Materialien

No. 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

Landesumweltamt
Nordrhein-Westfalen

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Preface

This final report presents the results of the "Dioxins Measurement Programme of North Rhine-Westphalia" which has been initiated and sponsored by the Ministry of the Environment in North Rhine-Westphalia. The very thorough and extensive investigations which were carried out between 1992 and 1995 provide an encompassing insight into the emissions of dioxins and furans by industrial plants in North Rhine-Westphalia; they contributed considerably to increase the knowledge on the occurrence of dioxins in North Rhine-Westphalia.

Only 14 plants emitting more than 1 ng I-TEQ/m^3 were found to account for almost the entire quantity emitted annually in North Rhine-Westphalia which according to the measurements amounted to 500 g I-TEQ/a. For about 70 % of the more than 50 plants included in the study which were thought to emit increased amounts of dioxins and furans this initial assumption could not be confirmed; in these cases the concentrations were below 0.1 ng I-TEQ/m^3. Thus the entry of dioxins into the atmosphere was caused by few large plants and not by numerous small ones which would have been difficult to monitor.

Immediately initiated abatement measures which instantly reduced the entry of PCDD/PCDF into the environment can be considered as the most important success of the programme. In addition to providing proof of the successful reduction of the emissions and of other changes (e.g. with regard to the equipment of waste incinerators) simultaneously conducted measurements in the ambient air in 4 large cities of the Rhine-Ruhr area confirmed a decrease of the ambient air pollution by about two thirds compared with 1987/88.

Moreover, the report on the measurement programme furnishes important information on the efficiency of waste gas cleaning methods and on the influence which input materials and operating conditions exert on the emissions of dioxins.

At this point may I express my gratitude to the companies involved in the programme. They all actively supported the programme with their voluntary work. The programme provides an excellent example of how fast effective measures to reduce the entry of dioxins into the atmosphere can be achieved by combining the forces of companies and the environmental protection agencies.

Dr. Irmer

Dr. Ing. Harald Irmer
President of the
North Rhine-Westphalia State Environment Agency

Essen, April 1997

North Rhine-Westphalia State Environment Agency
(Landesumweltamt Nordrhein-Westfalen)

Final Report

by the project group

"Dioxins Measurement Programme in North Rhine-Westphalia"

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The programme was carried out for the Ministry of Environment, Regional Planning and Agriculture of the state of North Rhine-Westphalia.

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1. Introduction

At the Symposium on dioxins in Karlsruhe in 1990 the majority of experts on the effects came out in support of limiting the long-term daily intake dose of chlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF) by humans for protective reasons to below 1 pg toxicity equivalents (I-TEQ) per kg body weight as proposed by the German Federal Bureau of Health (BGA) and the German Federal Environmental Protection Agency (UBA). The proposal received further backing at the "Second Symposium on Dioxins" in Berlin in November 1992.

The symposia on dioxins also clearly stated that in Germany approx. 95% of the daily intake of PCDD and PCDF occurs with the food and the daily average intake by adults amounts to 2 pg I-TEQ/kg body weight, which is above the proposed protective limit. For breast-fed babies the average daily intake with breast milk is much higher and amounts to approx. 150 pg I-TEQ/kg body weight. During the time the baby is nursed the dose limit proposed for protective reasons is clearly exceeded. Even though the German Federal Bureau of Health recommends to continue to breast-feed babies because of the positive effects of breast milk, the concentrations of dioxins are not acceptable.

At both symposia the BGA and UBA came to the conclusion that further measures appear necessary to reduce entry of dioxins and furans into the environment and into the food chain in order to protect the health of the population.

The conclusions by the experts on effects and by the top federal authorities as well as the legal requirement spelled out in Section 3.1.7 of the administrative provision on air quality control (TA Luft) to keep environmental pollution by dioxins and furans at a minimum form the basis for the dioxins measurement programme carried out in North Rhine-Westphalia which will be presented in the following. The programme was needed because knowledge of all relevant sources of dioxins and furans is an absolute necessity to accomplish an effective control. Several authors estimated the annual emissions of PCDD and PCDF into the ambient air in West Germany in the years 1990 and 1991 on the basis of the then existing knowledge. Table 1-1 provides two examples of such estimates.

In the public debate the origin of dioxins was narrowed to waste incinerators. For this reason, the contribution by that source was well known at the time the estimates were made. The estimates by the various authors differed hardly with regard to waste incinerators while great differences existed in the estimates of the contributions by further thermal sources such as domestic heating and primarily the metal industry. For some sources such as steelworks and smelting plants hardly any results of measurements had become known. At the first symposium on dioxins, therefore, the need for a research and development programme was spelled out which would lead to an extensive inventory of the emissions of important sources in the metal producing industry and likewise of all firing equipment.

Table 1-1: **Estimated annual emissions of PCDD/PCDF by thermal sources and trends in 1990; area of the former Federal Republic.**

	annual emissions, g I-TEQ/a		
emission source	Hagenmaier [1]	Fiedler [2]	comments, trends
garbage incineration	400	432	declining to 4 g I-TEQ/a (17. BImSchV)
hospital waste incineration	1.5	5.4	declining towards 0 (shut down)
hazardous waste incineration	1	1.6	declining to about 0.5 g I-TEQ/a
automobile exhaust gas	50	22	declining (prohibition of scavengers, catalysts)
domestic heating	?	-	20 g I-TEQ/a, mostly constant
cable burning installations	included	4.5	thermal installations shut down
industry			
production of secondary raw materials	400, estimated	38 to 380	up till now estimated too low, presumably ≥ 500 g I-TEQ/a; trend downward
steelworks	included	0.03	
total	800	504 to 846	> 1000, decline by > 500 g I-TEQ/a

In order to close the information gaps and to provide the necessary groundwork for efficient abatement measures the Ministry of the Environment of the state of North Rhine-Westphalia initiated a programme in 1992 with the goal to create an inventory of all industrial sources which emit dioxins and furans. At that time the State Agency of Air Pollution Control (meanwhile integrated into the State Environment Agency) determined the contribution by domestic firing and heating equipment through measurements of the emissions from various types of ovens and stoves using various kinds of fuels and a special test stand to take the measurements. According to the results of these measurements the contribution by domestic firing and heating equipment in general turned out to be rather low with the annual emissions amounting to less than 20 g I-TEQ/a. Although, in some locations (such as settlements with individual stoves) this source may contribute amounts to the ambient air which cannot be ignored.

2. Planning

Two groups of emission sources appeared to be of concern

- plants whose high concentrations of dioxins and furans (> 1 ng I-TEQ/m^3) affect the immediate neighbourhood because of inadequate discharge facilities (such as roof vents).

- plants producing high emissions of dioxins and furans with good discharge conditions (which do not pollute the immediate neighbourhood), but whose high-volume flows contribute considerably to the entry of PCDD/PCDF into the food chain.

2.1 Cataloguing potential emission sources of dioxins

In the year 1991 a list of 340 industrial plants subject to licensing was compiled in co-operation with the industrial inspection agencies in North Rhine-Westphalia. The list was confined to plants which were expected to emit dioxins and furans because of the applied technologies and prevailing conditions (such as temperatures of > 200°C, O_2-containing atmosphere, type of flue gas cleaning equipment used, chlorine-containing input material) and because of available results of measurements in similar plants.

A separate programme for reducing the emissions from waste incinerators is in progress in North Rhine-Westphalia. Therefore, these plants were excluded as were those plants to which the 17th administrative provision issued on the basis of the Federal Immission Control Law (17. BImSchV) applies.

From the list 76 plants were selected which were expected to emit relevant amounts of dioxins and furans and for which no results of measurements existed which would provide information on the variations of the emissions of PCDD/PCDF.

The plants were grouped into three categories according to following criteria:

- emissions of dioxins and furans of > 1 ng/m³ international toxicity equivalents (I-TEQ) are likely,
- the discharge conditions for the flue gases are unfavourable (such as discharge through low, scattered outlets with likely impact on the immediate neighbourhood or high flue gas volume flows carrying a high load),
- no results of measurements on comparable plants are available.

A total of 42 out of 76 plants subject to licensing were entered into categories 1 and 2 which were given high priority with regard to measurements, the remaining plants were put into category 3 with lower information need (Tables 2.1-1 to 2.1-2).

With this list of plants the measurement programme was started at the end of 1991 and continuously expanded according to need. Already existing results were integrated into the programme which was managed by a project group.

At the time of the first selection of plants reports of emission measurements which were in the hands of authorities in North Rhine-Westphalia were collected and evaluated. Because the list of plants requiring measurements which did not fall into category 1 was considered to be expandable, 19 plants were added to that group (Table 2.1-3).

In some plants of category 1 no measurements were performed. The reasons are explained below.

Company WEKA GmbH

In the plant of the company WEKA GmbH four electrically heated crucible furnaces are fed with primary aluminium and internally recycled scrap. Perchlorinated hydrocarbons are no longer used. Now "Flussum-NITRAL-C(19)" is used for final treatment of the melt. Because of the results of measurements on comparable plants no local exhaust system for the crucible furnaces was required by the inspection agency; therefore the plant is equipped with only an exhaust system for drawing off the air in the room.

Table 2.1-1: Plants in category I

no.	company	location	comment
1	Aluminium Norf GmbH	Neuss	no measurements, cf. text for explanations
2	B. Hausmann GmbH & Co. KG	Blomberg	measurement performed
3	Deutsche Solvay Werke	Rheinberg	measurement performed
4	Felten & Guillaume	Cologne	plant shut down, no measurement
5	GEHÜ GmbH	Heiligenhaus	hexachloroethane no longer used, no measurement
6	Grillo-Werke	Duisburg	measurement performed
7	Heinrich Schneider	Drolshagen	measurement performed
8	Hoogovens Aluminium	Voerde	measurement performed
9	Leichtmetall-GmbH	Essen	measurement performed
10	Metallhüttenges. Schumacher GmbH	Rommerskirchen	measurement performed
11	Metallwerk Dinslaken GmbH	Dinslaken	measurement performed
12	Metallwerk Olsberg & Co.	Essen	measurement performed
13	R. Linnemann GmbH & Co. KG	Sassenberg	measurement performed
14	Rheinische Motoröl GmbH & Co. KG	Duisburg	plant shut down, no measurement
15	W. Prym	Stolberg	measurement performed
16	Willi Kampmann GmbH	Velbert	perchlorinated hydrocarbons are no longer used, no measurements

Table 2.1-2: Plants in category II

No.	company	location	comment
1	Alugral GmbH	Neuss	measurement performed
2	Aluminiumwerk Unna AG	Düren	shut down, no measurement
3	Berzelius MHD GmbH	Duisburg	measurement performed
4	Degussa AG	Hürth	flue gas volume 600 m^3/h, source not relevant, no measurement
5	Dynamit Nobel AG	Troisdorf	shut down, no measurement
6	Erbslöh GmbH	Velbert	inhouse recycled scrap, no chlorination, no measurement
7	Ford-Werke AG	Cologne	measurement outside the dioxin measurement project
8	Gebr. Goldschmidt GmbH	Heiligenhaus	flue gas flux not determined, no measurement
9	Gottschol-Aluminium GmbH	Nachrodt	flue gas ducts not suitable for measurements, no measurements
10	Gottschol-Metallwerke	Hagen	measurement performed
11	H. Twillingmeier KG	Rietberg	no measurement because several other wood-fired furnaces were investigated
12	Hoesch-Stahl AG	Dortmund	measurement performed
13	Honsel-Werke AG	Meschede	measurement outside the dioxin measurement project
14	Honselwerke AG	Soest	operations were modified, no measurements
15	Messingwerk Hohenlimburg	Hagen	shut down, no measurement
16	Metallhandelsges. Tacke & Co.	Wipperfürth	measurement performed
17	Metallhüttengesells. Schumacher GmbH	Rommerskirchen	measurement performed

Continuation of Table 2.1-2: Plants in category II

no.	company	location	comment
18	Nolte-Möbel	Delbrück	measurement performed
19	Pfleiderer Industrie GmbH & Co. KG	Arnsberg	no measurement because several other wood-fired furnaces were investigated
20	Pfleiderer Industrie GmbH & Co. KG	Rheda	fibre board production, no measurement
21	Roland Legierungsmetall	Oberhausen	no measurement
22	VAW	Bonn	predominantly clean materials, no measurements
23	VAW Erftwerk	Grevenbroich	results of measurements performed by a third party
24	Wirus Werk	Gütersloh	fibre board production, no measurement
25	Wuppermetall GmbH	Wuppertal	measurement outside the dioxin measurement project
26	Zeller Recycling	Gelsenkirchen	measurement performed

Table 2.1-3: Plants which were added to the project and investigated plants in category III

no.	company	location	comment
1	Bayer AG	Leverkusen	residue incineration
2	Bayer AG	Dormagen	central waste gas incineration
3	Busch Jäger	Lüdenscheidt	brass foundry
4	Deumu GmbH	Recklinghausen	shredder
5	Deutsche Gasrußwerke	Dortmund	residual gas burning
6	Duisburger Kupferhütte AG	Duisburg	sintering plant
7	Gerresheimer Glas AG	Düsseldorf	glass recycling
8	Hornitex Werke GmbH	Duisburg	fibre board production
9	Hüttenmann Holz GmbH & Co. KG	Olsberg	incineration of bark
10	Isola Werke AG	Düren	residue incineration
11	Krupp Stahl AG	Duisburg	Bessemer steel works
12	Metallhüttenwerke Bruch GmbH	Dortmund	secondary aluminium smelter
13	Metallhüttenwerke Bruch GmbH	Dortmund	lead and tin smelter
14	Muschert & Gierse	Neuenrade	thermal paint removal
15	Niehoff	Everswinkel	wood burning furnace
16	Norsk Hydro Magnesium GmbH	Gelsenkirchen	secondary magnesium smelter
17	Otto Fuchs Metallwerke	Meinerzhagen	aluminium foundry
18	RAG Kokerei Kaiserstuhl	Dortmund	coking plant
19	Recyclingwerk Olsberg	Essen	aluminium and non-ferrous metal smelter
20	Ruhr-Zink GmbH	Datteln	calcining plant
21	Seppelfricke GmbH	Gelsenkirchen	brass foundry
22	Siegfried Jacob Metallwerke	Ennepetal	copper smelter
23	Stadt Duisburg	Duisburg	crematorium
24	Thyssen Stahl AG	Duisburg	sintering plant
25	Vinnolit Kunststoff GmbH	Cologne	vinyl chloride production, drier

The plant was placed into category I at first. Because the additives which were originally used were substituted, no justification for priority measurements within the programme existed any longer.

Company GEHÜ GmbH & Co.

The company GEHÜ GmbH & Co. feeds primary aluminium and internally recycled scrap to three crucible furnaces. Hexachloroethane has been substituted by other substances. There are no sources with local exhaust. The plant had been placed into category 1 originally. After substitution of a substance known to be involved in the formation of dioxins no reason for priority measurements of the emissions of dioxins existed any more.

Company Alu-Norf

This plant was entered into category I because of its chlorination facility. The company Alu-Norf operates 10 furnaces for melting pure aluminium scrap, scrap consisting of aluminium alloys and scrap from hot-strip and cold-rolling mills. The scrap may be contaminated with lubricants used for rolling. Each liquid aluminium charge is chlorinated. The chlorination process lasts 20 to 30 minutes. In 24 hours 4 chlorination processes are carried out. The chlorinating gas is distributed in the melt with enameled metal lances; no graphite pipes are used. The developing fumes, approx. 2000 m^3/h (aspirator), are cleaned in a scrubber (NaOH-slurry) and are entered into the exhaust system which draws off the fumes from the casting ladle. The project group decided not to conduct measurements in that plant because of the relatively low amounts of fumes, use of enameled pipes and because data are available from similar chlorination processes.

The plants operated by the companies Felten & Guillaume as well as Rheinische Motoröl GmbH & Co. KG were shut down.

2.2 Project group

In order to carry out the programme a "Project Group on the Measurement of Dioxins" managed by Dr. Bröker was created in the State Environment Agency LUA. The project group included Dr. Bruckmann of the Ministry of Environment, Regional Planning and Agriculture (MURL) as well as five staff members of the LUA who are specialists in the fields of measurement technology (Dr. Geueke), analyses (Dr. Hiester), mechanical engineering (Hoffmann, Gliwa) and effects (Radermacher).

The programme was timed to have results of measurements from that geographical area available for which an air quality control plan was being worked. In order to accomplish that goal the first measurements between fall of 1992 and spring 1993 were taken in the eastern Ruhr area. They were followed by the main Ruhr area. After completion of these measurements focus was placed on the remaining plants in North Rhine-Westphalia.

The following procedure was pursued in every area that was investigated:

- The project group of the LUA worked out proposals on the emitters and sources that needed to be investigated. The basis for this was the list of emission sources presented by the LUA in 1991 and which has been updated continuously according to the expanding knowledge (among other things intermediate results of the programme as well as of other programmes, for example the one conducted by the German Federal Environmental Protection Agency UBA, were taken into consideration).

- The proposals were co-ordinated with the affected industrial inspection agencies and offices of the Ministry of Environment, Regional Planning and Agriculture (MURL).

- The final decision on which of the proposed industrial plants needed to be put on the priority list was made by the project group together with the MURL.

- Preliminary discussions were conducted by the LUA with the industrial inspection agencies and state environment authorities and the sites of the measurements in the companies were inspected.

- The measurements were carried out by the LUA or by external laboratories which were asked by the LUA to conduct the measurements.

- The project group made sure that a high standard of quality was maintained by conducting round-robin tests, performing analyses reference samples and visiting the external laboratories while they performed the measurements.

- The measurement reports were passed on to the MURL after the LUA had checked them for plausibility. Each state inspection authority and company received a copy of the report that concerned them.

- The individual reports issued during the measurements were used to plan and initiate measures for reducing the emissions and for working out air quality control plans.

