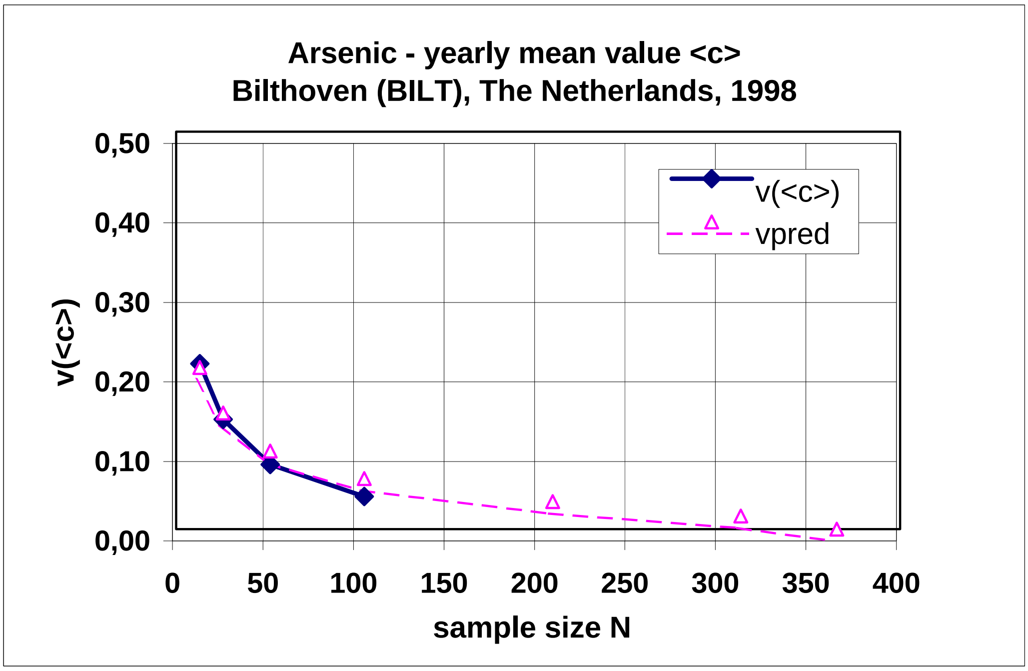
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Bilthoven, The Netherlands**	**units:**	**ng/m³**
poll:	**Arsenic**	**data:**	**1998**

N	<c>	u(<c>)	v(<c>)	vpred
13	0,9	0,18	0,21	0,20
26	0,8	0,12	0,14	0,15
52	0,9	0,07	0,08	0,10
104	0,9	0,04	0,04	0,06
208	0,9			0,03
312	0,9			0,02
365	0,9			0,00
Nmax:	159		s =	0,65



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	143
0,10	50
0,15	24

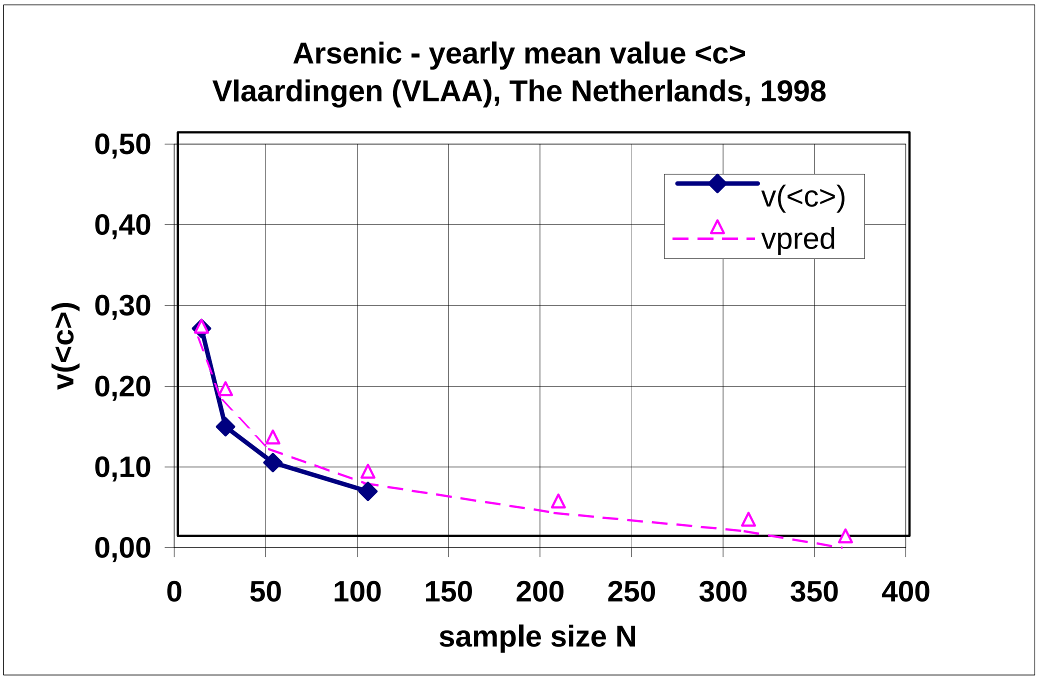
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Vlaardingen, The Netherlands**	**units:**	**ng/m³**
poll:	**Arsenic**	**data:**	**1998**

N	<c>	u(<c>)	v(<c>)	vpred
13	0,9	0,22	0,26	0,26
26	0,9	0,12	0,14	0,18
52	0,9	0,08	0,09	0,12
104	0,9	0,05	0,06	0,08
208	0,9	0,00		0,04
312	0,9			0,02
365	0,9			0,00
Nmax:	161		s =	0,82



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	182
0,10	73
0,15	36

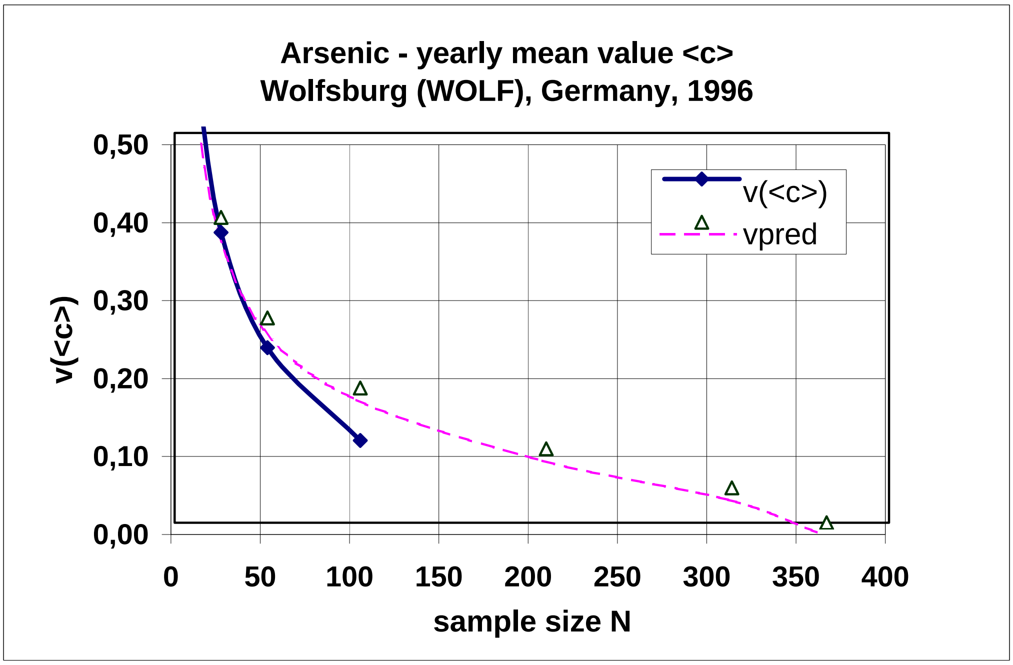
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size**
<c>:	**mean value**	**vpred:**	**s*SQRT(1/N - 1/ 365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>) =	**u(<c>)/<c>**		

site:	**Wolfsburg, Germany**	**units:**	**ng/m³**
poll:	**Arsenic**	**data:**	**1996**

N	<c>	u(<c>)	v(<c>)	vpred
13	1,7	0,96	0,56	0,56
26	1,7	0,63	0,37	0,39
52	1,7	0,38	0,22	0,26
104	1,7	0,18	0,11	0,17
208	1,7			0,09
312	1,7			0,04
365	1,7			0,00
Nmax:	150		s =	3,5