2.3 Programme Management

External contractors were engaged according to the rules for contracting out research projects which required that invitations to bid had to be sent out. The measurements which were contracted out concerned primarily four sites in North Rhine-Westphalia. The sites were selected because they required PCDD/PCDF measurements according to Articles 26 and 28 of the Federal Immission Control Law (BImSchG) as was announced in the circular published on 6 January 1992 in the Ministerialblatt No. 11. In cases not suitable for issuing invitations to bid because the bidder had already extensive experience and knowledge of the plant where the measurements needed to be taken a sole source contract was granted.

Extensive additional efforts, such as erecting scaffolds on the measurement site and setting up experimental filters, were necessary in some cases to be able to carry out the measurements.

During the programme, 303 waste gas samples, on the average 3 samples per source, were obtained and analysed for the concentrations of dioxins. Frequently, measurements had to be performed at several sources per plant. The highest number of 11 individual sources was found in a coking plant.

In addition to the above mentioned waste gas samples, 61 samples of dust collected in dust separators were analysed. For quality control the LUA conducted 91 duplicate analyses. Disagreements led to multiple analyses by all other participating laboratories as well. These analyses were not included in the above given figures.

3. Measurements

3.1 Methods

3.1.1 Filtering/cooling method (condensation method)

The guideline VDI 3490, Part 1 (draft) [3] and the standard DIN EN 1948-1 [4] describe the method. It is based on placing a filter after the probe in the flue gas duct or after the sampling tube outside the flue gas duct. The temperature of the filter is kept below 125 °C and above the dew point of water. For high dust loads a quartz wool filter or cyclone is used to precede the filter. After the filter the gas sample is cooled to below 20 °C in a cooler. The PCDD/PCDF present in the gaseous phase or as aerosols are collected in impingers or in an adsorber.

3.1.2 Condensation method (simplified version)

The gas sample is drawn through a water-cooled sampling tube with internal glass tube. Together with the condensate that is formed it is then passed through an adsorption unit consisting of a solid adsorber with preceding quartz-wool filter. The method is explained in the LIS-Report No.109 [5] and in the standard DIN EN 1948-1 [4].

3.1.3 Condensation method with cooled sampling tube

The method is described in the guideline VDI 3499, Part 3 (draft) [6] and in the standard DIN EN 1948-1 [4]. The gas sample flows through the probe and water-cooled sampling tube and is cooled to below 20 °C. The condensate which forms is collected in a flask. The flask is followed by impingers and/or solid adsorber for collection of the gaseous PCDD/PCDF. Aerosols and small particles are separated in a filter preceding the last impinger or the solid adsorber.

3.1.4 Dilution method

This method is described in the guideline VDI 3499, Part 1 (draft) [7] and in the standard DIN EN 1948-1 [4]. The gas sample is passed through a sampling tube heated to the flue gas temperature (or a higher temperature). The waste gas sample is then quenched to temperatures below 40°C by mixing it with dried, filtered and if necessary cooled air in a mixing tube. The dilution prevents a temperature drop of the gas sample below the dew point of water. The particle-bound PCDD/PCDF are collected in a filter which is followed by a solid adsorber for collection of the gaseous PCDD/PCDF.

3.2 Quality control

The agreements with the contractors contained an appendix in which the contractor who performed measurements was obliged to provide following information to simplify quality control:

- state the standards used (distinguish between sampling standard, internal standard, recovery standard)

- state the used standard concentration

- state the total blank value (sampling and analysis)

- state the recovery rate of the sampling standard

- state the recovery rates of all internal standards

- supply the chromatographs upon request.

All extracts were divided; half of them were kept to provide the possibility of performing duplicate analyses by the LUA for quality control. This option was also put into the contract. Together with the extract samples for duplicate analyses following information had to be supplied:

- drawn off sampling volume,
- sampling standard used
- solvent used.

Following further quality control measures were agreed upon:

- random inspections by staff members of the LUA during the measurements

- random duplicate measurements by the LUA.

During the random inspections the staff members of the LUA had to check whether the terms of the contract were fulfilled and the measurements were carried out with the necessary expertise. At the inspections no mistakes which would put the measurements into jeopardy were observed.

The duplicate analyses of extract samples yielded mostly satisfactory agreement between the results of the contractors and those obtained by the LUA. However, in some cases discrepancies occurred because samples were mixed up or the supplied information on the type and concentration of added standards was incorrect.

Duplicate measurements and additional investigations led in most cases to a satisfactory agreement between the results (cf. Table 3.2-1). Of the measurements which were checked approx. 25% led to complaints requiring further investigations to solve the problems.

The experiences with the dioxins measurement programme stress the importance of setting the terms for quality control in order to be able to judge the results of the measurements. At the extent at which measurements of dioxins are meanwhile performed quality control is an absolute necessity. It can be performed in steps beginning with local inspections (to observe the measurement procedure on site) and duplicate analyses followed by duplicate measurements conducted by an independent laboratory.

3.3 Measurements

Checking compliance with limit values did not belong to the tasks of the project group. Therefore, in co-operation with the involved companies the contractors were asked to conduct the measurements during the operating conditions that are typical for the respective plant. In exceptional cases measurements were taken during a trial operation or during the start-up; such measurements are identified accordingly.

The goal of the measurements was to obtain those concentrations which are representative of the PCDD/PCDF emissions of the sampled plants. Operating conditions which are expected to lead to maximum concentrations in the emissions were deliberately avoided. The operating conditions which are normal for the plant can be found by checking the past operations documented in diaries or on printouts of automatic recorders. In order to compensate for the large deviations produced by the PCDD/PCDF measurement methods each measurement was repeated twice. In one case the measurement had to be repeated because the results appeared improbable.

Table 3.2.-1: Results of duplicate measurements (in ng/m^3)

congeners/ homologues	LUA	laboratory	deviation, %
sum TCDD	2.0	2.8	+40
sum PeCDD	1.8	2.5	+39
sum HxCDD	2.4	2.8	+17
sum HpCDD	1.6	1.3	-19
OCDD	0.4	0.5	+25
PCDD	8.1	9.9	+22
2,3,7,8-TCDD	0.06	0.09	+50
1,2,3,7,8-PeCDD	0.19	0.40	+110
1,2,3,4,7,8-HxCDD	0.09	0.19	+111
1,2,3,6,7,8-HxCDD	0.21	0.26	+24
1,2,3,7,8,9-HxCDD	0.10	0.18	+80
1,2,3,4,6,7,8-HpCDD	0.70	0.66	-6
sum TCDF	61	58.7	-4
sum PeCDF	34.0	32.5	-4
sum HxCDF	18.0	13.5	-25
sum HpCDF	2.0	2.2	10
OCDF	nd	0.4	
PCDF	116	107	-8
2,3,7,8-TCDF	2.7	1.9	-30
1,2,3,7,8/1,2,3,4,8-PeCDF	2.8	2.7	-3
2,3,4,7,8-PeCDF	3.0	2.4	-20
1,2,3,4,7,8/1,2,3,4,7,9-HxCDF	1.4	1.7	+21
1,2,3,6,7,8-HxCDF	2.5	1.6	-35
1,2,3,7,8,9-HxCDF	< 0.01	0.12	
2,3,4,6,7,8-HxCDF	1.4	1.3	-5
1,2,3,4,6,7,8-HpCDF	2.0	1.9	-3
1,2,3,4,7,8,9-HpCDF	< 1.2	< 0.04	
PCDD + PCDF	124	117	-6
TE(I-TEQ)	*2.6*	*2.4*	*-8*

(nd = not detectable)

4. Results

All concentrations measured in the emissions together with the mass flows derived from them (mg I-TEQ/h) are listed in Table 4-1. In addition, this table provides the results of multiple measurements, test measurements, measurements in the uncleaned flue gases and measurements in the emissions from scattered sources. For providing a better survey over the companies involved in the measurements they are presented in the table in alphabetical order. The measurements were in most cases repeated twice. In the table the average over all repetitions is given. The sum total over all measurements of the emissions in cleaned waste gases amounts to approx. 58 mg I-TEQ/h.

In Table 4-2 those plants are listed in which concentrations of >1 ng I-TEQ/m³ were measured in the cleaned waste gases. In order to provide an idea of the range of concentrations obtained by the individual measurements, the averages and individual values of 10 plants listed in Table 4-2 are illustrated in Fig. 4-1 as examples.

Table 4-3 lists the plants with concentrations of $\leq$ 1 ng I-TEQ/m³ and $\geq$ 0.1 ng I-TEQ/m³. These plants cause an average total emission of 0.64 mg I-TEQ/h constituting about 1% of the total mass flow obtained. In Fig. 4-2 the range of individual values in that group of plants is illustrated for some of them. The results provided in that Figure for a bath of molten copper were measured on a membrane filter which was tested and the results presented for a wood-fired furnace were measured in a plant which is not subject to licensing.

The plants with concentrations of < 0.1 ng I-TEQ/m³ in the cleaned gas are listed in Table 4-4. In the plant of the company Vinnolit GmbH in Cologne no dioxin was detected. For the group of plants with concentrations of < 0.1 ng I-TEQ/m³ a mass flow of 0.09 mg I-TEQ/h was obtained. For assessing the importance of these plants the discharge conditions need to be taken into consideration as well.

In Table 4-5 emitters with an emission mass flow of > 0.005 mg I-TEQ/h are listed. The threshold of 0.005 mg I-TEQ/h was selected because a modern 16t waste incinerator with a concentration of 0.05 ng I-TEQ/m³ in the cleaned gas and a waste gas amount of approx. 100,000 m³/h emits a mass flow of dioxins of 0.005 mg I-TEQ/h. The average hourly emissions of the plants mentioned in Table 4-5 amount to a total of 58 mg I-TEQ/h. The results of the analyses of dust samples from the dust collectors are presented in Table 4-6. Further explanations of the results of the measurements are provided for selected plants in Section 5.

Table 4-1: Listing of all mean values of the emission measurements, including measurements of raw gas and pilot measurements.

company	**type of installation**	**emission flux, mg I-TEQ/h**	**concentration, ng I-TEQ/m³**
Alugral GmbH Metallwerk	secondary aluminium smelter	0.031	0.19
Bayer AG, Werk Dormagen	central waste gas incineration	pilot operation	0.013
Bayer Werke Leverkusen	residue incineration	0.00006	0.0059
Berzelius MHD	Imperial smelting plant, Kastrup filter	0.0001	0.0032
Berzelius MHD	sintering plant, high-capacity filter (source 118)	0.00004	0.004
Berzelius MHD	sintering plant, scrubber, mixing cylinder (source 9)	0.0002	0.009
Berzelius MHD	sintering plant, dust removal from sintering belt behind double contact plant	0.0007	0.01
Berzelius MHD	sintering plant, charging installation (source 13)	0.003	0.034
Berzelius MHD	cowper, recuperator	0.009	0.096
Berzelius MHD	tin plant, short rotary furnace 2	0.092	5.9
Berzelius MHD	rotating cylinder	1.04	20.8
Berzelius MHD	hot-briquetting unit	3.69	70
Blomberger Holzindustrie B. Hausmann GmbH & Co. KG	wood-waste incineration	0.000055	0.002
Blomberger Holzindustrie B. Hausmann GmbH & Co. KG	wood-waste incineration, start-up operation	start up operation	0.007
Busch Jäger	smelter for oil containing brass chips	0.0001	0.002
DEUMU Deutsche Erz- und Metallunion GmbH	shredder	0.0028	0.032
Deutsche Gasrußwerke GmbH & Co.	boiler with residual gas incineration	0.0005	0.007
Deutsche Solvay-Werke GmbH	vinyl chloride production	0.00034	0.053

Table 4-1: **continuation**

company	type of installation	emission flux, mg I-TEQ/h	concentration, ng I-TEQ/m³
Duisburger Kupferhütte AG	dust removal from the blast furnace area in the foundry	0.0003	0.003
Duisburger Kupferhütte AG	recuperator at the blast furnace	0.0015	0.021
Duisburger Kupferhütte AG	sintering plant	13.2	46.7
Ford Werke AG	secondary aluminium smelter	0.003	0.13
Gerresheimer Glas AG	tank furnace	0.0002	0.0054
Gottschol Aluminium GmbH	secondary aluminium smelter, hearth	0.0007	0.023
Grillo-Werke AG	plant for the production of sulphur dioxide	0.0007	0.029
Grillo-Werke AG	zinc smelter, including secondary smelter	0.0052	0.097
Heinrich Schneider	copper and brass smelter	0.0001	0.02
Heinrich Schneider	copper and brass smelter	0.0006	0.023
Hoesch Stahl AG	iron ore sintering plant, sintering belt 3, pilot plant	pilot plant	4.38
Hoesch Stahl AG	iron ore sintering plant, sintering belt 4, pilot plant	pilot plant	6.44
Hoesch Stahl AG	iron ore sintering plant, sintering belt 4, pilot plant	pilot plant	22.68
Hoesch Stahl AG	iron ore sintering plant, sintering belt 3, pilot plant	pilot plant	8.38
Hoesch Stahl AG	iron ore sintering plant, loading of sintering belt 3	0.00009	0.0007
Hoesch Stahl AG	iron ore sintering plant, loading of sintering belt 4	0.00024	0.0016
Hoesch Stahl AG	iron ore sintering plant, dust removal from sintering belt 3	0.0024	0.0109
Hoesch Stahl AG	iron ore sintering plant, dust removal from sintering belt 4	0.272	0.619
Hoesch Stahl AG	iron ore sintering plant, dust removal from sintering belt	5.8	11.55

Table 4-1: continuation

company	type of installation	emission flux, mg I-TEQ/h	concentration, ng I-TEQ/m^3
Hoesch Stahl AG	iron ore sintering plant, sintering belt 3, dust removal	20.4	43.2
Hoogovens Aluminium Hüttenwerk GmbH	anode plant	0.0005	0.002
Hoogovens Aluminium Hüttenwerk GmbH	fusion electrolysis	0.0037	0.0037
Homitex Werke. Gebr. Cloos GmbH	fibre board plant, press	0.0005	0.0059
Homitex Werke. Gebr. Cloos GmbH	fibre board plant, rotary drier with hot gas production	0.019	0.25
Hüttenmann Holz GmbH & Co. KG	bark burning	0.000173	0.018
Isola Werke AG	incineration of residues	0.00001	0.0023
Krupp-Stahl AG	Bessemer steel works	0.02	0.038
Leichtmetall Gesellschaft mbH	aluminium foundry with chlorinating plant	0.000008	0.026
Linnemann GmbH & Co.	incineration of wood waste and plastics , ca. 7 MW, old boiler	0.0008	0.05
Metallhandelsgesellschaft Tacke & Co.	zinc smelter	0.0003	0.028
Metallhütten- und Recyclinggesellschaft Schuhmacher mbH & Co.	secondary non-ferrous metal smelter	0.064	1.63
Metallhüttenwerke Bruch GmbH	secondary aluminium smelter, waste gases from hearths are ducted	measurement of the uncleaned gas	0.27
Metallhüttenwerke Bruch GmbH	secondary aluminium smelter, waste gases drawn off from hearths	0.0004	0.0038
Metallhüttenwerke Bruch GmbH	secondary aluminium smelter, waste gases drawn off from hearths	pilot operation	0.0039
Metallhüttenwerke Bruch GmbH	secondary aluminium smelter, waste gases drawn off from hearths	second measurement	0.0069
Metallhüttenwerke Bruch GmbH	secondary aluminium smelter, exhaust ventilation	0.00255	0.0113
Metallhüttenwerke Bruch GmbH	secondary aluminium smelter, waste gases drawn off from hearths	measurement of the uncleaned gas	0.07

Table 4-1: continuation

company	type of installation	emission flux, mg I-TEQ/h	concentration, ng I-TEQ/m³
Metallhüttenwerke Bruch GmbH	metal chip recycling plant	0.038	1.05
Metallhüttenwerke Bruch GmbH	lead and tin smelter	0.038	2.7
Metallhüttenwerke Bruch GmbH	secondary aluminium smelter, waste gases drawn off from hearths	measurement of the uncleaned gas	6.1
Metallhüttenwerke Bruch GmbH	secondary aluminium smelter, waste gases drawn off from hearths	measurement of the uncleaned gas	6.1
Metallwerk Dinslaken GmbH & Co.	zinc recovery and secondary smelter	comparison measurement	0.121
Metallwerk Dinslaken GmbH & Co.	zinc recovery and secondary smelter	0.0009	0.0417
Metallwerk Dinslaken GmbH & Co.	zinc recovery	0.0022	0.052
Metallwerk Olsberg GmbH	secondary aluminium smelter	0.262	2.68
Muschert & Gierse	plant for cleaning paint shop equipment	0.00000014	0.0039
Niehoff	burning of wood waste, 0.97 MW	pilot operation	3.06
Niehoff	burning of wood waste, 0.97 MW	pilot operation	8.79
Niehoff	burning of wood waste, 0.97 MW	pilot operation	0.62
Niehoff	burning of wood waste, 0.97 MW	0.0086	5.77
Nolte Möbel	boiler with furnace for burning wood waste, 7 MW thermal capacity	0.0001	0.008
Norsk Hydra Magnesiumgesellschaft mbH	secondary magnesium smelter	0.0012	0.203
Otto Fuchs Metallwerke	aluminium foundry without chlorination	0.00016	0.002
RAG Kokerei Kaiserstuhl	surplus gas from dry cooling of coke	no source	0.002
RAG Kokerei Kaiserstuhl	flue battery II	0.000711	0.003
RAG Kokerei Kaiserstuhl	flue battery I	0.0014	0.006

Table 4-1: continuation

company	type of installation	emission flux, mg I-TEQ/h	concentration, ng I-TEQ/m^3
RAG Kokerei Kaiserstuhl	dust removal from coking plant	0.0011	0.006
RAG Kokerei Kaiserstuhl	dust removal from dry cooling of coke	0.0003	0.006
RAG Kokerei Kaiserstuhl	emissions from gas pipes	0.000004	0.009
RAG Kokerei Kaiserstuhl	flue battery II	pilot operation	0.01
RAG Kokerei Kaiserstuhl	quenching tower	0.00004	0.012
RAG Kokerei Kaiserstuhl	emissions from charging openings	0.0005	0.012
RAG Kokerei Kaiserstuhl	coke cooling	0.0013	0.014
RAG Kokerei Kaiserstuhl	leakage gas	0.0018	0.05
Recyclingwerk Olsberg	secondary aluminium and non-ferrous metal smelters	0.0081	0.062
Ruhr-Zink GmbH	calcining installation for the production of zinc oxide	0.00009	0.0018
Seppelfricke GmbH & Co.	foundry for brass bolts	0.0002	0.003
Siegfried Jacob Metallwerke	copper smelter	0.001	0.08
Siegfried Jacob Metallwerke	copper smelter	pilot operation	0.19
Siegfried Jacob Metallwerke	copper smelter	pilot operation	0.26
Siegfried Jacob Metallwerke	crucible type induction furnace	0.0001	0.01
Stadt Duisburg	crematorium	0.00003	0.004
Stadt Duisburg	crematorium	measurement of uncleaned waste gas	0.38
Thyssen Stahl AG	blast furnace 1, dust removal from air in foundry	0.002	0.0024
Thyssen Stahl AG	sintering plant 4, roof vents, scattered source (source 79)	no volume flow measurements	0.0083

Table 4-1: continuation

company	**type of installation**	**emission flux, mg I-TEQ/h**	**concentration, ng I-TEQ/m³**
Thyssen Stahl AG	blast furnace 1, recuperator	0.01	0.0322
Thyssen Stahl AG	sintering plant 4, roof vents, scattered source (source 78)	no volume flow measurements	0.0781
Thyssen Stahl AG	sintering plant 4, dust removal from drawn off air	0.317	0.463
Thyssen Stahl AG	sintering plant 3, dust removal from sintering belts	1.95	1.89
Thyssen Stahl AG	sintering plant 4, dust removal from sintering belts	1.62	2.37
VAW Vereinigte Aluminiumwerke AG, Erftwerk	secondary aluminium smelter	0.6	4.34
Vinnolit Kunststoff GmbH, Werk Köln	polyvinyl chloride production	nd	nd
W. Prym	copper and brass smelter	0.0003	0.005
Zeller Recycling	incineration of photographic film for the recovery of silver	0.00005	0.009

nd: not detectable

total emission:
58.54 mg I-TEQ/h

Table 4-2: Emitters with waste gas concentrations > 1 ng I-TEQ/m^3

company	type of installation	emission flux, mg/h	concentration ng I-TEQ/m^3	level of emission, m
Berzelius MHD	hot briquetting plant	3.69	70	
Duisburger Kupferhütte AG	sintering plant	13.2	46.7	250
Hoesch Stahl AG	iron ore sintering plant, sintering belt 4, dust removal from the belt	29.4	43.2	140
Berzelius MHD	rotating cylinder	1.04	20.8	81
Hoesch Stahl AG	iron ore sintering plant, sintering belt 3, dust removal from the sintering belt	5.8	11.55	140
Berzelius MHD	tin plant, short rotary furnace	0.092	5.9	
Niehoff	burning of wood waste, 0.97 MW	0.0096	5.77	11
VAW Vereinigte Aluminiumwerke AG, Erftwerk	secondary aluminium smelter	0.6	4.34	31
Metallhüttenwerke Bruch GmbH	lead and tin smelter	0.038	2.7	16
Metallwerk Olsberg GmbH	secondary aluminium smelter	0.262	2.68	26
Thyssen Stahl AG	sintering plant 4, dust removal from sintering belt	1.62	2.37	250
Thyssen Stahl AG	sintering plant 3, dust removal from sintering belt	1.95	1.89	250
Metallhütten- und Recyclinggesellschaft Schumacher mbH & Co.	secondary non-ferrous metal smelter	0.064	1.63	39
Metallhüttenwerke Bruch GmbH	metal chip recycling	0.038	1.05	15

total emission:
57.80 mg I-TEQ/h

Figure 4-1: Plants with average emission concentrations of ≥ ng I-TEQ/m³

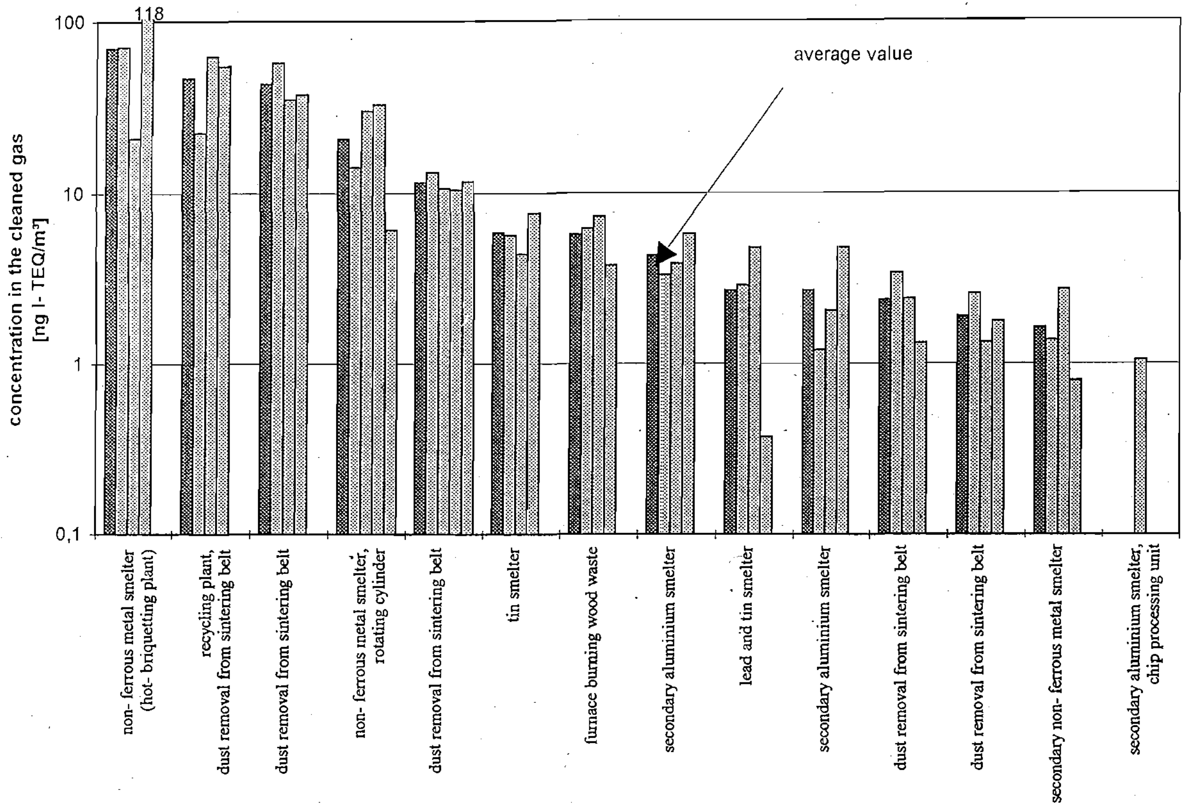


Table 4-3: Emitters with waste gas concentrations ≤ 1 and ≥ 0.1 ng ng I-TEQ/m^3

company	type of installation	emission flux, mg/h	concentration ng I-TEQ/m^3	level of emission, m
Hoesch Stahl AG	iron ore sintering plant, sintering belt 4, dust removal	0.272	0.619	40
Thyssen Stahl AG	sintering plant 4, dust removal	0.317	0.463	60
Homitex Werke, Gebr. Cloos GmbH	fibre board plant, rotary drier with hot gas production	0.019	0.25	80
Norsk Hydro Magnesium gesellschaft mbH	secondary magnesium smelter	0.0012	0.203	13
Alugral GmbH Metallwerk	secondary aluminium smelter	0.031	0.19	50
Ford Werke AG	secondary aluminium smelter	0.003	0.13	25

total emission:
0.64 mg I-TEQ/h

Figure 4-2: Plants with average emission concentrations of
< 1 and > 0,1 ng I-TEQ/m³

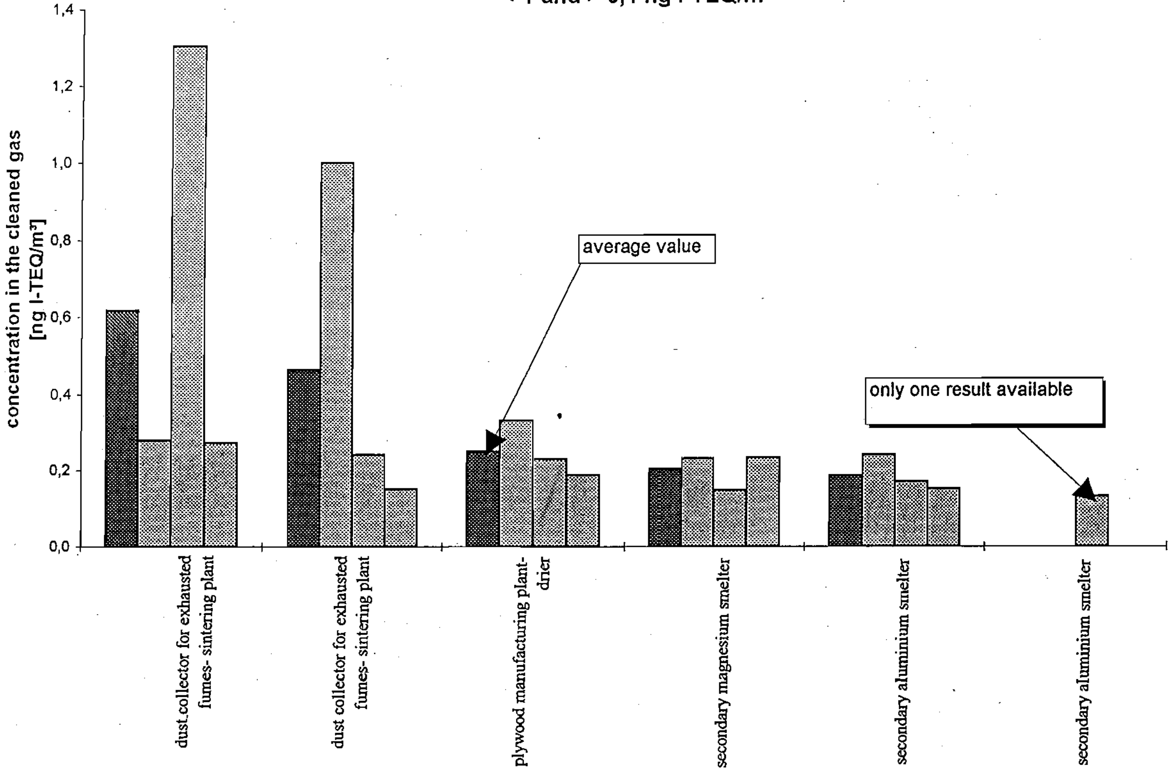


Table 4-4: Emitters with a mean waste gas concentration < 0.1 ng I-TEQ/m³

company	type of installation	emission flux, mg/h	concentration ng I-TEQ/m³	level of emission, m
Grillo-Werke AG	zinc smelters, including secondary smelters	0.0052	0.097	97
Berzelius MHD	cowper/recuperator	0.009	0.096	
Siegfried Jacob Metallwerke	copper smelter	0.001	0.08	22
Recyclingwerk Olsberg	secondary aluminium and non-ferrous metal smelter	0.0081	0.062	26
Deutsche Solvay-Werke GmbH	vinyl chloride production	0.00034	0.053	40
Metallwerk Dinslaken GmbH & Co.	zinc recovery plant	0.0022	0.052	5
RAG Kokerei Kaiserstuhl	emissions from gas leaks	0.0018	0.05	
Linnemann GmbH & Co.	burning of wood waste, paper and plastics, ca. 7 MW, old boiler	0.0008	0.05	32
Metallwerk Dinslaken GmbH & Co.	zinc recovery plant and secondary zinc smelter	0.0009	0.0417	45
Krupp-Stahl AG	Bessemer steel works	0.02	0.038	
Berzelius MHD	sintering plant, charging installation (source 13)	0.003	0.034	30
Thyssen Stahl AG	blast furnace 1, recuperator	0.01	0.0322	145
DEUMU Deutsche Erz- und Metallunion GmbH	shredder	0.0028	0.032	16
Grillo-Werke AG	installation for the production of sulphur dioxide	0.0007	0.029	
Metallhandelsgesellschaft Tacke & Co.	zinc smelter	0.0003	0.028	12
Leichtmetall Gesellschaft mbH	aluminium foundry with chlorination plant	0.000008	0.026	18
Heinrich Schneider	copper and brass smelter	0.0006	0.023	15
Gottschol Aluminium GmbH	secondary aluminium smelter, hearth	0.0007	0.023	11
Duisburger Kupferhütte AG	recuperator at the blast furnace	0.0015	0.021	60

Table 4-4: continuation

company	type of installation	emission flux, mg/h	concentration ng I-TEQ/m^3	level of emission, m
Heinrich Schneider	copper and brass smelter	0.0001	0.02	15
Hüttermann Holz GmbH & Co. KG	burning of bark	0.000173	0.018	20
RAG Kokerei Kaiserstuhl	coke cooling	0.0013	0.014	62
RAG Kokerei Kaiserstuhl	quenching tower	0.00004	0.012	50
RAG Kokerei Kaiserstuhl	emissions from charging openings	0.0005	0.012	
Metallhüttenwerke Bruch GmbH	secondary aluminium smelter, exhaust air	0.00255	0.0113	11
Hoesch Stahl AG	iron ore sintering plant, dust removal from sintering belt 3	0.0024	0.0109	28
Siegfried Jacob Metallwerke	crucible type induction furnace	0.0001	0.01	22
Berzelius MHD	sintering plant, dust removal from sintering belt behind the double contact installation	0.0007	0.01	22
Zeller Recycling	incineration of photographic film for the recovery silver of	0.00005	0.009	18
RAG Kokerei Kaiserstuhl	emissions from gas pipes	0.000004	0.009	
Berzelius MHD	sintering plant, scrubber and mixing cylinder (source 9)	0.0002	0.009	21
Nolte Möbel	boiler for wood waste, 7 MW thermal capacity	0.0001	0.008	26
Deutsche GasrußwerkeGmbH & Co.	boiler installation with residual gas incineration	0.0005	0.007	41
RAG Kokerei Kaiserstuhl	flue battery I	0.0014	0.006	165
RAG Kokerei Kaiserstuhl	dust removal from coke	0.0011	0.006	40
RAG Kokerei Kaiserstuhl	dust removal from dry cooling of coke	0.0003	0.006	54
Homitex Werke, Gebr. Cloos GmbH	fibre board production, press	0.0005	0.0059	70
Bayer Werke, Leverkusen	incineration of residues	0.00006	0.0059	37

Table 4-4: continuation

company	type of installation	emission flux, mg/h	concentration ng I-TEQ/m³	level of emission, m
Gerresheimer Glas AG	tank furnace	0.0002	0.0054	70
W. Prym	copper and brass smelter	0.0003	0.005	20
Stadt Duisburg	crematorium	0.00003	0.004	0
Berzelius MHD	sintering plant high capacity filter (source 118)	0.00004	0.004	23
Muschert & Gierse	installation for cleaning paint shop equipment	0.00000014	0.0039	
Metallhüttenwerke Bruch GmbH	secondary aluminium smelter, drawn-off hearth gas	0.0004	0.0038	80
Hoogovens Aluminium Hüttenwerk GmbH	fusion electrolysis	0.0037	0.0037	130
Berzelius MHD	Imperial smelting plant, Kastrup filter	0.0001	0.0032	
Seppelfricke GmbH & Co.	foundry for brass bolts	0.0002	0.003	18
RAG Kokerei Kaiserstuhl	flue battery II	0.000711	0.003	165
Duisburger Kupferhütte AG	dust removal from the blast furnace area in the foundry	0.0003	0.003	35
Thyssen Stahl AG	dust removal from the foundry shed in the area of blast furnace 1	0.002	0.0024	31
Isola Werke AG	incineration of residues	0.00001	0.0023	20
Otto Fuchs Metallwerke	aluminium foundry without chlorination	0.00016	0.002	23
Hoogovens Aluminium Hüttenwerk GmbH	production of anodes	0.0005	0.002	45
Busch Jäger	smelter for oil containing brass chips	0.0001	0.002	18.5
Blomberger Holzindustrie B. Hausmann GmbH & Co. KG	burning of wood waste	0.000055	0.002	70
Ruhr-Zink GmbH	calcining plant for the production of zinc oxide	0.00009	0.0018	
Hoesch Stahl AG	iron ore sintering plant, sinter transfer, sintering belt 4	0.00024	0.0016	25
Hoesch Stahl AG	iron ore sintering plant, sinter transfer, sintering belt 3	0.00009	0.0007	25

total emission:
0.09 mg I-TEQ/h

Table 4-5: Emitters with a mean emission mass flux > 0.005 mg I-TEQ/h

company	**type of installation**	**emission flux, mg/h**	**concentration ng I-TEQ/m^3**	**level of emission, m**
Hoesch Stahl AG	iron ore sintering plant, sintering belt 4, dust removal	29.4	43.2	140
Duisburger Kupferhütte AG	sintering plant	13.2	46.7	250
Hoesch Stahl AG	iron ore sintering plant, sintering belt 3, dust removal	5.8	11.55	140
Berzelius MHD	hot briquetting plant	3.69	70	
Thyssen Stahl AG	sintering plant 3, dust removal from the sintering belt	1.95	1.89	250
Thyssen Stahl AG	sintering plant 4, dust removal from the sintering belt	1.62	2.37	250
Berzelius MHD	rotating cylinder	1.04	20.8	81
Thyssen Stahl AG	sintering plant 4, dust removal	0.317	0.463	60
Hoesch Stahl AG	iron ore sintering plant, dust removal from sintering belt 4	0.272	0.619	40
Metallwerk Olsberg GmbH	secondary aluminium smelter	0.262	2.68	26
Berzelius MHD	tin plant, short rotary furnace	0.092	5.9	
Metallhütten- und Recyclinggesellschaft Schumacher mbH & Co.	non-ferrous metal smelter	0.064	1.63	39
Metallhüttenwerke Bruch GmbH	lead and tin smelter	0.038	2.7	16
Metallhüttenwerke Bruch GmbH	metal chip recycling	0.038	1.05	15
Algural GmbH Metallwerk	secondary aluminium smelter	0.031	0.19	50
Krupp-Stahl AG	Bessemer steelworks	0.02	0.038	
Hornitex Werke, Gebr. Cloos GmbH	fibre board plant, rotary drier with hot gas production	0.019	0.25	80
Thyssen Stahl AG	blast furnace 1, recuperator	0.01	0.0322	145
Berzelius MHD	cowper, recuperator	0.009	0.096	