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	302
0,10	198
0,15	126

Resampling of mean values

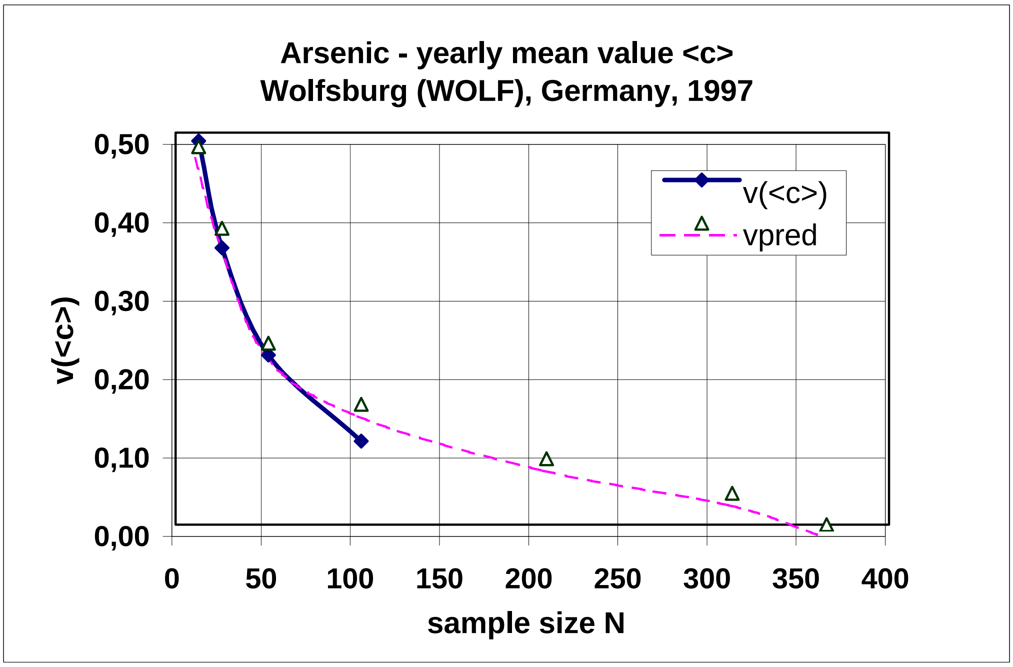
(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size**
<c>:	**mean value**	**vpred:**	**s*SQRT(1/N - 1/ 365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>) =	**u(<c>)/<c>**		

site:	**Wolfsburg, Germany**	**units:**	**ng/m³**
poll:	**Arsenic**	**data:**	**1997**

N	<c>	u(<c>)	v(<c>)	vpred
13	1,1	0,55	0,49	0,48
26	1,0	0,35	0,35	0,38
52	1,1	0,24	0,22	0,23
104	1,1	0,12	0,11	0,15
208	1,1			0,08
312	1,1			0,04
365	1,1			0,00

Nmax: 166 s = 2



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	288
0,10	177
0,15	108

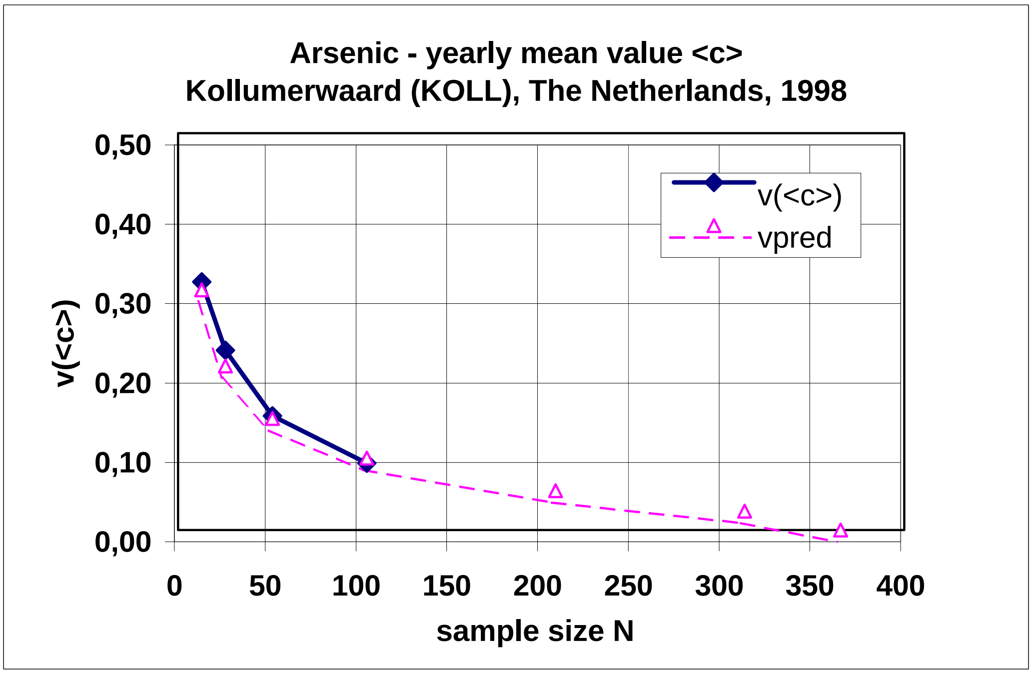
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Kollumerwaard, The Netherlands**	**units:**	**ng/m³**
poll:	**Arsenic**	**data:**	**1998**

N	<c>	u(<c>)	v(<c>)	vpred
13	0,6	0,20	0,31	0,30
26	0,6	0,15	0,23	0,21
52	0,6	0,09	0,14	0,14
104	0,6	0,05	0,08	0,09
208	0,6			0,05
312	0,6			0,02
365	0,6			0,00
Nmax:	182		s =	0,7



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	207
0,10	90
0,15	46

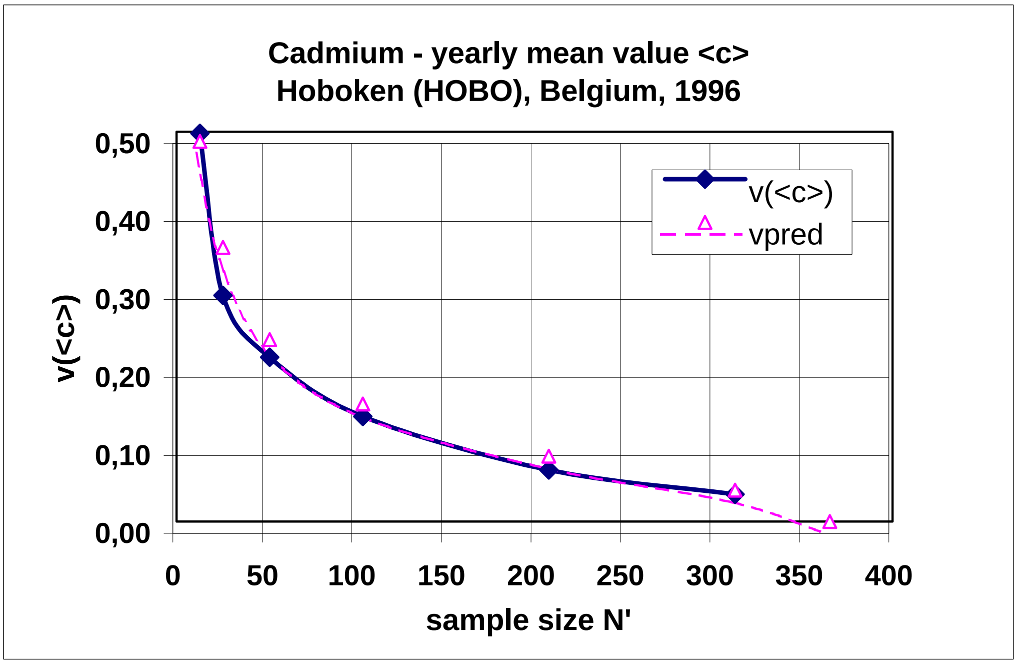
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Hoboken, Belgium**	**units:**	**ng/m³**
poll:	**Cadmium**	**data:**	**1996**

N	<c>	u(<c>)	v(<c>)	vpred
13	1,3	0,67	0,50	0,49
26	1,3	0,37	0,29	0,35
52	1,3	0,28	0,21	0,23
104	1,3	0,18	0,13	0,15
208	1,3	0,09	0,07	0,08
312	1,3	0,05	0,03	0,04
365	1,3			0,00
Nmax:	362		s =	2,4