Table 4-5: **continuation**

company	type of installation	emission flux, mg/h	concentration ng I-TEQ/m^3	level of emission, m
Niehoff	burning of wood waste, 0.97 MW	0.0086	5.77	11
Recyclingwerk Olsberg	secondary aluminium and non-ferrous metal smelter	0.0081	0.062	26
Grillo-Werke AG	zinc smelter, including secondary smelter	0.0052	0.097	97

total emission:
57.89 mg I-TEQ/h

Table 4-6: Results of the analyses of dust samples

no.	company	installation	type of sample	dioxin content, µg I-TEQ/kg
1	Berzelius MHD	hot briquetting-plant	dust from electrostatic precipitator	42
2	Berzelius MHD	tin plant	dust from electrostatic precipitator	3.1
3	Berzelius MHD	tin plant	cooling tower dust	1.8
4	Berzelius MHD	sintering plant	filter dust	0.1
5	Berzelius MHD	sintering plant	dust from a vacuum cleaner	0.1
6	Berzelius MHD	tin plant	dust from the flue	0.1
7	Berzelius MHD	tin plant	input material	0.1
8	Berzelius MHD	sintering plant	scrubber sludge	0.003
9	Berzelius MHD	sintering plant	recycled material	nd
10	Metallhüttenwerke Bruch	lead and tin smelter	filter dust	12
11	Metallhüttenwerke Bruch	lead and tin smelter	filter dust	5.3
12	Metallhüttenwerke Bruch	secondary aluminium smelter	mixed samples of filter dust	2.5
13	Metallhüttenwerke Bruch	secondary aluminium smelter	mixed samples of filter dust	2.4
14	Niehoff	wood-fired furnace	mixed samples of filter dust	80
15	Niehoff	wood-fired furnace	mixed samples of filter dust	44
16	Niehoff	wood-fired furnace	mixed samples of cyclone dust	43
17	Niehoff	wood-fired furnace	mixed samples of cyclone dust	27
18	Recyclingwerk Olsberg	secondary aluminium and non-ferrous metal smelter	filter dust	38

Table 4-6: continuation

no.	company	installation	type of sample	dioxin content, µg I-TEQ/kg
19	Recyclingwerk Olsberg	secondary aluminium and non-ferrous metal smelter	filter dust	29
20	Recyclingwerk Olsberg	secondary aluminium and non-ferrous metal smelter	filter dust	23
21	Seppelfricke GmbH & Co.	brass foundry	filter dust	1.1
22	Seppelfricke GmbH & Co.	brass foundry	filter dust	1
23	Seppelfricke GmbH & Co.	brass foundry	filter dust	0.9
24	Seppelfricke GmbH & Co.	brass foundry	dust from the first filter stage	0.04
25	Seppelfricke GmbH & Co.	brass foundry	dust from the first filter stage	0.03
26	Seppelfricke GmbH & Co.	brass foundry	dust from the first filter stage	0.02
27	Thyssen Stahl AG	dust removal from indoor air	mixed sample	2.1
28	Thyssen Stahl AG	dust removal from sintering belts	dust from electrostatic precipitator	1.2
29	Thyssen Stahl AG	dust removal from sintering belts	dust from electrostatic precipitator	0.7
30	Berzelius MHD	hot briquetting plant	input pellets	0.4
31	Berzelius MHD	Imperial smelting plant	dust from electrostatic precipitators	0.08
32	Duisburger Kupferhütte	sintering plant	dust from electrostatic precipitator	1
33	Duisburger Kupferhütte	sintering plant	purple ore	0.6
34	Duisburger Kupferhütte	sintering plant	filter sludge	0.051
35	Duisburger Kupferhütte	sintering plant	raw material for sintering	0.023

Table 4-6: continuation

no.	company	installation	type of sample	dioxin content, µg I-TEQ/kg
36	Duisburger Kupferhütte	sintering plant	dusts from steelworks	0.009
37	Duisburger Kupferhütte	sintering plant	finished sinter	0.002
38	Ford-Werke AG	secondary aluminium smelter	filter dust	0.002
39	Gottschol Aluminium GmbH	secondary aluminium smelter	mixed filter dust samples	54
40	Krupp Hoesch Stahl AG	dust removal from sintering belts	dust from electrostatic precipitator	7.2
41	Krupp Hoesch Stahl AG	dust removal from sintering belts	dust from electrostatic precipitator	6.2
42	Krupp Hoesch Stahl AG	dust removal from sintering belts	dust from electrostatic precipitator	4.3
43	Krupp Hoesch Stahl AG	dust removal from sintering belts	dust from electrostatic precipitator	3.8
44	Krupp Hoesch Stahl AG	dust removal from sintering belts	dust from electrostatic precipitator	2.7
45	Krupp Hoesch Stahl AG	dust removal from sintering belts	dust from electrostatic precipitator	2.7
46	Krupp Hoesch Stahl AG	dust removal from sintering belts	dust from electrostatic precipitator	2.7
47	Krupp Hoesch Stahl AG	dust removal from sintering belts	dust from electrostatic precipitator	0.39
48	Krupp Hoesch Stahl AG	sintering plant	blast furnace charge	0.01
49	Krupp Hoesch Stahl AG	sintering plant	blast furnace charge	0.006

Table 4-6: continuation

no.	company	installation	type of sample	dioxin content, µg I-TEQ/kg
50	Krupp Hoesch Stahl AG	sintering plant	used sand	0.003
51	Krupp Hoesch Stahl AG	sintering plant, sinter loading	finished sinter	0.001
52	Krupp Hoesch Stahl AG	sintering plant, sinter loading	finished sinter	0.001
53	Krupp Stahl AG/Duisburg	Bessemer steelworks	secondary filter dust	0.3
54	Krupp Stahl AG/Duisburg	Bessemer steelworks	primary filter dust	0.004
55	Metallwerke Dinslaken	zinc recovery plant	mixed filter dust samples	7.7
56	Siegfried Jacob Metallwerke	copper smelter	mixed filter dust samples	2
57	Siegfried Jacob Metallwerke	copper smelter	filter dust	6.3
58	Siegfried Jacob Metallwerke	copper smelter	filter dust	5.1
59	Siegfried Jacob Metallwerke	copper smelter	filter dust	5.4

nd: not detectable

5. Description of selected plants

5.1 Wood-fired furnace of the company Niehoff

This company operates a furnace fired with wood waste which is equipped with a fabric-filter. The wood waste comprises wood chips, saw dust, wood meal from abrasive operations and wood blocks containing the remains of lacquer and glue. The fuel stems from the manufacture of solid-wood furniture and enters the combustion chamber via an underfeed grate. The heat production is controlled by intermittent operation of the furnace. The measurements were taken during standard operation.

In the fabric-filter for cleaning the flue gas of the furnace the dust concentrations are reduced to < 10 mg/m³. The fabric-filter has been designed for a waste gas temperature of 250 °C. The filter is preceded by a cyclone.

The measurements were taken during following operating conditions:

operating condition A
standard operation, measurement of the emissions before and after the fabric-filter using lime as additive;

operating condition B
standard operation, measurement of the emissions before and after the fabric-filter using lime and lignite coke.

In addition, four dust samples collected in the filter were analysed for the content of PCDD/PCDF.

Six samples were taken each from the uncleaned and cleaned flue gases from the wood-fired furnace. In planning the measurements under the two operating conditions it was assumed that approximately similar operating conditions would produce approximately similar concentrations in the uncleaned flue gases. The concentrations in Table 5.1-1 show, however, that the range of concentrations is wide. Primarily, the concentrations of furans differed between the two operating conditions.

The operating condition A without use of lignite coke produced in some cases much higher concentrations of dioxins and furans - Fig. 5.1-2. The operating condition B with use of lignite coke produced much lower concentrations of dioxins and furans in samples 2 and 3 taken in the cleaned gas. The first samples which were taken revealed lower concentrations for some congeners in the uncleaned gas than in the cleaned gas - Fig. 5.1-3.

Taking the toxicity equivalents (I-TEQ) as a measure, a collection efficiency of 34 % is obtained on the average for the operating condition A. For the simultaneous use of lignite coke the collection efficiency is 79 %.

In the present case the dust collected in the cyclone and the fabric-filter was analysed. Table 5.1-1 shows the sum totals of 8 PCDD/PCDF according to appendix V, No.3 of the German hazardous substances act (Gefahrstoff-Verordnung, Anhang V, Nr.3). In the collected dusts the concentrations of these substances ranged from 103 to 312 µg/kg and were higher by one order of magnitude than the threshold limit value of 5 µg/kg. The threshold limit value for 2,3,7,8-TCDD of 2 µg/kg provided by the German hazardous substances act was also exceeded in all samples.

Table 5.1-1: Concentrations of PCDD and PCDF in dust collected in the cyclone and the fabric-filter*

	dust from cyclone operating condition A (µg/kg)	dust from cyclone operating condition B (µg/kg)	dust from filter operating condition B (µg/kg)	dust from filter operating condition B (µg/kg)
hazardous substances act	102.7	154.2	311.6	164.9
I-TEQ	27.2	43.5	80.0	44.3
2378-TCDD	2.73	4.78	4.1	3.1

* All results are based on dried matter

Both the concentrations in the gaseous emissions as well as the high concentrations of dioxins and furans in the dust collected in the separators led to the initiation of abatement measures by the company.

Figure 5.1-1: Concentrations in the uncleaned waste gas ahead of the fabric filter for both operating conditions (wood- fired furnace)

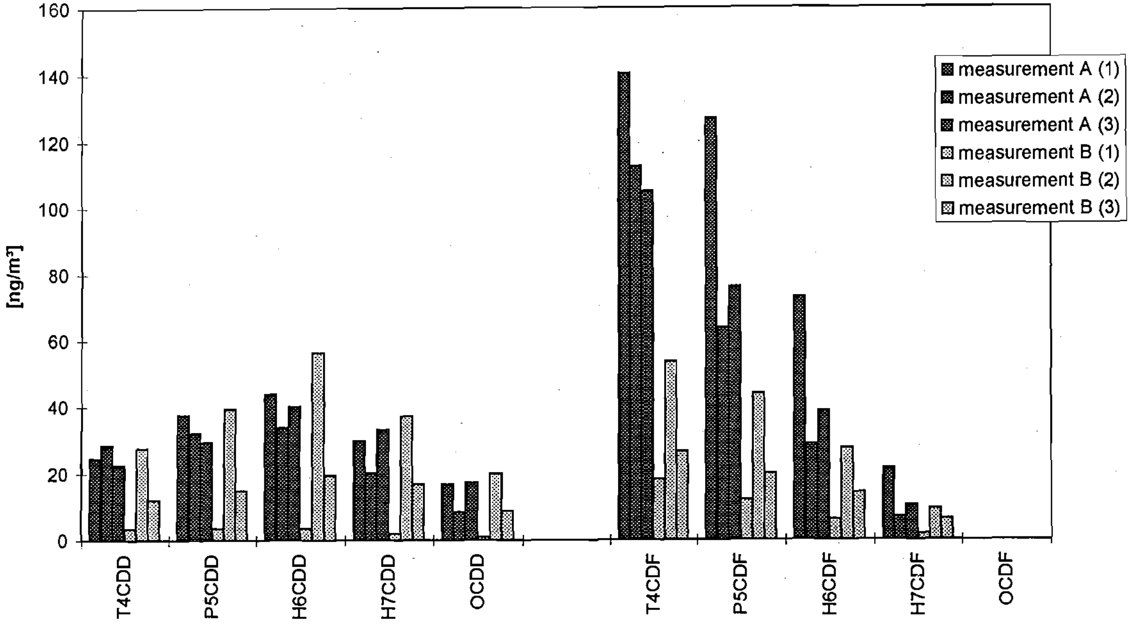


Figure 5.1-2: Concentrations of PCDD/PCDF when calcium hydrate is used for waste gas cleaning

(wood- fired furnace with fabric filter- operating condition A)

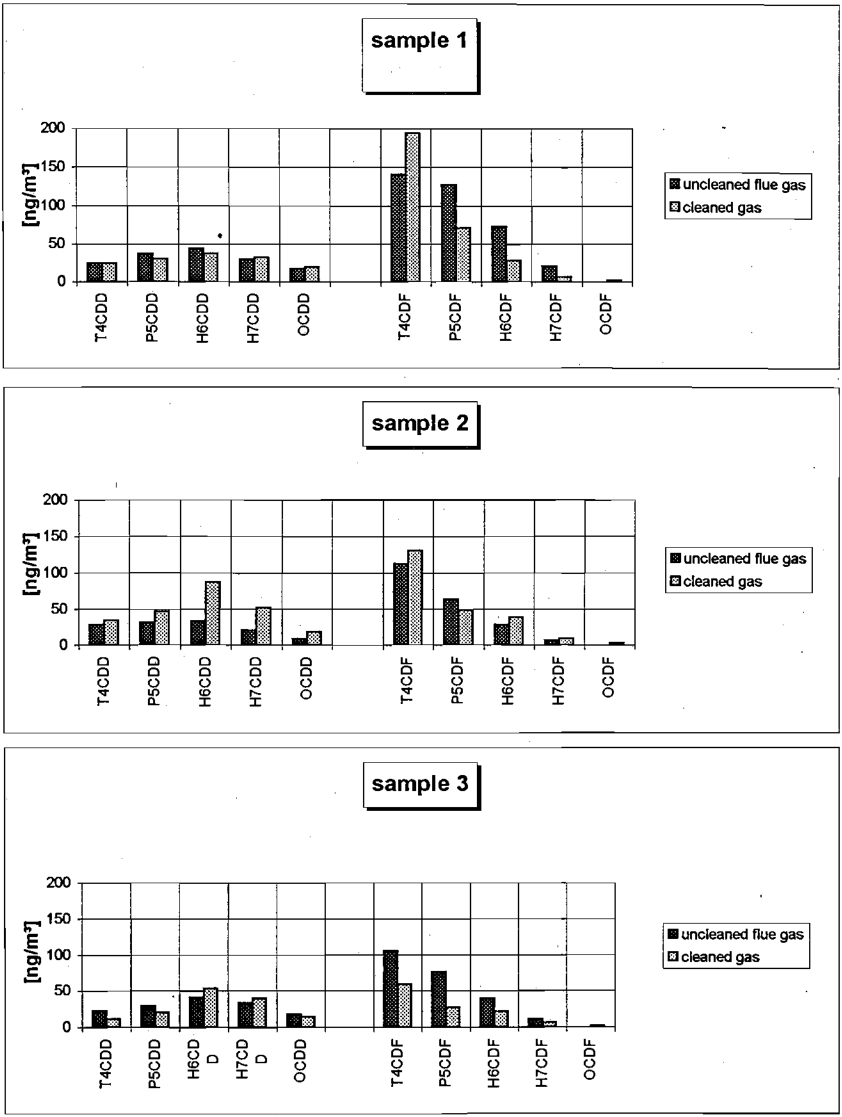
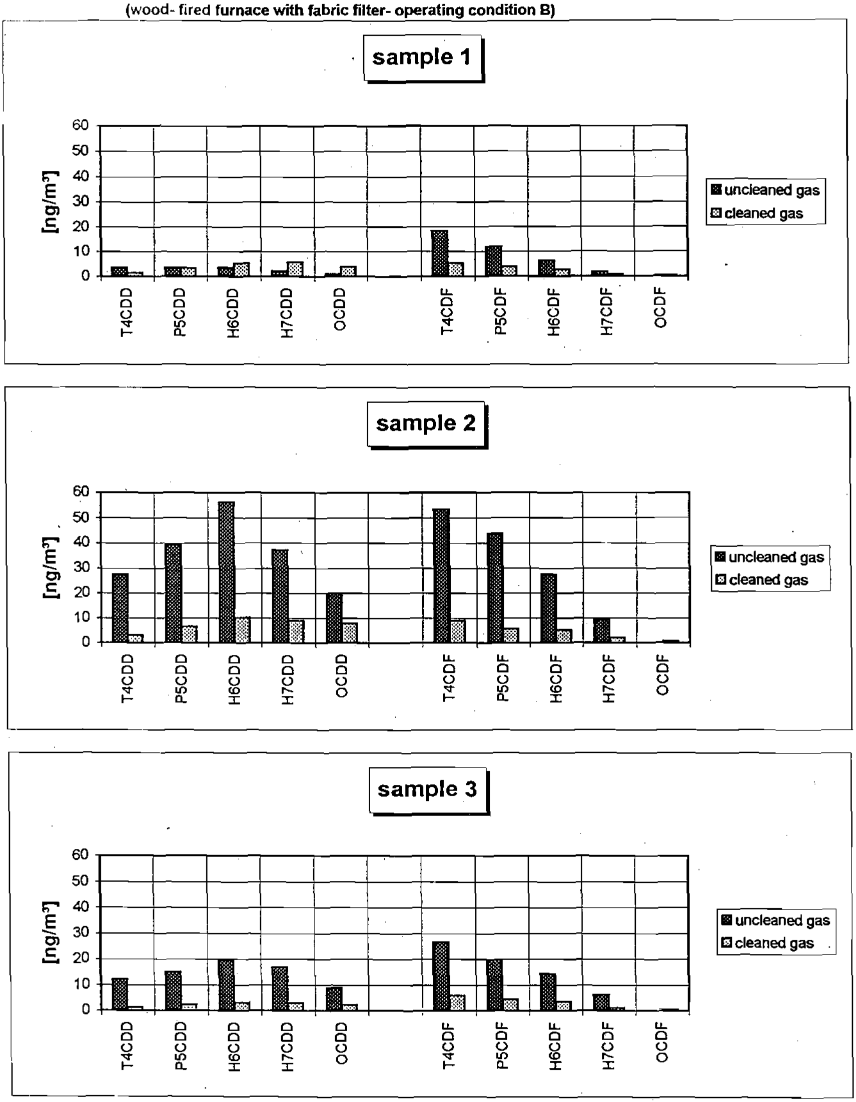


Figure 5.1-3: Concentrations of PCDD/PCDF when calcium hydrate and coke are used for flue gas cleaning

(wood- fired furnace with fabric filter- operating condition B)



5.2 Company Blomberger Holzindustrie B. Hausmann GmbH & Co. KG

This company produces mainly plywood panels which are made from sheets of beechwood which are glued together. Some of the panels are treated with flame retardants or with pesticides. The company claims that the amounts they produce of various products remain pretty constant. Following residual materials are left from the manufacture of the plywood panels:

beech bark
pieces of veneer
trimming residues
grinding dust
wood shavings

Larger residual pieces are comminuted in a chopper and transported to a fuel storage bunker. Wood dust from abrasive operations and wood shavings are compressed (without dust binders) and are also stored in the fuel storage bunker. Alternatively, wood shavings and wood dust can be directly injected into the combustion chamber when more energy is needed. The residence time of the fuels in the bunker with a volume of 150 m^3 usually amounts to approx. 20 hours. The energy which is produced is used for steaming, drying, compressing, for heating and power generation.

For combustion an incinerator with traveling grate producing 11 MW of thermal power and an oil-fired stand-by furnace are used. The capacity of the traveling-grate incinerator is controlled by varying the depth of the layer of combustible material and by the speed with which the traveling grate is moved. The supply of primary air for combustion is manually controlled. The primary air is passed through an air preheater. The incinerator is followed by a two-stage flue gas cleaning system comprising a cyclone dust collector and an electrostatic precipitator. The electrostatic precipitator is installed in the updraft flue where an underpressure prevails. The exhaust fan for the flue gas can be adjusted to the incinerator output by a control. The wood-fired incinerator is started up daily from Monday through Friday. Output fluctuations are caused by interruptions, reduced production and low heat demand.

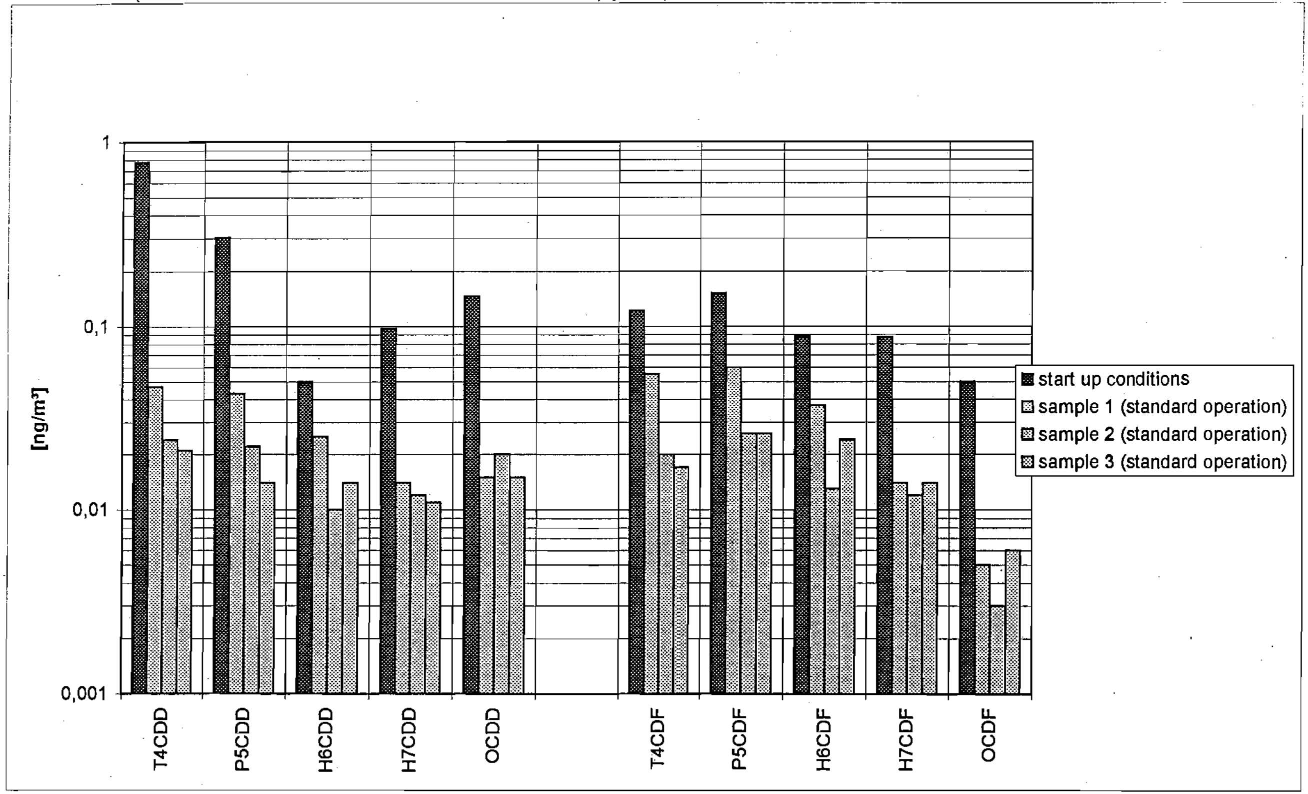
Measurements were conducted during following operating conditions:

1. Standard operation with heat output as high as possible using fuel from the storage bunker and when wood shavings and wood dust were injected provided standard operating conditions continued to prevail during injection.

2. Samples were taken during start-up and shut-down operations on three days.

As Figure 5.2-1 shows, the emissions of dioxins and furans were markedly higher during start-up than during standard operation.

Figure 5.2-1: Standard and Start- up operations
(incinerator fired with residues from the manufacture of plywood)



5.3 Company Siegfried Jacob Metallwerke

This company operates among others one 3 t induction furnace (crucible furnace) and one 5 t Thomas rotary furnace.

In the crucible furnace raw materials are molten which have a low tendency to produce slag. The rotary furnace is operated under reducing conditions when dross is processed and under oxidising conditions when, for example, Fe- and Mn-containing copper scrap is processed. At this furnace a filter for the separation of extremely fine particles with a capacity of 5000 m^3/h was tested.

Following measurements were taken in that plant:

1. Measurement in the cleaned gas of the crucible furnace
2. Measurement in the cleaned gas of the rotary furnace during oxidising conditions
3. Measurement in the cleaned gas of the rotary furnace during reducing conditions
4. Measurement in the uncleaned and cleaned gases in the test filter manufactured by the company Gore

Simultaneously with taking the samples for the measurements of the dioxins during oxidising operation of the rotary furnace when the test filter was in operation dust measurements were taken at following locations:

in the cleaned gas after the fabric-filter	M1
in the uncleaned gas ahead of the test filter	M2
in the cleaned gas after the test filter	M3

The dust concentrations measured at the various sampling locations are given in Table 5.3-1.

Table 5.3-1: Dust concentrations at the sampling locations M1, M2 and M3

sample no.	M1 (mg/m^3)	M2 (mg/m^3)	M3 (mg/m^3)
1	1.0	268	1.0
2	0.7	268	1.5
3	0.8	344	2.3

In both filters comparable dust concentrations were found in the cleaned gas. The international toxicity equivalents I-TEQ which were obtained for the dioxins are given in Table 5.3-2.

Table 5.3-2: Results of the measurements of dioxins

measurement site	sample 1 (ng/m³)	sample 2 (ng/m³)	sample 3 (ng/m³)
M1	0.04	0.05	0.06
M2	2.6*	0.27	0.11
M3	0.16	0.52	0.09
reducing conditions	0.06	0.08	0.2

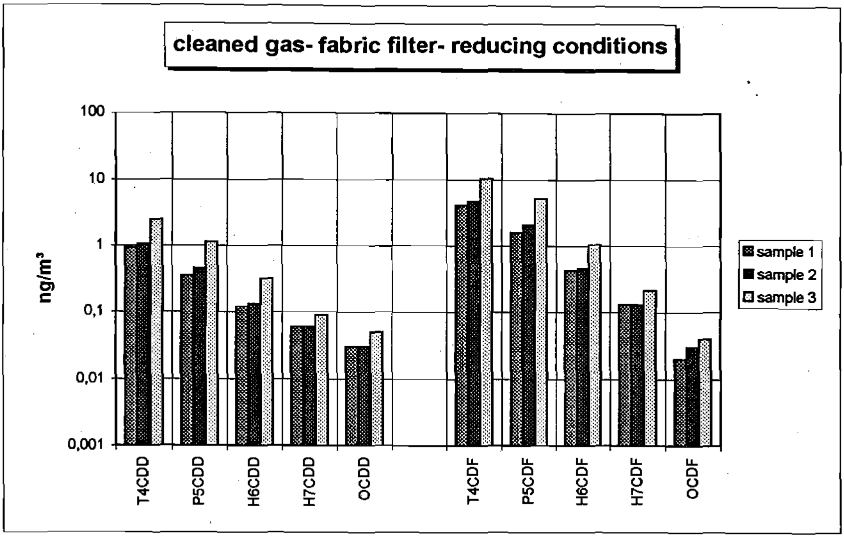
* This value was probably produced by a mistake in the operation of the test filter and was removed from the valid results.

No significant differences between the oxidising and reducing conditions became apparent. In the cleaned gas coming from the test filter two values were obtained which exceeded 0.1 ng I-TEQ/m³. However, from the relatively small number of values it cannot be concluded that the collection efficiency of the test filter is generally lower.

The results obtained for the various operating conditions are illustrated in Figures 5.3-1 to 5.3-3. Figure 5.3-1 provides the concentrations of the various TCDD/TCDF homologues in the cleaned gas coming from the fabric-filter during both the oxidising and reducing conditions in the rotary furnace. The values in the cleaned gas correspond largely to the values in the uncleaned gas presented in Figure 5.3-2. The values in the cleaned gas coming from the test filter are completely different. The reason for this probably lies in the different collection mechanisms of the test filter as compared with the fabric-filter. A comparison of the values during oxidising conditions in the rotary furnace obtained with the two filters is given in Figure 5.3-3.

Figure 5.3-1: Cleaned gas coming from the fabric filter during oxidising and reducing conditions

(melting of non- ferrous metal, rotary furnace)



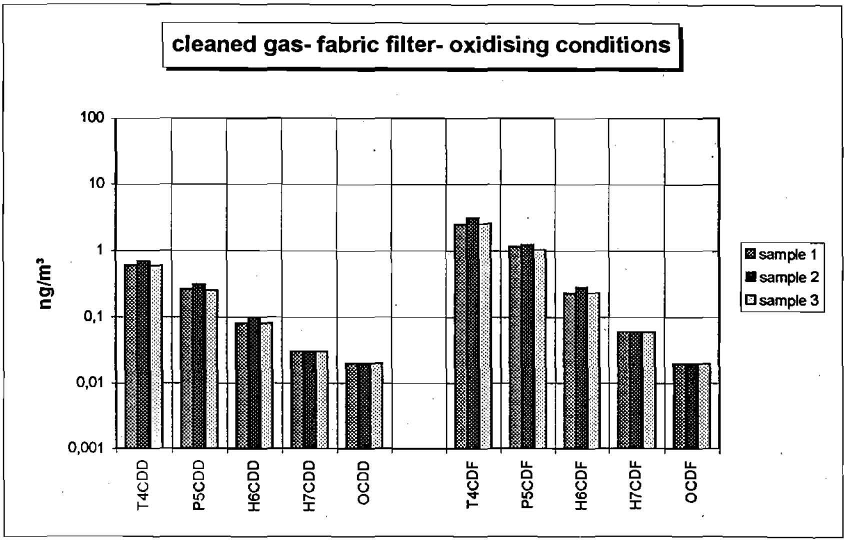
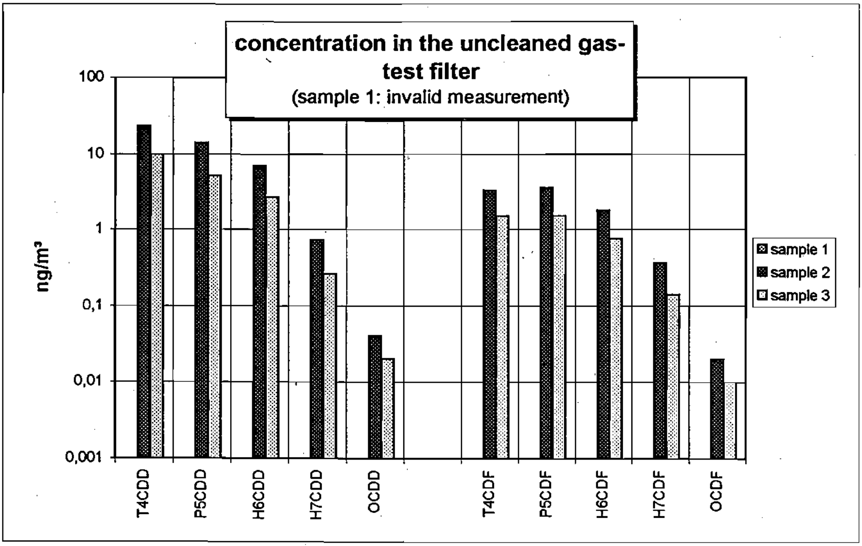


Figure 5.3- 2: Concentrations in the uncleaned and cleaned gases before and after the test filter

(melting of non- ferrous metal, rotary furnace, test filter)



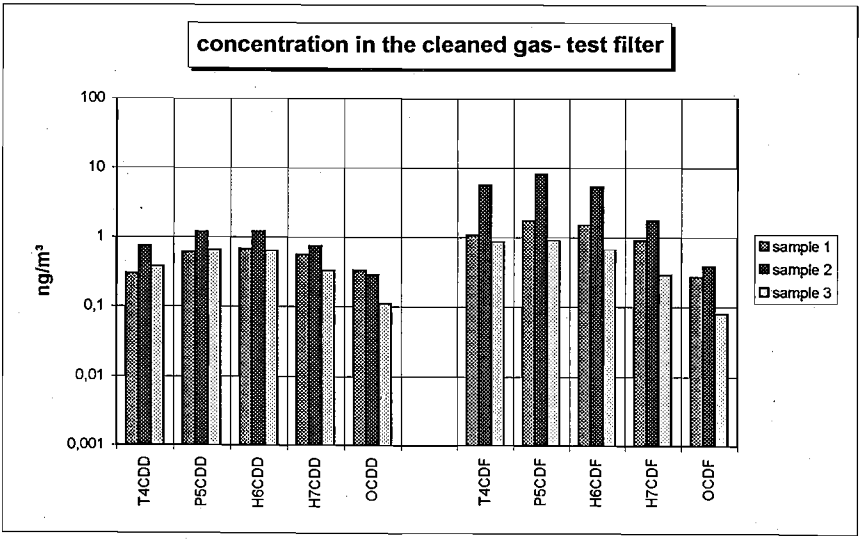
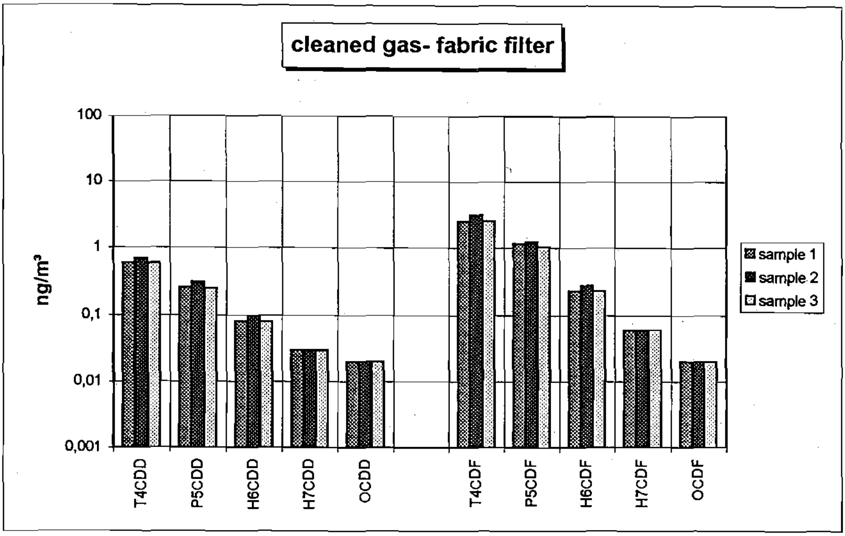
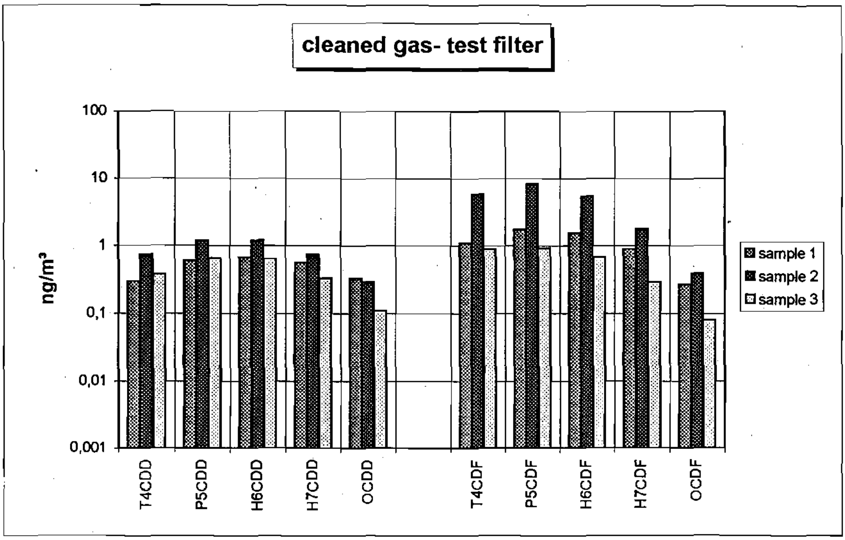


Figure 5.3-3: Comparison of fabric filter with test filter during oxidising conditions
(melting of non- ferrous metal, rotary furnace)





5.4 Company Metallwerk Dinslaken GmbH & Co.

This company recovers zinc from used materials. Following units are in operation:

Indirectly fired melting furnace for used zinc

Used zinc is molten in an indirectly heated furnace. The melt is pumped into a liquation hearth and finally cast into billets. The waste air from the burner is directly discharged into the atmosphere via a roof vent. The waste gases emitted by the bath of molten metal are drawn off and passed to the waste gas cleaning equipment. The zinc-containing slag which is obtained as by-product is sold on the market. Zinc-containing dross which is also obtained is molten in a second furnace for recovery of the metal.