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	289
0,10	178
0,15	108

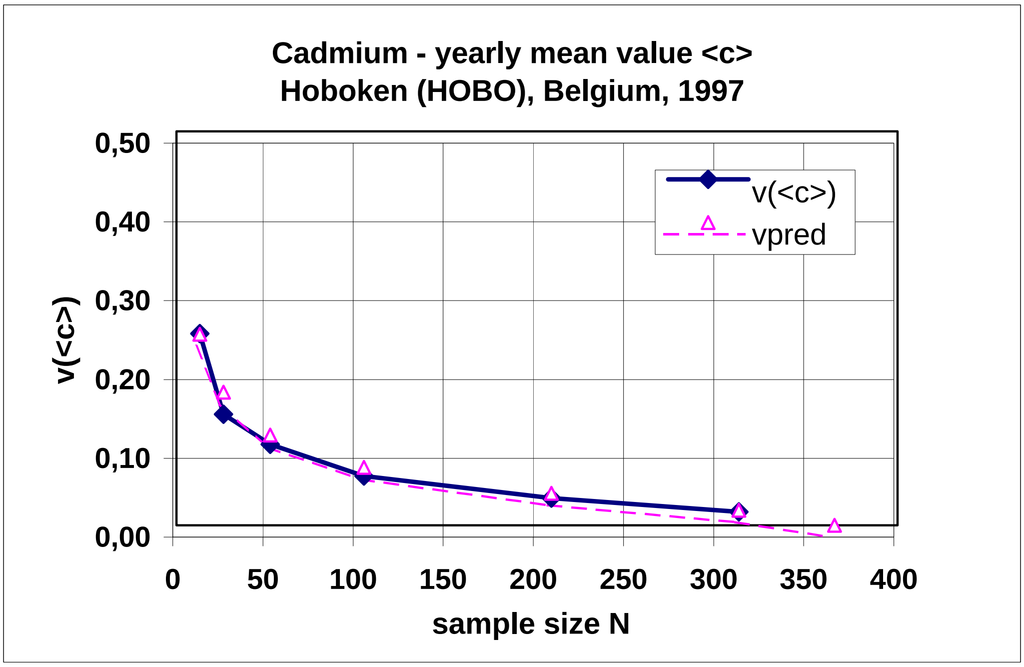
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Hoboken, Belgium**	**units:**	**ng/m³**
poll:	**Cadmium**	**data:**	**1997**

N	<c>	u(<c>)	v(<c>)	vpred
13	2,5	0,60	0,24	0,24
26	2,5	0,35	0,14	0,17
52	2,5	0,25	0,10	0,11
104	2,5	0,16	0,06	0,07
208	2,5	0,09	0,03	0,04
312	2,5	0,04	0,02	0,02
365	2,5			0,00
Nmax:	365		s =	2,2



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	170
0,10	65
0,15	32

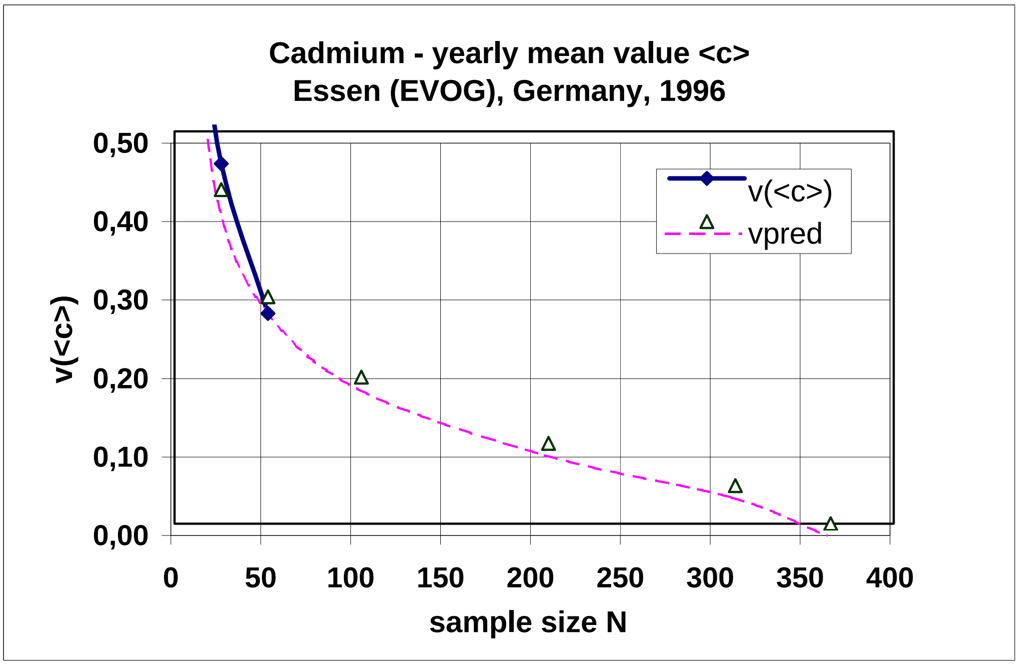
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Essen, Vogelheim, Germany**	**units:**	**ng/m³**
poll:	**Cadmium**	**data:**	**1996**

N	<c>	u(<c>)	v(<c>)	vpred
13	2,3	1,58	0,68	0,67
26	2,5	1,16	0,46	0,43
52	2,5	0,68	0,27	0,29
104	2,5			0,19
208	2,5			0,10
312	2,5			0,05
365	2,5			0,00
Nmax:	100		s =	5,7



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	310
0,10	214
0,15	141

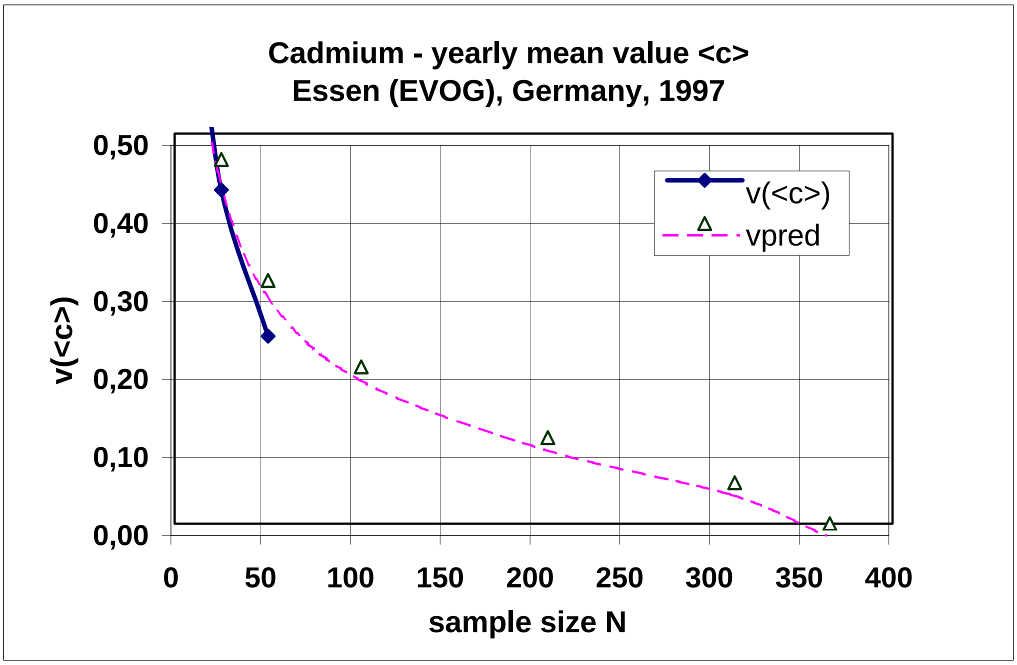
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Essen, Vogelheim, Germany**	**units:**	**ng/m³**
poll:	**Cadmium**	**data:**	**1997**

N	<c>	u(<c>)	v(<c>)	vpred
13	1,7	1,12	0,67	0,67
26	1,7	0,71	0,43	0,47
52	1,7	0,41	0,24	0,31
104	1,7			0,20
208	1,7			0,11
312	1,7			0,05
365	1,7			0,00
Nmax:	94		s =	4,1



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	315
0,10	223
0,15	150

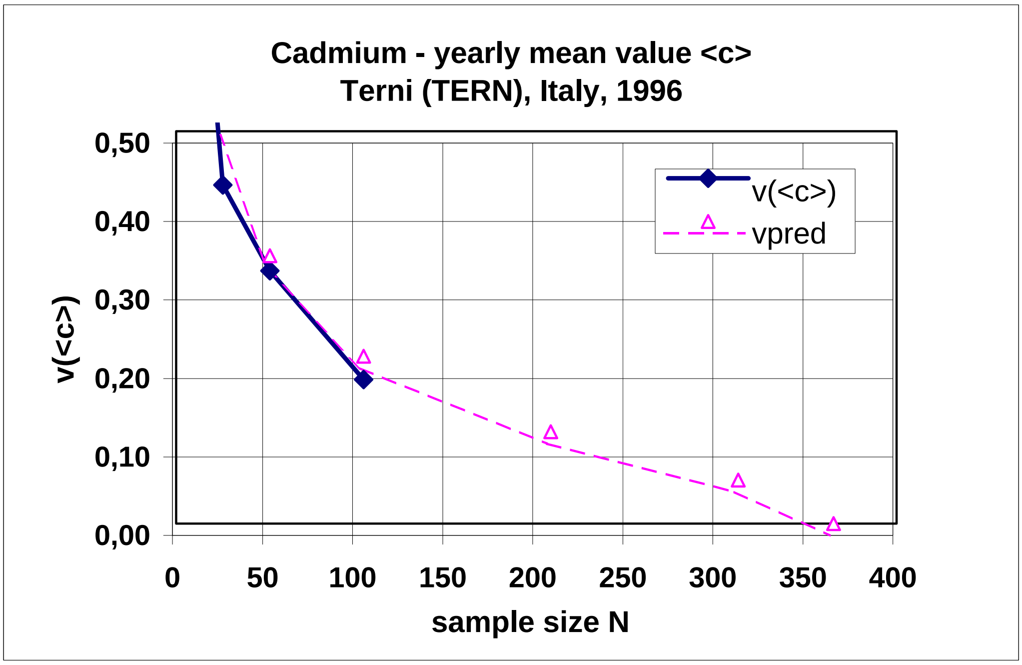
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Terni, Italy**	**units:**	**ng/m³**
poll:	**Cadmium**	**data:**	**1996**