Directly fired melting furnace

In this directly with natural gas fired furnace zinc containing alloys and zinc containing scrap are molten. All waste gases are passed to the waste gas cleaning equipment. Visible emissions leaking from several untight sections of the furnace during the melting process leave the room via roof vents.

Furnace 2

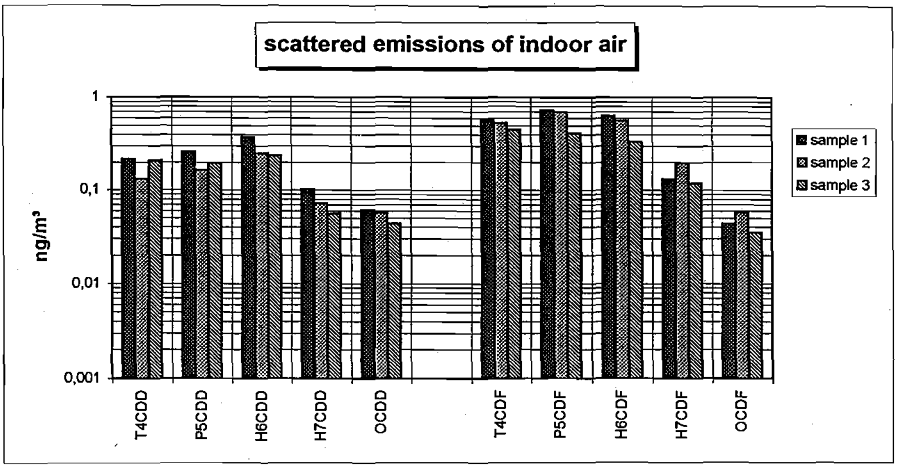
This furnace comprises an indirectly fired steel hearth with agitator. In this furnace the dross produced by melting used zinc is molten and degassed by adding NaCl/F as fluxing agent.

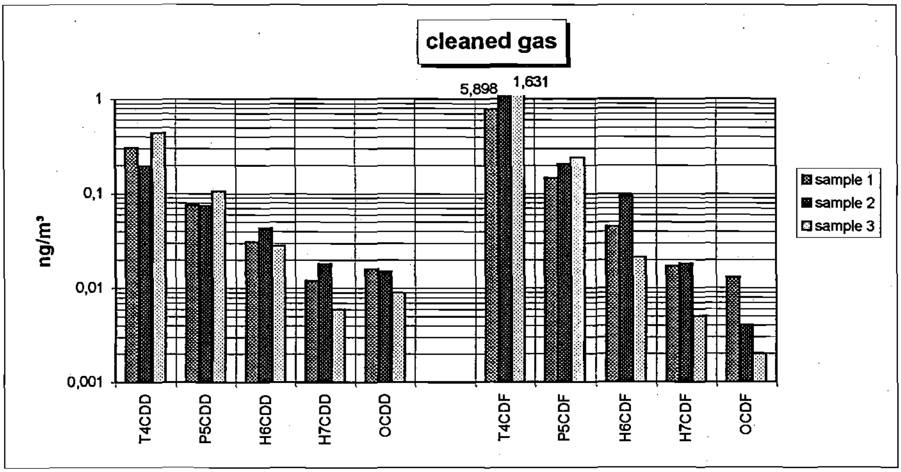
Furnace 4.4a

In this furnace zinc alloy is molten in two steel hearths and cast into billets. All fumes which are drawn off are combined. If necessary the fumes are cooled before they are passed through a fabric-filter. They are discharged via the approx. 45 m high brick stack.

In the cleaned gas coming from the fabric-filter three measurements were taken. In addition, samples were taken in indoor air which was discharged through various vents. Figure 5.4-1 presents the concentrations of dioxins and furans in both waste gas flows. The mass flow of indoor air emitted in a height of 5 m amounted to about 0.002 mg I-TEQ/h with the concentration of dioxins in this emission measuring 0.05 ng I-TEQ/m^3. About 0.0009 mg I-TEQ/h were emitted over the 45 m high stack with the concentration in that waste gas flow amounting to 0.04 ng I-TEQ/m^3.

Figure 5.4-1: Concentrations in the cleaned waste gas and in the indoor air discharged via scattered vents
(melting of zinc)





5.5 Company Metallhüttenwerke Bruch GmbH

This company operates in Dortmund a secondary aluminium smelter. In addition, a plant for treatment of alkali salts from the aluminium smelting plant is operated on the company premises. The gases and dusts from that plant are drawn off and cleaned in Venturi and other gas scrubbers and are passed to a fabric-filter together with the waste gases from the melting furnaces. The total waste gas quantity amounts to 105,000 m^3/h. The salt treatment plant contributes 21,000 m^3/h.

One of the goals of the measurements was to study the influence of the ammonia-containing waste gases from the salt treatment plant on the concentration of dioxins in the cleaned gas. In order to achieve this goal measurements were taken in the uncleaned and cleaned gases while the salt treatment plant was not in operation and approximately four weeks later the measurements in the uncleaned and cleaned gases were repeated during standard operation which included the waste gases from the salt treatment plant. During both measurements a mixture of lime with 5 % lignite coke was used as additive. With regard to the uncleaned gases measurements had to be taken in two uncleaned gas flows separately although they are combined in the end (namely in the flue gas and in the fumes drawn off by exhaust hoods).

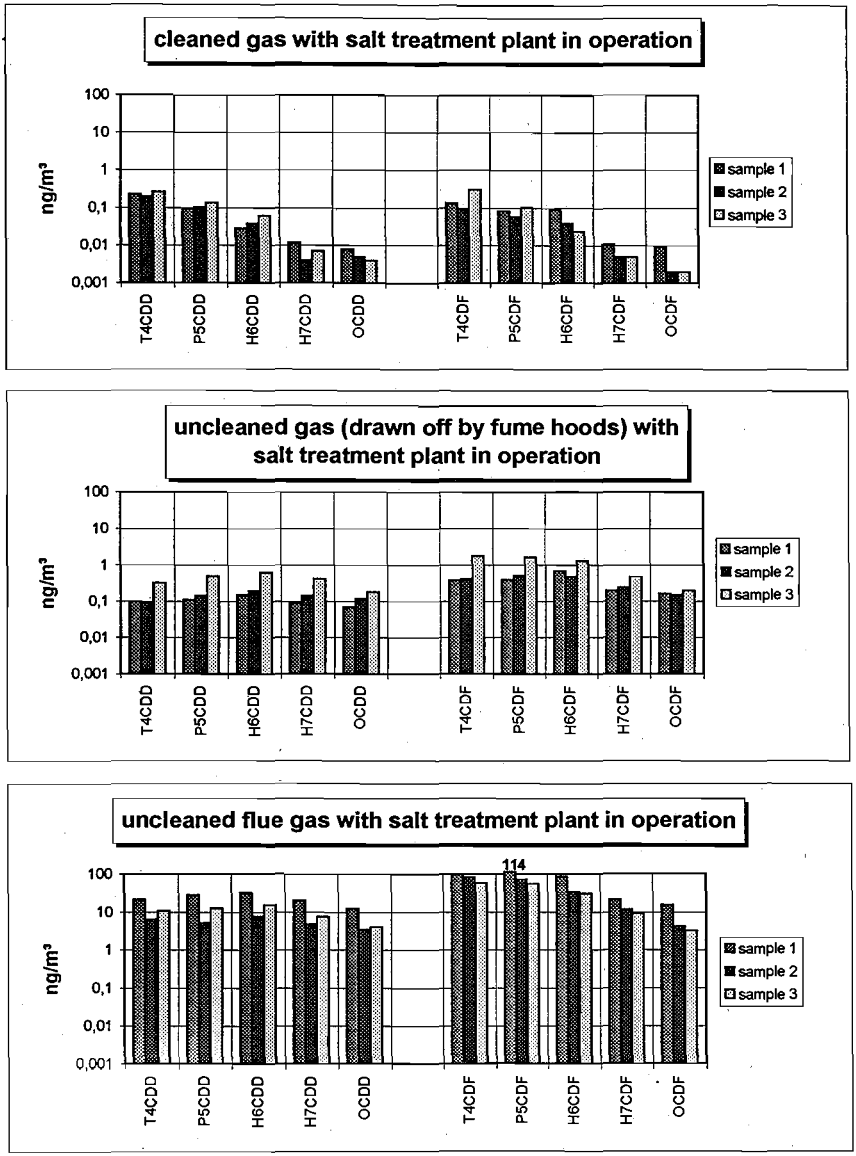
Figure 5.5-1 presents the concentrations which were obtained in the cleaned gas and in the two flows of uncleaned gas. Remarkably high concentrations in the flue gas flow were found.

Figure 5.5-2 presents the results obtained while the salt treatment plant was shut down. The concentrations in the cleaned gas are nearly identical with those provided in Figures 5.5-1 and 5.5-3.

First measurements were taken in the plant back in 1992. These measurements likewise yielded low concentrations of dioxins when additives were used. Figure 5.5-3 shows the obtained concentrations of dioxins and furans. These first measurements were taken during standard operation when the waste gases from the salt treatment plant were added to the waste gases from the melting furnaces. During the measurements in the cleaned gases 23-hour samples of the scattered emissions of waste air from indoors were taken as well. The concentrations are likewise illustrated in Figure 5.5-3. For the waste air from indoors a concentration of 0.01 ng I-TEQ/m^3 was obtained and for the cleaned stack gases the concentration was 0.004 ng I-TEQ/m^3. The indoor waste air which is emitted was found to amount to 225,000 m^3/h which yields an emitted mass flow of 0.003 mg I-TEQ/h. The secondary aluminium smelter alone emits 105,000 m^3/h of waste gas with only 0.0004 mg I-TEQ/h via an 80 m high stack. No influence of the NH_4-containing waste gas from the salt treatment plant on the emission of dioxins was detectable.

Figure 5.5-1: Concentations in the uncleaned and cleaned waste gases which include the waste gases from the salt treatment plant

(secondary aluminium smelting plant)



cleaned gas with salt treatment plant in operation

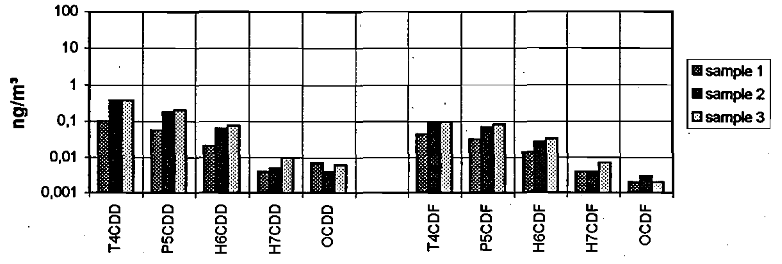
uncleaned gas (drawn off by fume hoods) with salt treatment plant in operation

uncleaned flue gas with salt treatment plant in operation

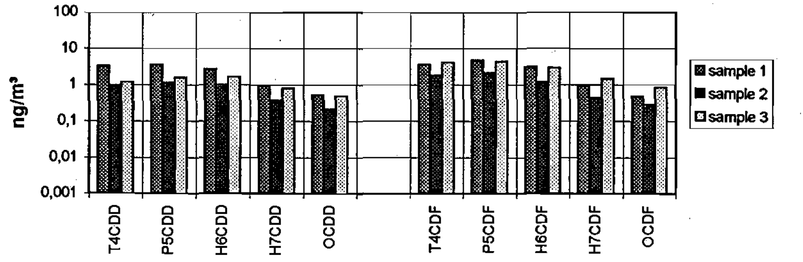
Figure 5.5-2: Concentrations in the uncleaned and cleaned gases without those from the salt treatment plant

(secondary aluminium smelting plant)

cleaned gas without salt treatment plant



uncleaned fumes drawn off by fume hoods



uncleaned flue gas without salt treatment plant

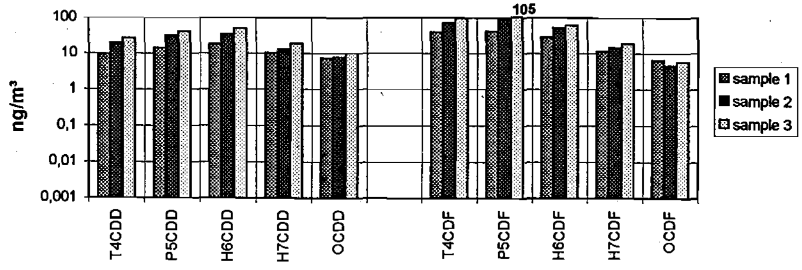
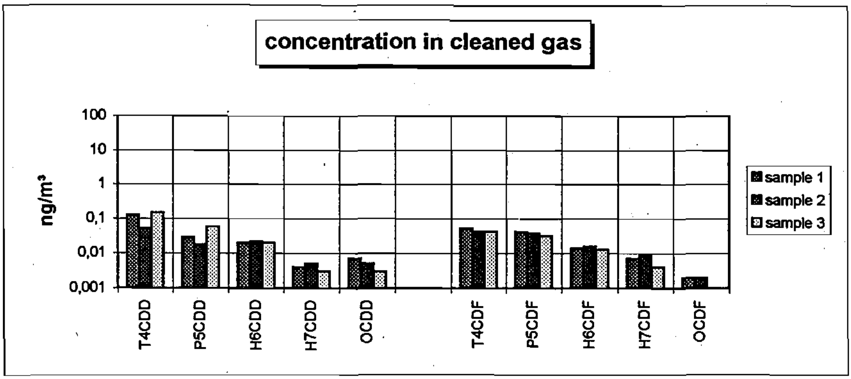
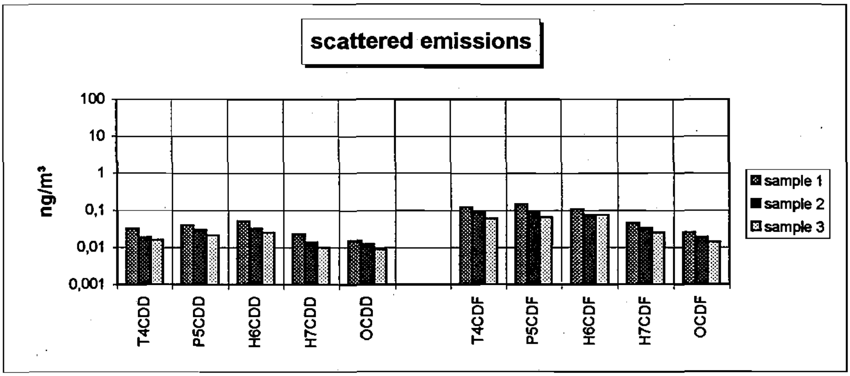


Figure 5.5-3: Concentrations in the cleaned and in scattered emissions

(secondary aluminium smelter)





5.6 City of Duisburg - Crematorium

The automatically operated, natural gas-fired furnace in this crematorium comprises 3 combustion zones. The heat is recovered in a recuperator to provide the combustion air for the cremation process.

The flue gas coming from the recuperator is passed into a cooling unit where it is cooled to a temperature of about 60 °C by injection of water. Fresh air can be added as well via a bypass if needed. The conditioned flue gas is passed into a biofilter from where it is discharged into the atmosphere. The biofilter covers an area of 150 m^2 and is equipped with a gas distribution system made of concrete pipes. The biomass is made up of a 0.5 m high layer of special compost (such as composted garbage, shredded foliage and porous granules). The filter can be loaded with 50 m^3/m^2 per hour.

The biofilter can be considered to be an emitter with multiple sources scattered over the filter area. Therefore, for sampling the entire filter was covered with a foil. The front side had a 1.9 m wide and 0.9 m high outlet. In that outlet the sample of the cleaned gas was drawn and the volume of the flow was determined.

The concentrations found in the uncleaned and cleaned gases are listed in Table 5.6-1.

Table 5.6-1: Concentrations in the uncleaned and cleaned gases from a crematorium

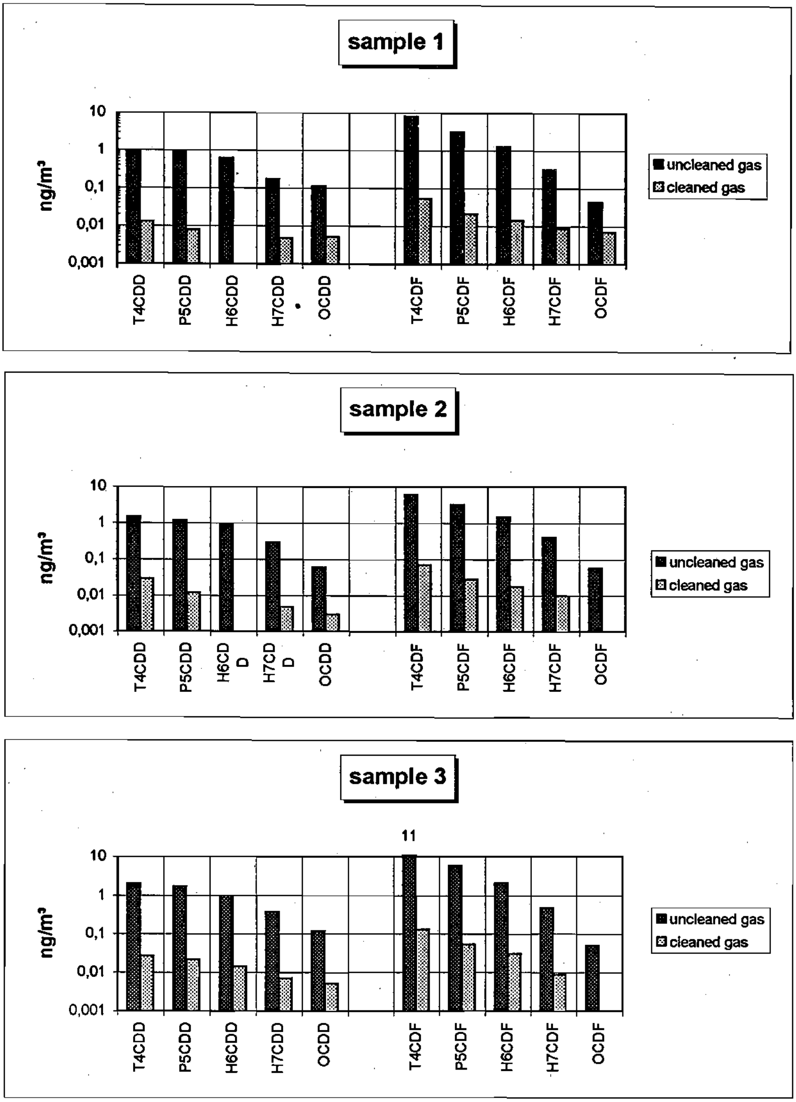
sample	**uncleaned gas (ng I-TEQ/m^3)**	**cleaned gas (ng I-TEQ/m^3)**
1	0.35	0.003
2	0.33	0.004
3	0.47	0.006
average	0.38	0.004

The average waste gas volume flow is 6,700 m^3/h. With this figure an average collection efficiency of 98.9 % I-TEQ is obtained for the biofilter.

Figure 5.6-1 presents the concentrations of various PCDD/PCDF which are emitted. The ranges obtained for the 3 samples are pretty uniform in this case too. In samples 2 and 3 no OCDF could be detected any more.

Figure 5.6-1: Collection of dioxins by a biofilter

(crematorium)



5.7 Company Thyssen Stahl AG

The first measurements in the company Thyssen Stahl AG were taken in 1992. They covered only sintering belt 3. Because of the high emission values found in other sintering plants, the necessity arose to conduct additional measurements on sintering belt 4 of Thyssen Stahl AG. The second series of measurements took place one year later. It appeared to be necessary to include also other potentially relevant sources besides the dust removal system of the sintering belts. Furthermore, the measurements were taken during operating conditions which were expected to be the standard operating conditions once the altered operating licence had been obtained. These operating conditions were defined as follows:

- application of SO_3 conditioning (10 to 20 vppm)
- addition of 40 kg of coke breeze/t sintered material
- no change of the belt capacity.

For the experimental addition of SO_3, nozzles had to be installed for dosage. The following sources were measured:

Cleaned waste gas drawn off from belt 4

The source is rated as having a volume flow of 600,000 m³/h. The waste gases drawn off from the sintering belt are conducted into two separate ducts of which one is equipped with a SO_2 scrubber. Behind the scrubber the two ducts join and the measurements cover the total waste gas flow.

Cleaned waste gases drawn off from other sources

Waste gases drawn off from other sources contribute a flow of about 700,000 m³/h of which 50 % come from waste air drawn off at transfer points, crushers and similar equipment. The other 50 % are waste gas from the circular cooler. This gas is exhausted from the 800 °C hot section of the cooler; before it is combined with the waste gas from the transfer points and crushers it is led through an oil-filled heat exchanger.

Scattered sources

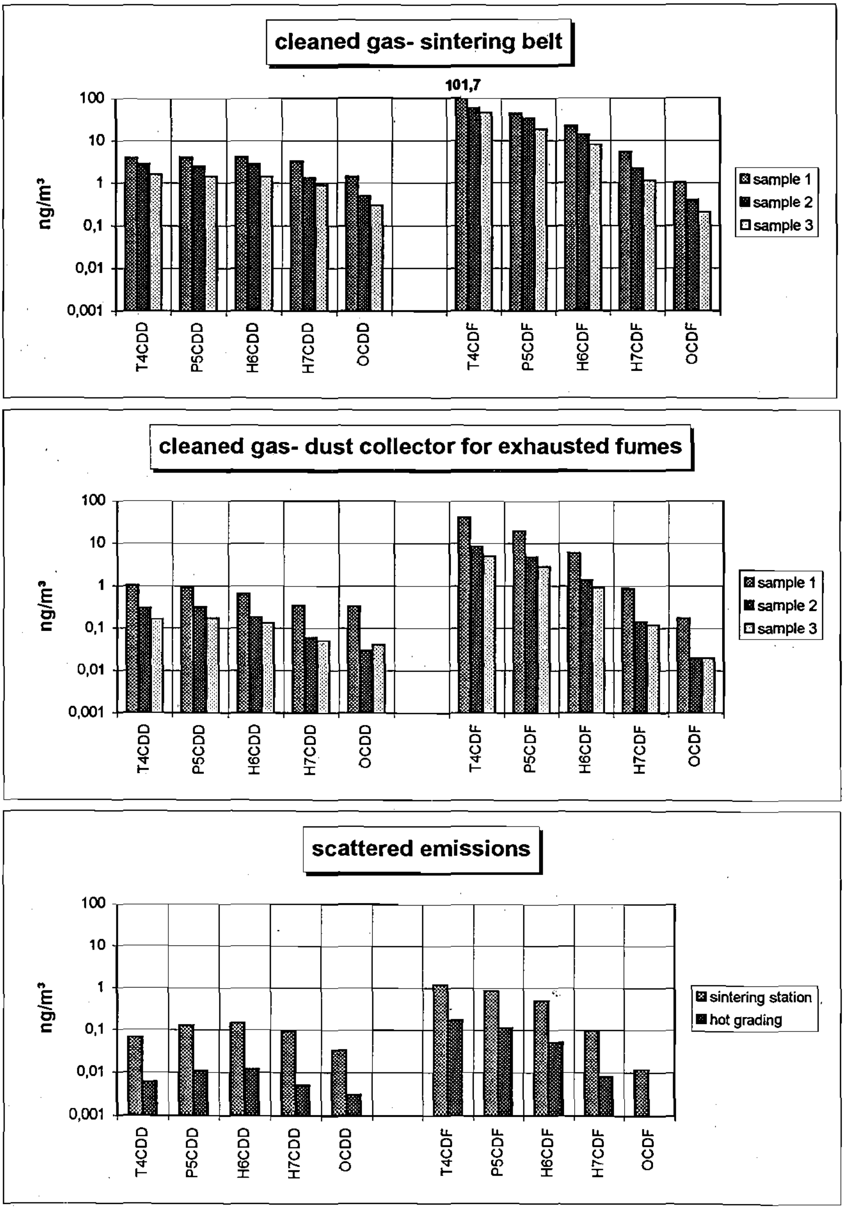
Because of the high energy consumption of the sintering process a large number of air exchanges (30 per hour) in the sintering room are to be expected. As a consequence, large quantities of waste gas escape diffusely through the roof. They had to be taken into account for the purposes of this project. The waste gases diffusing out of the sinter cooler cannot be measured for technical reasons.

Results

The dioxin and furan concentrations of the various sources are graphically presented in Figure 5.7-1. The concentrations in the waste gas of the dust removal system of the sintering belts as well as of the cleaned air of other sources (such as waste gas cooling, sinter cooling, hot grading, transfer points of belt conveyors) distinctly exceed the concentrations of the diffusely emitted waste gas from the sintering room or the hot grading station. But because the scattered emissions involve very large volume flows, emissions have to be expected which are of the same order of magnitude as those from the exhausted air flows whose mean emission mass flow is 0.32 mg I-TEQ/h.The cleaned gases coming from the dust removal system for the sintering belts emit 1.6 mg I-TEQ/h which is significantly higher.

Figure 5.7-1: Cleaned air from sintering belts and other equipment and scattered emissions

(sintering plant)



5.8 Company MHD Berzelius

In this metal smelter, measurements were performed at the following units in several measurement series:

- Imperial smelting plant
- cowper and recuperator
- hot-briquetting plant
- charging installation with several sources
- sintering plant, dust removal from the sintering belts
- tin smelting plant (short rotary furnace).

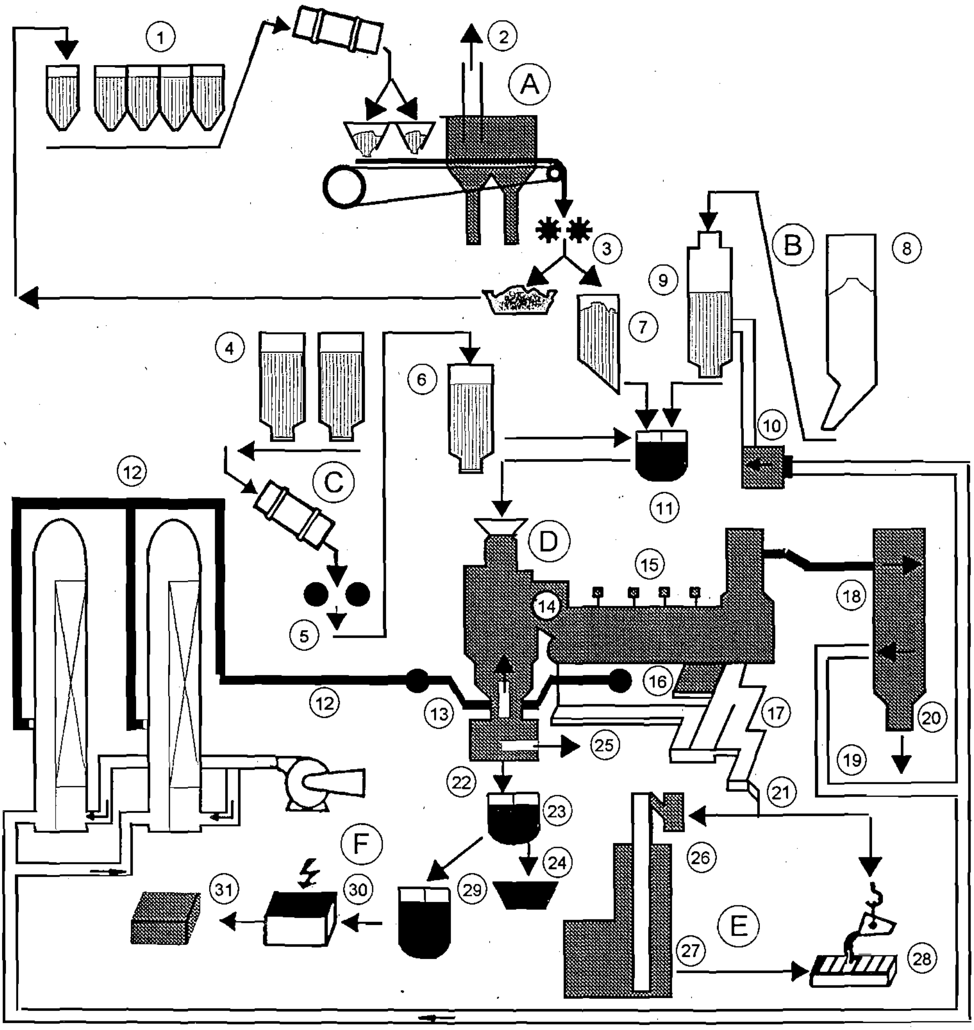
The processes are depicted in the flow diagram of Figure 5.8-1. The different units are explained as follows:

The shaft furnace (D) is charged with a mixed zinc and lead sinter material and with briquettes. The sinter material contains about 40 % Zn and 20 % Pb. It comes from unit (A) where the Pb/Zn concentrate is calcined. The briquettes consist of about 55 % Zn and 15 % Pb. They are produced by the hot-briquetting unit (C) from oxydic secondary Pb-Zn material.

The coke required for reducing, smelting and vapourizing is preheated in two coke preheaters to 800 °C. These are fired by top gas. In the charging unit (B) weighed amounts of sintering material and coke are filled into two charging buckets which are transported by a crane to the shaft furnace (D). There they are fed into the furnace via two double bell seals.

Sixteen nozzles blow 36,000 standard m^3 hot air per hour into the shaft furnace. The hot air is heated to a temperature of 1,100 °C in a recuperator (cowper) consisting of three units.

Figure 5.8- 1: Flow diagram of the operations of the zinc smelter



Ⓐ sintering plant
- 1 Storage bin, lead-zinc concentrate
- 2 waste gas from the calcening process
- 3 sintering material

Ⓒ hot-briquetting
- 4 storage bin for the oxidic zinc-lead material
- 5 hot-briquettes
- 6 storage bin of the hot briquettes

Ⓑ charging unit
- 7 storage bin for sintering material
- 8 coke bin
- 9 coke preheater
- 10 furnace for top gas
- 11 charging bucket

Ⓓ lead-zinc shaft furnace
- 12 main blast pipe
- 13 nozzles
- 14 lead pump
- 15 lead spray condenser
- 16 cooling troughs
- 17 zinc-lead separator
- 18 waste gas scrubber
- 19 cleaned top gas
- 20 zinc and lead sponge
- 21 crude zinc
- 22 primary crude lead
- 23 copper extraction
- 24 secondary crude lead
- 25 dross

Ⓔ fine zinc unit
- 26 fine zinc condenser
- 27 fine zinc
- 28 foundry

Ⓕ copper unit
- 29 copper-leaching
- 30 electrolytic copper unit
- 31 cathodic copper

The zinc and lead oxides are reduced in the shaft furnace at temperatures up to 1,400 °C (in front of the nozzles). Lead and dross are tapped every hour from the crucible into a receiver where they separate. The dross is granulated and the primary crude lead goes to the copper extraction unit. The copper contained in the slurry produced there is leached out and recoverd electrolytically. The secondary crude lead, now without copper, is shipped to a refinery.

Zinc leaves the furnace as part of the 1,050 °C hot top gas. In the lead spraying condenser the sprayed liquid lead quenches the top gas down to a temperature of about 500 °C and takes up most of the zinc.

Subsequently the lead-zinc alloy is transferred by two pumps to a systems of troughs which are equipped with dip coolers. At a temperature of about 450 °C part of the dissolved zinc floates on the surface of the lead which comes from the condenser. It is skimmed off in the separator unit, cleaned and either sold as smelter zinc or shipped to a refinery. The zinc-free lead flows back into the furnace.

Connected to the condenser is the top gas scrubber where the still remaining zinc is removed. The slurry is recycled to the calcining unit (A). The cleaned top gas may contain as much as 30 % CO and is used in the smelter for

- heating the cowper
- heating the coke.

Figure 5.8-2 shows the flow diagram of the Imperial smelting plant.

Besides the described installations for producing smelter and fine zinc a tin smelter is in operation on the premises of MHD.

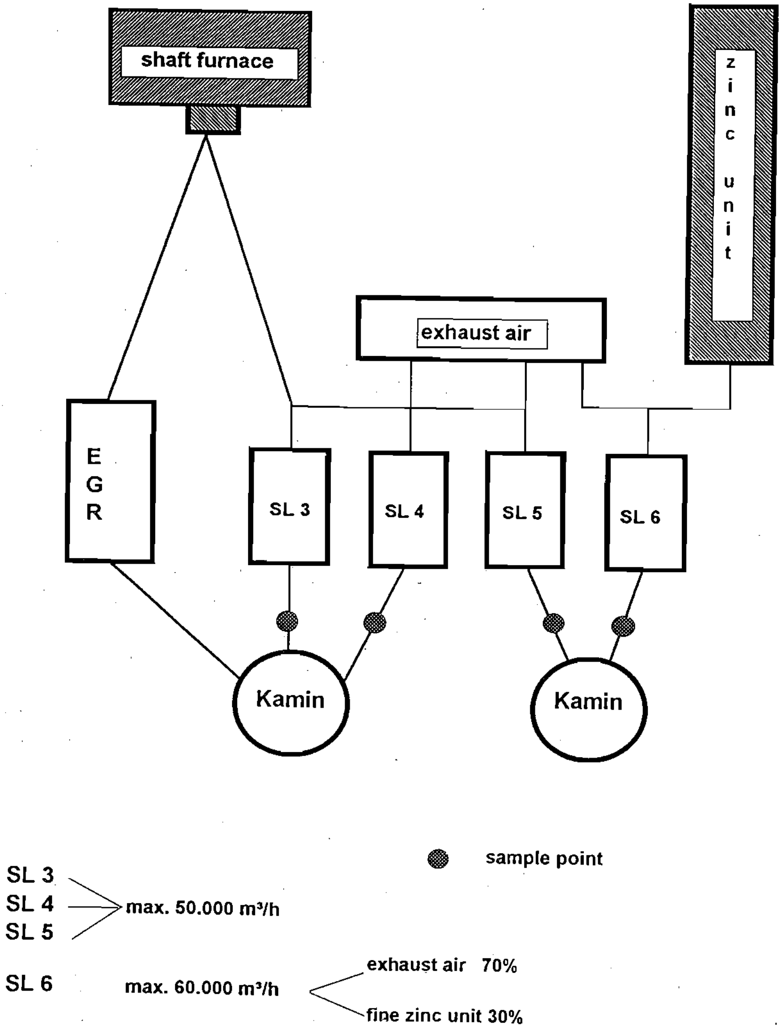
Crude tin is produced in a short rotary furnace by batch processes. The raw material is waste material with large contents of lead and tin. According to information supplied by the company, the origins of the raw material are hardly traceable. One batch takes about 6 hours which covers the melting of the raw material and the tapping of dross and metal. For one batch about 7 t material is charged. The furnace is fired with fuel oil EL and 1,400 m^3 pure oxygen.