N	<c>	u(<c>)	v(<c>)	vpred
13	5,1	3,99	0,78	0,76
26	5,3	2,29	0,43	0,51
52	5,4	1,75	0,32	0,34
104	5,6	1,03	0,18	0,21
208	5,6			0,12
312	5,6			0,06
365	5,6			0,00
Nmax:	195		s =	14,4



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	321
0,10	235
0,15	163

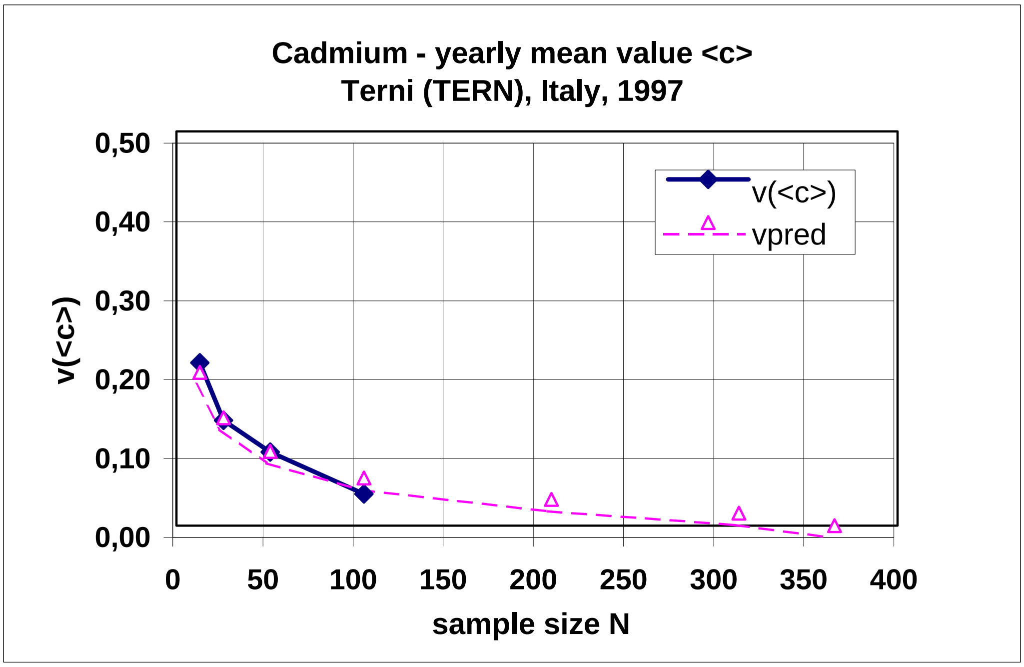
Resampling of mean values

(100 samples of size N without replacement)

N: **sample size**
<c>: **mean value**
u(<c>): **standard deviation of the mean value <c>**
v(<c>): **u(<c>) / <c>**
Nmax: **maximum sample size available**
vpred: **s * SQRT(1/N - 1/365) / <c>**

site: **Terni, Italy**
poll: **Cadmium**
units: **ng/m³**
data: **1997**

N	<c>	u(<c>)	v(<c>)	vpred
13	2,1	0,43	0,21	0,19
26	2,1	0,28	0,13	0,14
52	2,1	0,19	0,09	0,09
104	2,1	0,08	0,04	0,06
208	2,1			0,03
312	2,1			0,02
365	2,0			0,00
Nmax:	151		s =	1,5



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	136
0,10	47
0,15	23

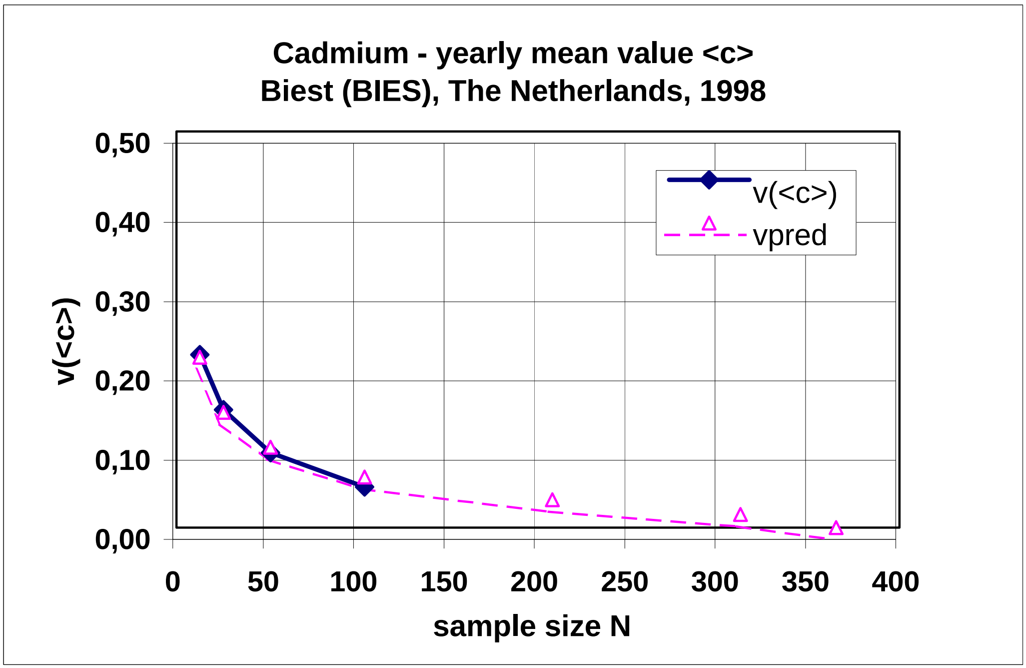
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Biest, The Netherlands**	**units:**	**ng/m³**
poll:	**Cadmium**	**data:**	**1998**

N	<c>	u(<c>)	v(<c>)	vpred
13	0,4	0,08	0,22	0,22
26	0,4	0,06	0,15	0,15
52	0,4	0,04	0,09	0,10
104	0,4	0,02	0,05	0,06
208	0,4	0,00		0,03
312	0,4			0,02
365	0,4			0,00
Nmax:	163		s =	0,3



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	144
0,10	51
0,15	25

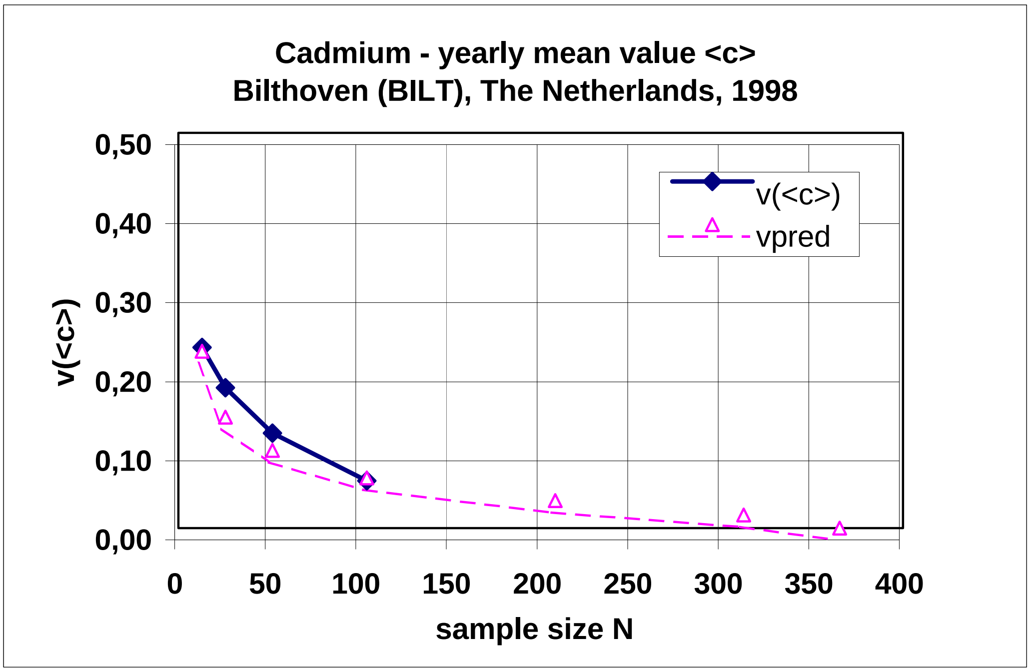
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Bilthoven, The Netherlands**	**units:**	**ng/m³**
poll:	**Cadmium**	**data:**	**1998**

N	<c>	u(<c>)	v(<c>)	vpred
13	0,3	0,06	0,23	0,22
26	0,3	0,06	0,18	0,14
52	0,3	0,04	0,12	0,10
104	0,3	0,02	0,06	0,06
208	0,3	0,00		0,03
312	0,3			0,02
365	0,3			0,00
Nmax:	159		s =	0,23



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	143
0,10	51
0,15	24

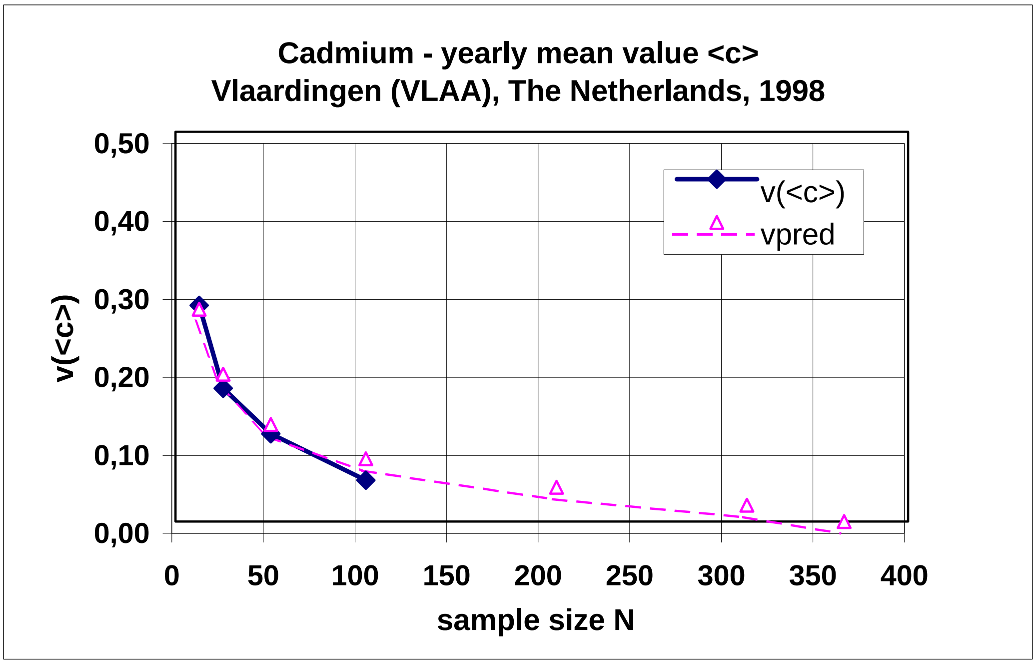
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Vlaardingen, The Netherlands**	**units:**	**ng/m³**
poll:	**Cadmium**	**data:**	**1998**

N	<c>	u(<c>)	v(<c>)	vpred
13	0,3	0,09	0,28	0,27
26	0,3	0,05	0,17	0,19
52	0,3	0,04	0,11	0,12
104	0,3	0,02	0,05	0,08
208	0,3			0,04
312	0,3			0,02
365	0,3			0,00
Nmax:	161		s =	0,31



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	185
0,10	75
0,15	37

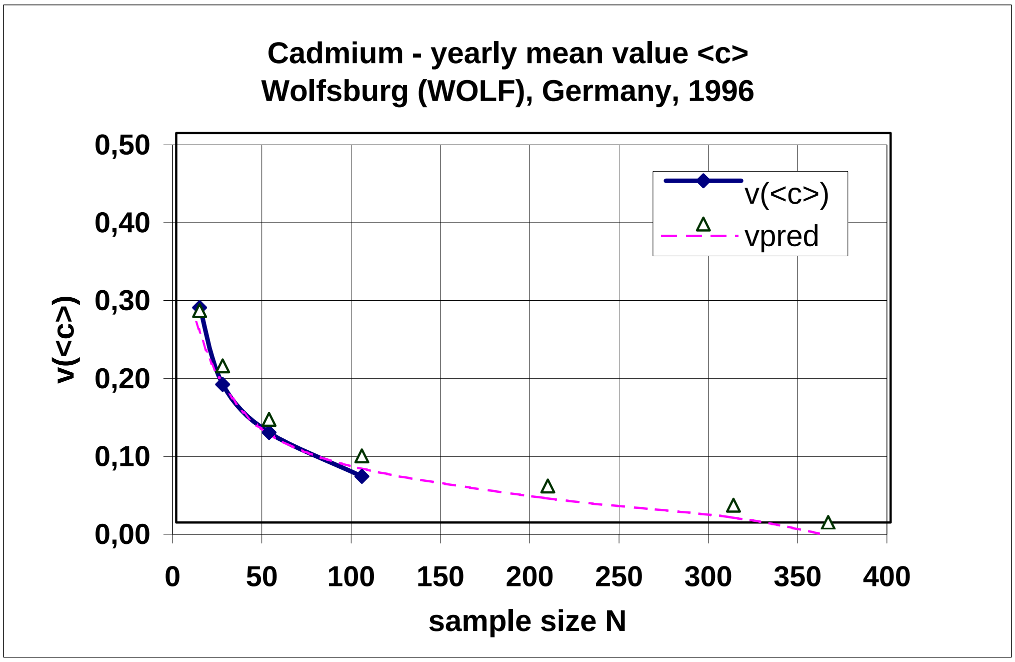
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size**
<c>:	**mean value**	**vpred:**	**s*SQRT(1/N - 1/ 365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>) =	**u(<c>)/<c>**		

site:	**Wolfsburg, Germany**	**units:**	**ng/m³**
poll:	**Cadmium**	**data:**	**1996**

N	<c>	u(<c>)	v(<c>)	vpred
13	0,33	0,091	0,28	0,27
26	0,31	0,055	0,18	0,20
52	0,32	0,037	0,12	0,13
104	0,32	0,019	0,06	0,09
208	0,32			0,05
312	0,32			0,02
365	0,32			0,00
Nmax:	150		s =	0,33



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	196
0,10	82
0,15	42

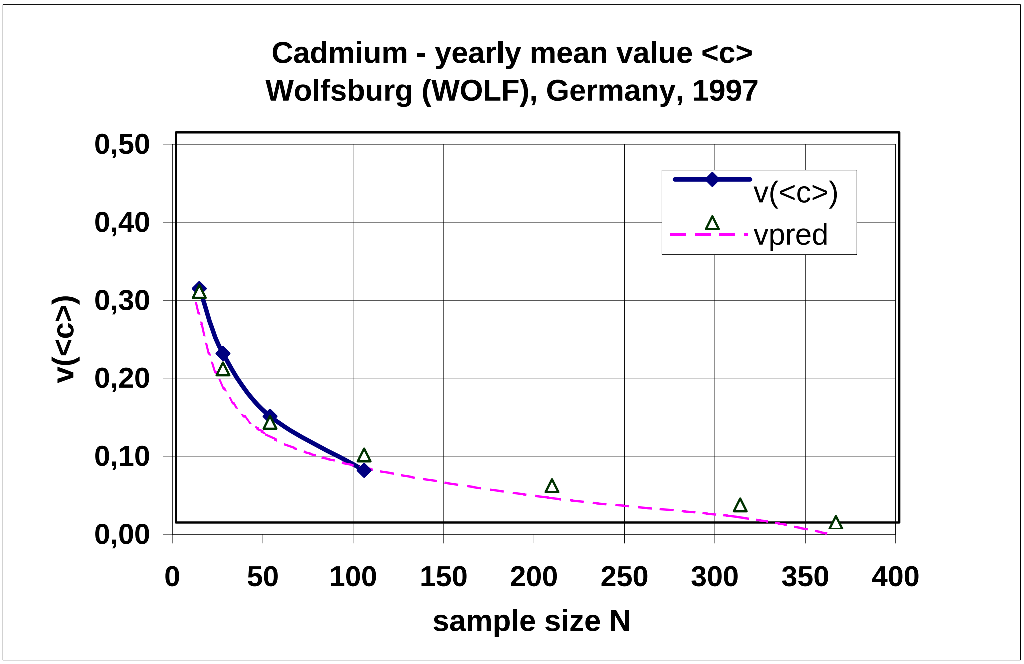
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size**
<c>:	**mean value**	**vpred:**	**s*SQRT(1/N - 1/ 365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>) =	**u(<c>)/<c>**		

site:	**Wolfsburg, Germany**	**units:**	**ng/m³**
poll:	**Cadmium**	**data:**	**1997**

N	<c>	u(<c>)	v(<c>)	vpred
13	0,2	0,07	0,30	0,30
26	0,2	0,05	0,22	0,20
52	0,3	0,03	0,14	0,13
104	0,2	0,02	0,07	0,09
208	0,2			0,05
312	0,2			0,02
365	0,2			0,00
Nmax:	169		s =	0,25



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	198
0,10	84
0,15	43

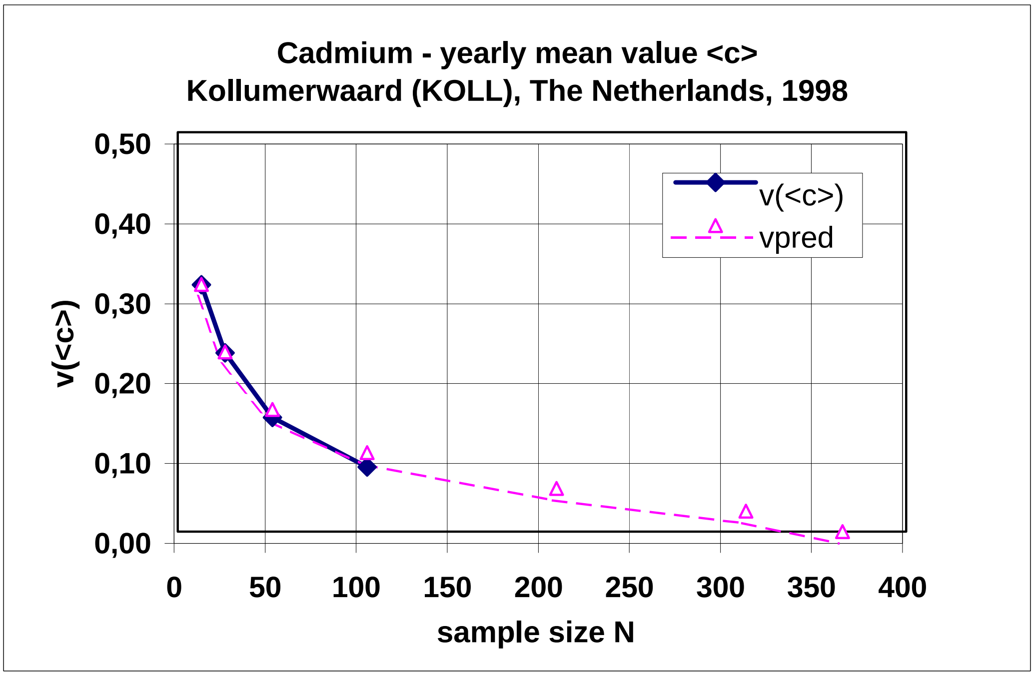
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

Site:	**Kollumerwaard, The Netherlands**	**units:**	**ng/m³**
Poll:	**Cadmium**	**data:**	**1998**

N	<c>	u(<c>)	v(<c>)	vpred
13	0,2	0,07	0,31	0,31
26	0,2	0,05	0,22	0,23
52	0,2	0,03	0,14	0,15
104	0,2	0,02	0,08	0,10
208	0,2			0,05
312	0,2			0,03
365	0,2			0,00
Nmax:	182		s =	0,25



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	222
0,10	102
0,15	54

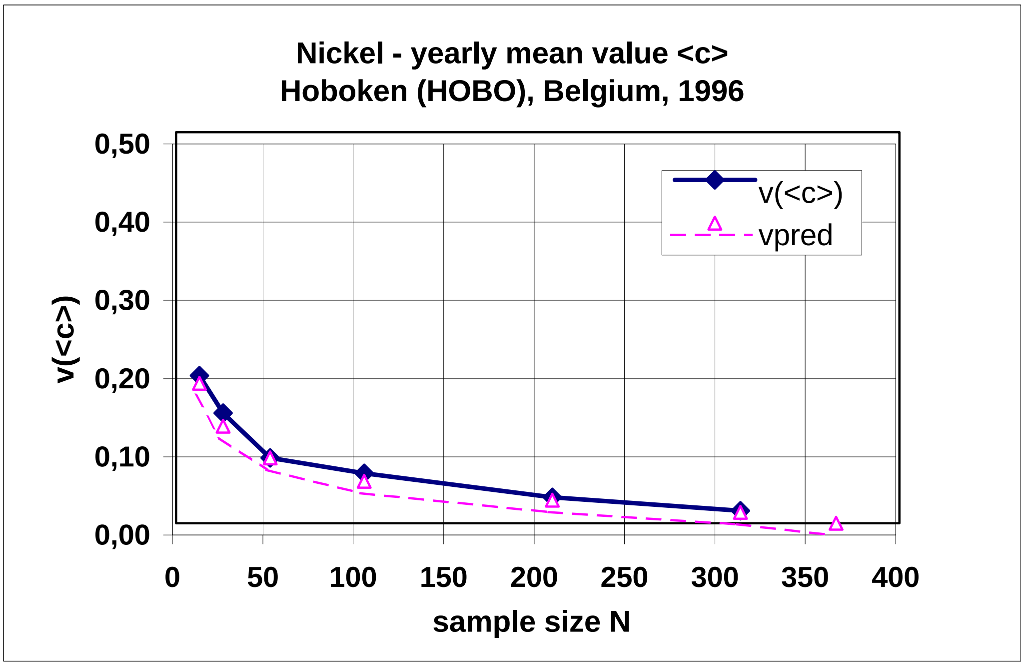
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Hoboken, Belgium**	**units:**	**ng/m³**
poll:	**Nickel**	**data:**	**1996**

N	<c>	u(<c>)	v(<c>)	vpred
13	2,1	0,40	0,19	0,18
26	2,1	0,30	0,14	0,12
52	2,2	0,18	0,08	0,08
104	2,2	0,14	0,06	0,05
208	2,2	0,07	0,03	0,03
312	2,2	0,03	0,02	0,01
365	2,2			0,00
Nmax:	362		s =	1,4



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	116
0,10	38
0,15	18

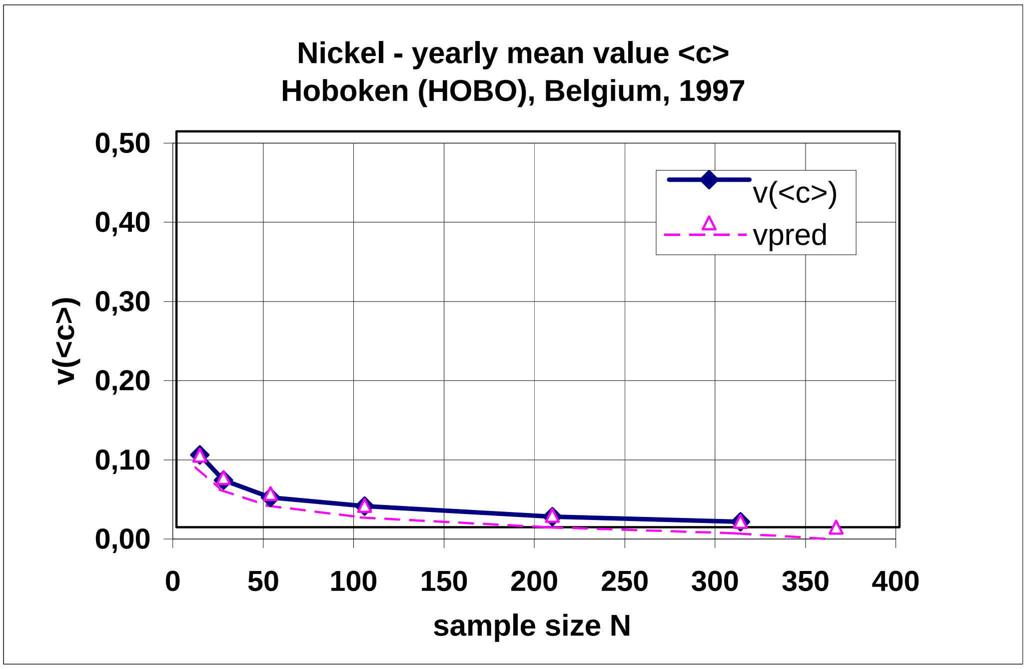
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Hoboken, Belgium**	**units:**	**ng/m³**
poll:	**Nickel**	**data:**	**1997**

N	<c>	u(<c>)	v(<c>)	vpred
13	5,4	0,49	0,09	0,09
26	5,4	0,32	0,06	0,06
52	5,4	0,20	0,04	0,04
104	5,4	0,14	0,03	0,03
208	5,4	0,07	0,01	0,02
312	5,4	0,04	0,01	0,01
365	5,4			0,00
Nmax:	365		s =	1,8



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	39
0,10	11
0,15	5

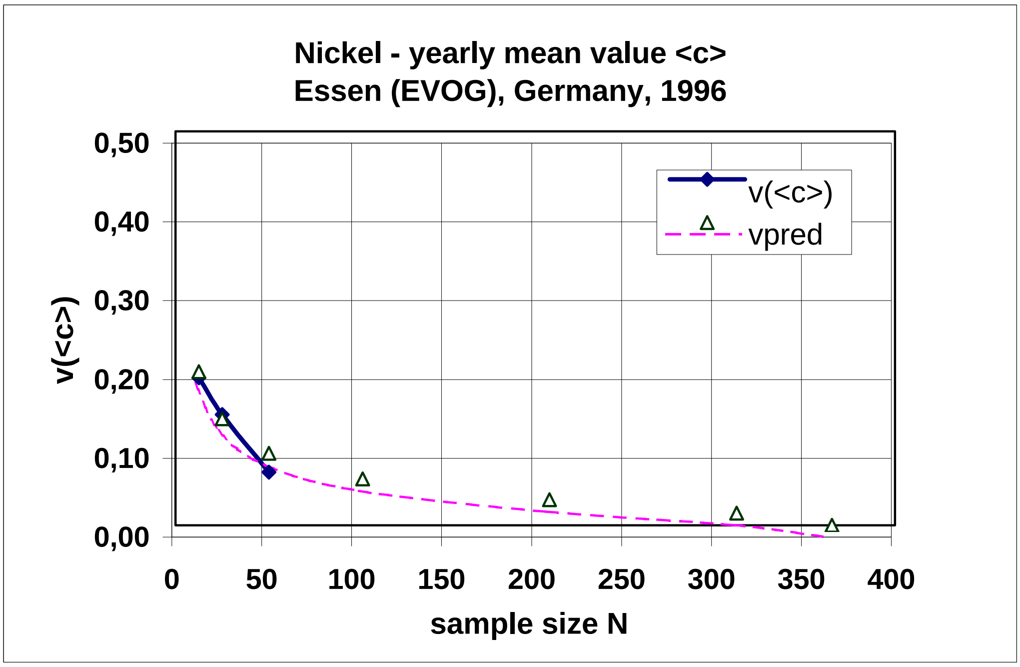
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Essen, Vogelheim, Germany**	**units:**	**ng/m³**
poll:	**Nickel**	**data:**	**1996**

N	<c>	u(<c>)	v(<c>)	vpred
13	7,0	1,31	0,19	0,20
26	7,0	0,98	0,14	0,14
52	7,0	0,47	0,07	0,09
104	7,0			0,06
208	7,0			0,03
312	7,0			0,02
365	7,1			0,00
Nmax:	100		s =	5



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	130
0,10	44
0,15	21

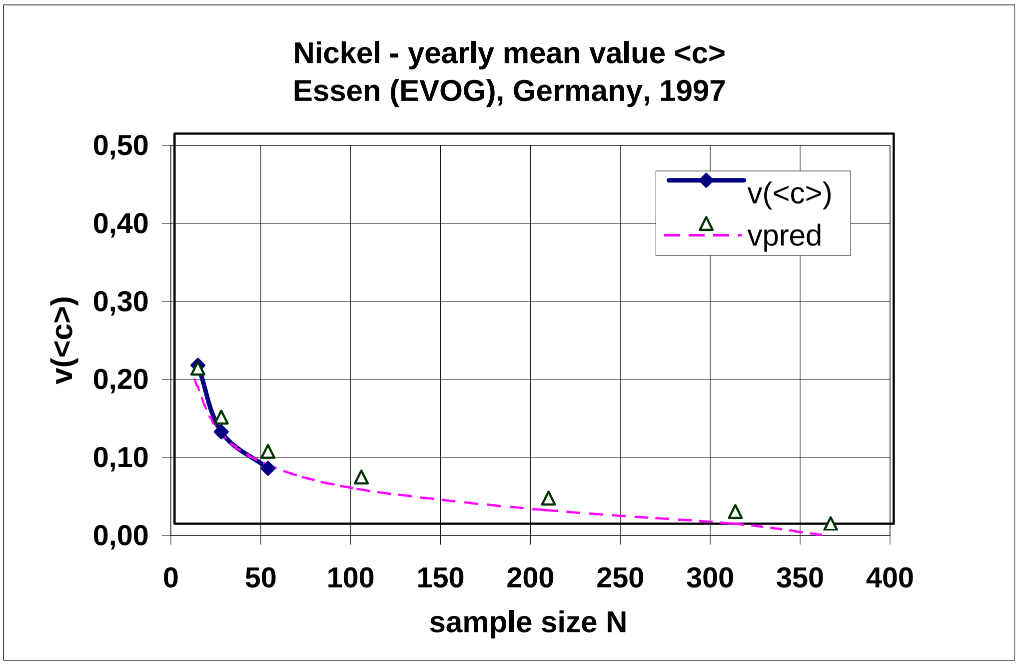
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Essen, Vogelheim, Germany**	**units:**	**ng/m³**
poll:	**Nickel**	**data:**	**1997**

N	<c>	u(<c>)	v(<c>)	vpred
13	7,1	1,44	0,20	0,20
26	7,2	0,85	0,12	0,14
52	7,2	0,51	0,07	0,09
104	7,2			0,06
208	7,2			0,03
312	7,2			0,02
365	7,2			0,00
Nmax:	92		s =	5,2



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	132
0,10	45
0,15	22

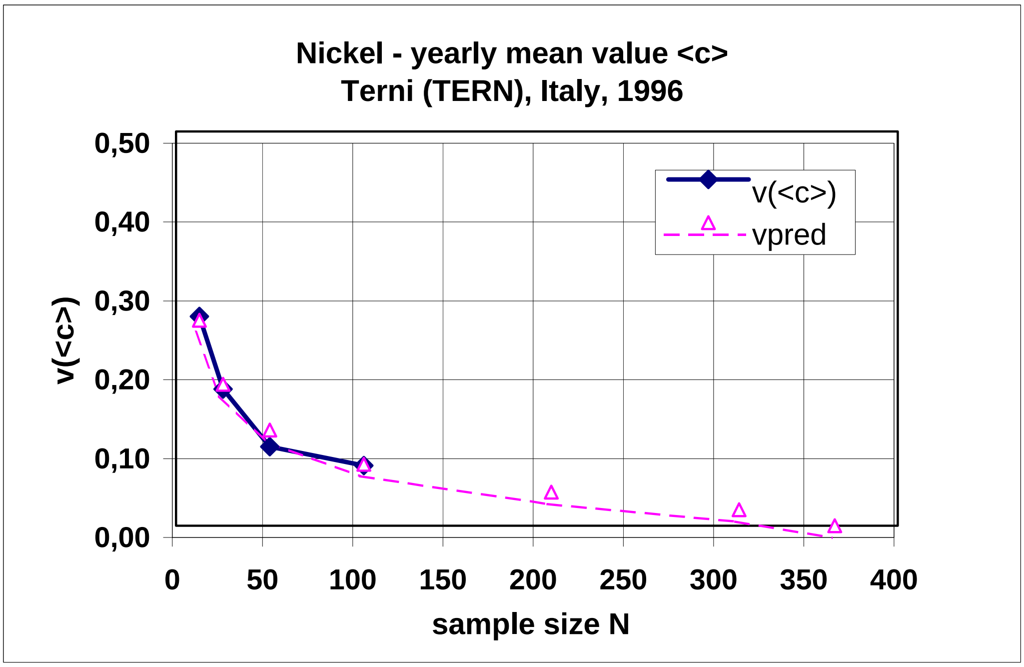
Resampling of mean values

(100 samples of size N without replacement)

N: sample size
<c>: mean value
u(<c>): standard deviation of the mean value <c>
v(<c>): u(<c>) / <c>
Nmax: maximum sample size available
vpred: s * SQRT(1/N - 1/365) / <c>

site: Terni, Italy
poll: Nickel
units: ng/m³
data: 1996

N	<c>	u(<c>)	v(<c>)	vpred
13	15,4	4,07	0,27	0,26
26	15,5	2,69	0,17	0,18
52	15,5	1,56	0,10	0,12
104	15,6	1,19	0,08	0,08
208	15,7	0,42		0,04
312	15,7			0,02
365	15,6			0,00
Nmax:	260		s =	14,7



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	180
0,10	71
0,15	36

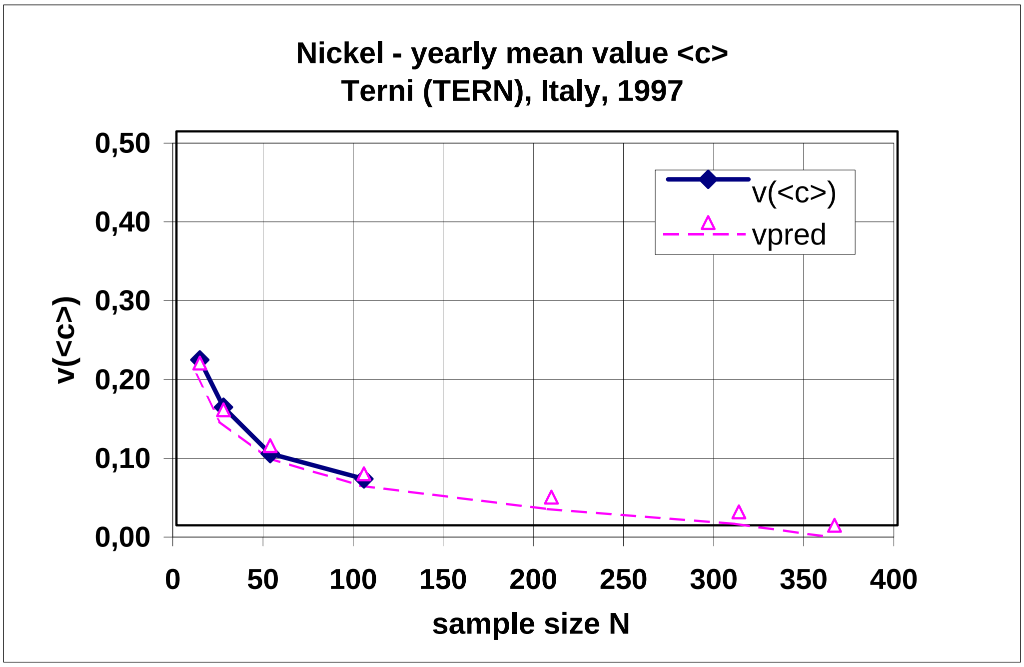
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size available**
<c>:	**mean value**	**vpred:**	**s * SQRT(1/N - 1/365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>):	**u(<c>) / <c>**		

site:	**Terni, Italy**	**units:**	**ng/m³**
poll:	**Nickel**	**data:**	**1997**

N	<c>	u(<c>)	v(<c>)	vpred
13	23,0	4,83	0,21	0,21
26	22,4	3,36	0,15	0,15
52	22,1	2,01	0,09	0,10
104	22,1	1,30	0,06	0,07
208	22,1			0,04
312	22,1			0,02
365	22,2			0,00
Nmax:	207		s =	17,4



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	147
0,10	53
0,15	25

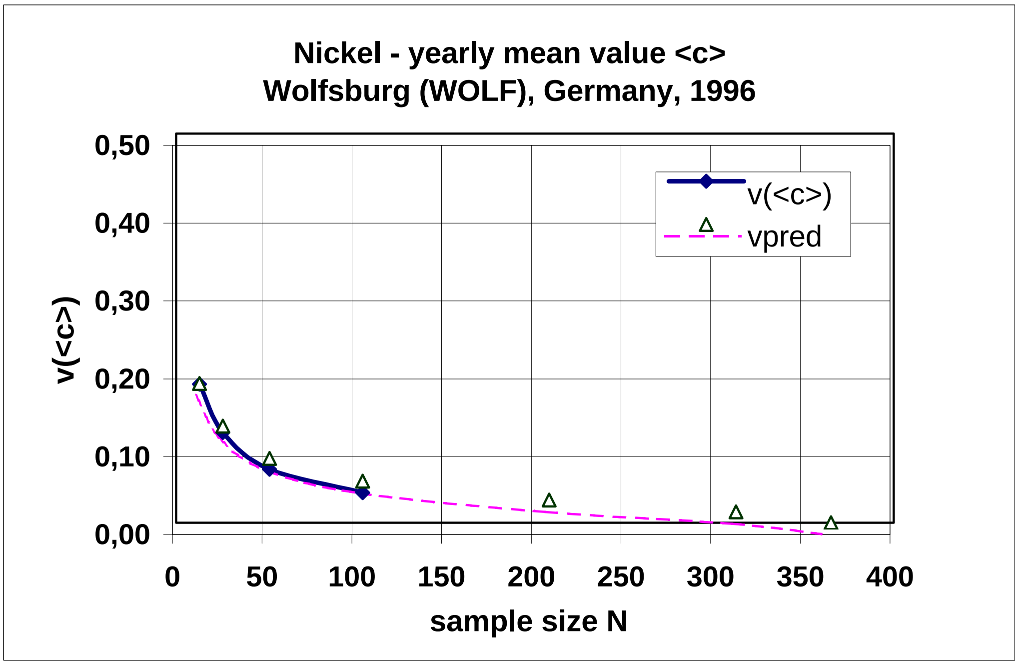
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size**
<c>:	**mean value**	**vpred:**	**s*SQRT(1/N - 1/ 365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>) =	**u(<c>)/<c>**		

site:	**Wolfsburg, Germany**	**units:**	**ng/m³**
poll:	**Nickel**	**data:**	**1996**

N	<c>	u(<c>)	v(<c>)	vpred
13	1,4	0,24	0,18	0,18
26	1,4	0,16	0,12	0,12
52	1,4	0,10	0,07	0,08
104	1,4	0,05	0,04	0,05
208	1,4			0,03
312	1,4			0,01
365	1,4			0,00
Nmax:	150		s =	0,9



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	114
0,10	37
0,15	17

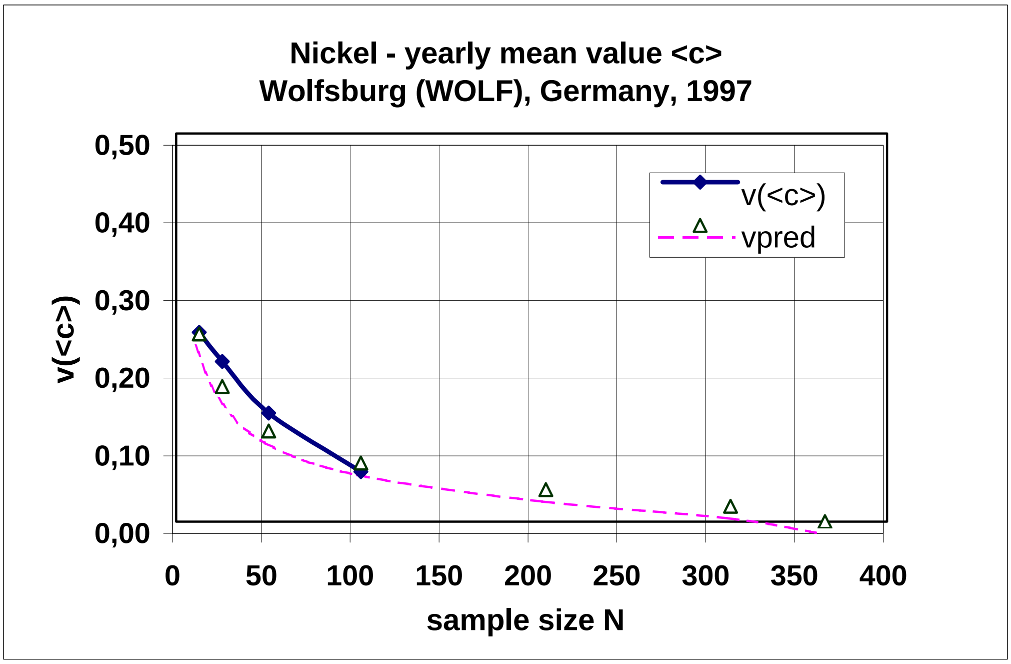
Resampling of mean values

(100 samples of size N without replacement)

N:	**sample size**	**Nmax:**	**maximum sample size**
<c>:	**mean value**	**vpred:**	**s*SQRT(1/N - 1/ 365) / <c>**
u(<c>):	**standard deviation of the mean value <c>**		
v(<c>) =	**u(<c>)/<c>**		

site:	**Wolfsburg, Germany**	**units:**	**ng/m³**
poll:	**Nickel**	**data:**	**1997**

N	<c>	u(<c>)	v(<c>)	vpred
13	1,7	0,41	0,24	0,24
26	1,6	0,34	0,21	0,17
52	1,7	0,23	0,14	0,12
104	1,7	0,11	0,06	0,08
208	1,7			0,04
312	1,7			0,02
365	1,7			0,00
Nmax:	166		s =	1,5



N = 1 / [(vpred*<c>/s)² + 1/365]

vpred	N
0,05	173
0,10	67
0,15	33

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30	Results of Measurements of the Emissions of Dioxins by Industrial Plants in North Rhine-Westphalia – Dioxins Measurement Programme North Rhine-Westphalia – Final Report 1996 English translation of the report LUA-Materialien No. 30 (1996); original edition published in German language – Translated by Edith Navé, Hohenbrunn, Germany Essen: Landesumweltamt NRW 1997, 102 S.	30,00 DM

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31	Umsetzung der TA Siedlungsabfall bei Deponien in NRW Fortbildungsveranstaltung am 27./28. Juni 1995 im Bildungszentrum für die Entsorgungs- und Wasserwirtschaft GmbH (BEW) in Essen Essen: Landesumweltamt NRW 1996, 189 S.	28,00 DM
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43	Identification of Relevant Industrial Sources of Dioxins and Furans in Europe (The European Dioxin Inventory) – Final Report – Essen: Landesumweltamt NRW 1997, 926 S.	50,00 DM

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No. 58

Ambient Air Pollution by As, Cd and Ni Compounds

Position Paper

Landesumweltamt Nordrhein-Westfalen

Luft

Wasser

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Verfahren