The waste gas of this furnace is cooled in a wet cooling tower and filtered by teflon filters.

Measurements were also taken at the rotary cylinder.

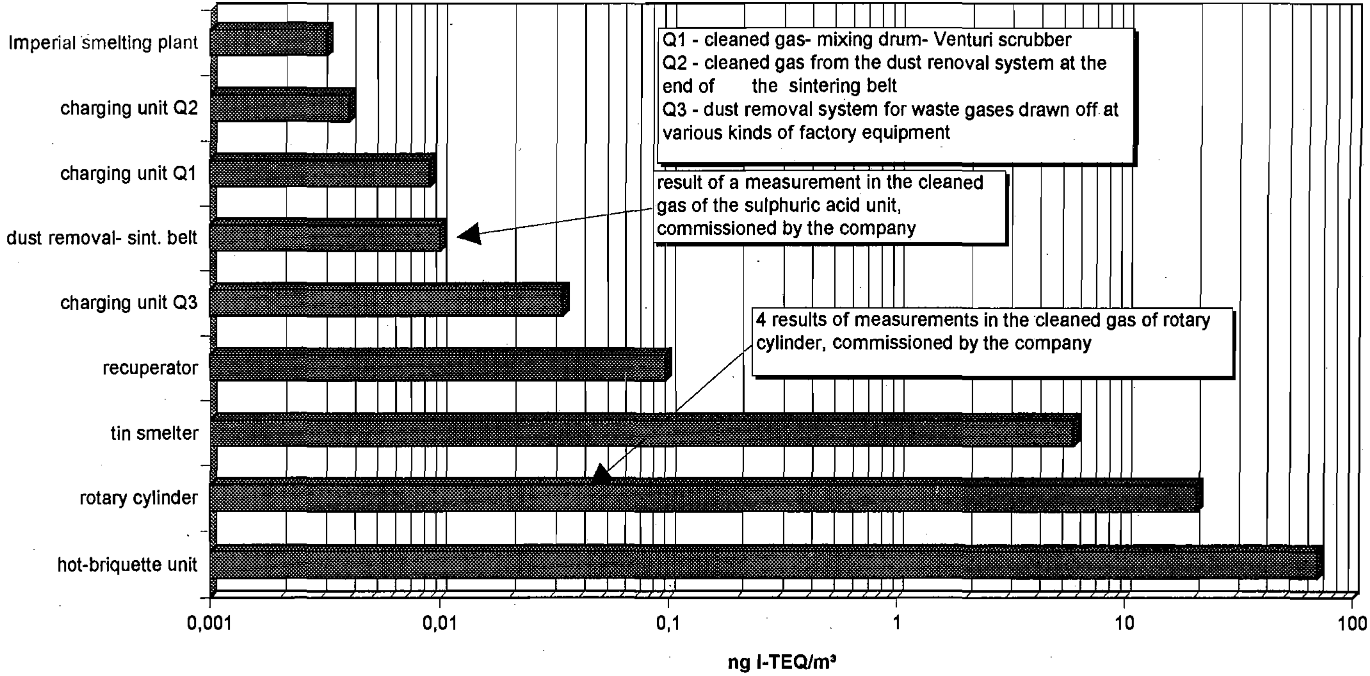
The emission concentrations determined at the various units are shown in Figure 5.8-3, the emission mass flows in Figure 5.8-4. Difficulties were encounterd while measuring the emissions from the dust removal systems for the waste gases drawn off from various kinds of equipment in the sintering plant because it was impossible to measure the cleaned gas flow. Therefore concentration measurements were conducted on three levels of the charging unit. Because of the high dust collection efficiency of the following cloth filter it could be safely assumed that the dioxin concentration would be reduced by at least 50 %. Consequently the estimate of the mean emission mass flow was based on one half of the concentration in the uncleaned gas.

Figure 5.8-2: Waste gas cleaning of the Imperial smelting plant



SL: bag filter, EGR: electrostatic precipitator

Figure 5.8-3: Emission concentrations of various sources at MHD; mean values

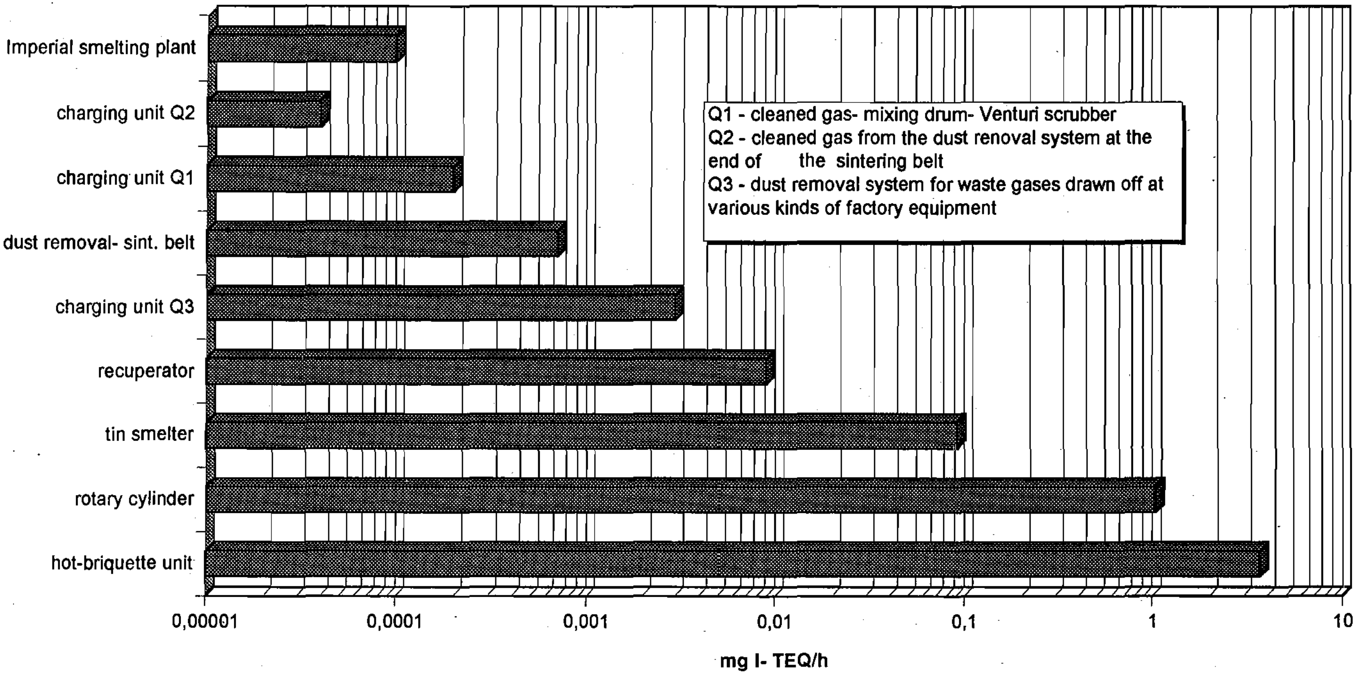


Q1 - cleaned gas- mixing drum- Venturi scrubber
Q2 - cleaned gas from the dust renoval system at the end of the sintering belt
Q3 - dust removal system for waste gases drawn off at various kinds of factory equipment

result of a measurement in the cleaned gas of the sulphuric acid unit, commissioned by the company

4 results of measurements in the cleaned gas of rotary cylinder, commissioned by the company

Figure 5.8-4: Mean emission mass flows in mg I-TEQ/h at MHD



The concentrations in air were measured on three days at different levels of the charging unit. Sampling lasted about eight hours, cf. Table 5.8-1.

Table 5.8-1: Concentration measurements in the charging area

level (m)	levels above respective floor where the samples were drawn (m)
5.4	1.5
15.5	1.5
19.3	4

The measured concentrations ranged from 0.03 to 0.07 ng I-TEQ/m³. The charging unit is enclosed. Because of the relatively low frequency of air exchanges the dust concentration inside this unit is considerable. The dust which deposits everywhere is regularly collected with industrial-strength vacuum cleaners. Results from analyses are presented in Table 5.8-2. From the values of the dioxin concentrations in the dust collected by the vacuum cleaner and from those determined in the air within the enclosures, a total dust concentration of 0.5 g/m³ inside the charging unit can be assumed in a first approximation. The results of the dioxin analyses of the dust samples are also listed in Table 5.8-2.

Table 5.8-2: Results of the analyses of dust samples

unit	dust sample	concentration µg I-TEQ/kg
hot -briquetting unit	pellets of raw material	0.35
	hot briquettes	0.24
	filter dust	42.21
tin smelter	dust from the electrostatic precipitator	3.09
	dust from the cooling tower	1.75
	dust from the flue stack	0.001
	raw material	0.097
Imperial smelting plant	dust from filters	0.077
charging unit	dust from filters of the mixer of sintering material	0.102
	dust collected by the vacuum cleaner	0.092
	mixing drum, sludge from the scrubber	0.003

Results of analyses of samples from the hot-briquetting unit have been obtained for the pellets of raw material, the hot briquettes and the dust collected by the dust removal system. The I-TEQ concentrations in the dust collected by the filters exceeded those of the raw materials and the briquettes by two orders of magnitude. The emissions from this area amounted to 70 ng I-TEQ/m³ on the average and reached a maximum value of 118 ng I-TEQ/m³.

5.9. Coking plant Kaiserstuhl

The coking plant which has been taken into operation in 1992 is worldwide the most modern plant of its type. Fig. 5.9-1 shows the plant equipment which is important for the measurements. As far as possible all sources emitting dioxins were included in the measurements.

The coking plant Kaiserstuhl has two batteries of coke ovens. Each of the batteries comprises 60 ovens which are usually heated with a top gas that has been enriched with carbon by mixing it with coke oven gas. Alternatively, the coke oven batteries can be heated with the coke oven gas they produce. The combustion air is composed of fresh air, a partial flow of the flue gas and leakage gas drawn off above the coke oven doors.

About 5,600 t of coke are produced daily which add up to 2 million t per year. The coking process takes 25 hours.

The produced coke of the coking plant Kaiserstuhl is cooled in dry condition, the availability of the drying facility is high. Only during shut down periods a wet quenching tower is used.

The coke leaves the drier with a temperature of about 200 °C via a rotary lock. The hot cooling gas is used in a boiler for producing steam.

Because the coke gives off gas, the cooling gas takes up combustible components such as H_2 and CO. The heating value is kept constant by adding air. A portion of the cooling gas is diverted as surplus gas and added to the top gas which fires the coke furnace batteries.

The waste gas from conveyor belts, sieves, mills, bins, runner troughs etc. is lead to dry dust filters. A second filter bag unit cleans the cooling air of the after-cooling facility.

The times of sampling at the various measurement points are listed in Table 5.9-1.

Figure 5.9-1: Schematic diagram of the operations in the coking plant

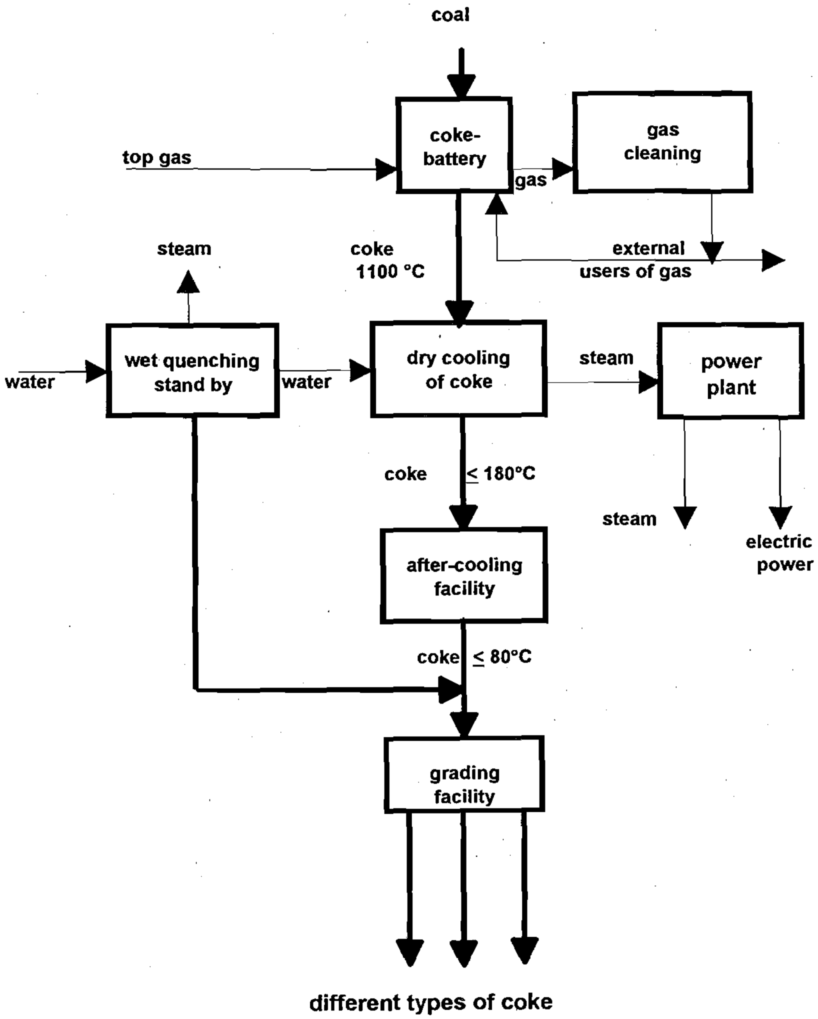


Table 5.9-1: Duration of sampling at the various measurement points

unit	number of measurements	duration of one measurement	operating conditions
flue stack of battery I	3	28.5 h	standard operation 100% mixed gas
flue stack of battery II	3	28.5 h	standard operation 50% mixed gas, 50% coke gas
flue stack of battery II	3	28.5 h	100% coke gas
dust removal from coke	3	12 h	standard operation
dust removal from dry coke cooling	3	12 h	standard operation
after-cooling of coke	1	6 h	standard operation
surplus gas from dry coke cooling	1	6 h	standard operation
leakage gas	3	12 h	pilot measurement
quenching tower	1	13.5 h	pilot measurement
charging openings	1	8 h	pilot measurement
gas pipess	1	3 h	pilot measurement

The following has to be said with regard to the pilot measurements:

Leakage gas collection

In order to avoid short term emissions from leaky furnace doors and other openings leakage gas is drawn off by a central exhaust system via hoods above all doors.

The control of the exhaust system allows to give priority to those four coke furnace chambers which were filled last and to manually set the exhaust system to draw off from those doors which are visibly leaky. About 10 % of the exhaust capacity are available for the rest of the furnaces.

There are separate exhaust systems for battery I and battery II with separate ducts for each side which are combined before the forced draft flue stack.

The leakage gas collected by the local exhaust system is mixed with fresh air and used as combustion air in battery I and battery II.

During the PCDD/PCDF measurements no visible leaks were detected at the furnace doors. The emission events could be evaluated by means of the measured and recorded contents of gaseous organic carbon compounds.

Each measurement with a sampling period of 12 hours covered about 50 discharges of battery I and battery II.

Quenching tower

The quenching tower is used as stand-by for the dry cooling facility. Because the availability of the dry cooling facility is about 95%, there are about 5 quenchings per 24 hours. In order to obtain a statistically acceptable sample size for the determination of PCDD/PCDF, 16 quenchings on each of two days were conducted with the quenching towers. During the PCDD/PCDF measurements, the following mean operational parameters prevailed:

day of measurement		**1**	**2**
origin of the coke		battery 1	batteries 1 and 2
temperature of battery 1	°C	1250	1237
temperature of battery 2	°C	1204	1213
number of charges		16	16

Charging openings (scattered sources)

The scattered emissions were sampled at one closed charging opening out of the 480 charging openings. The emissions of PCDD/PCDF were measured during the first eight process hours.

At the beginning of the measurement the lid on the charging opening was sealed by plant personnel with the appropriate sealant.

Gas pipes

The uncleaned gas coming from the coke furnace is conducted to a collecting pipe via gas mains. The gas mains are equipped with a lid which is opened prior to discharging the coke. Simultaneously a shutter at the end of the gas main is closed whereby the furnace is disconnected from the collecting pipe. The coke gas leaving the gas main is burned in a flare. This operation lasts for about 10 minutes and is concluded at the beginning of the charging process.

A representative PCDD/PCDF measurement was performed at an opened gas main. In contrast to normal operations which last 10 minutes, the gas main stayed open for 180 minutes during the measurement. The individual results of all emission measurements are listed for average operating conditions. The mass flow was calculated on the basis of an emission duration of 10 minutes per gas main.

During the measurement the shutter of the gas main was open and the furnace was disconnected from the collecting pipe. The plane of measurement was within the combustion chamber which could be well observed through the maintenance opening in the bend of the gas main. This opening admitted additional oxygen so that an optimised combustion of the flue gas could be assumed for the time of the measurement.

Results

Figures 5.9-2 to 5.9-4 show the distribution of the different stages of chlorination of the dioxins and furans for the various emission sources. Figure 5.9-2 provides the concentrations in the cleaned gas for the different fuel compositions. In Figure 5.9-4 the results are compiled of three individual measurements at the most important sources. For comparison, the results of the pilot measurements which are based on one sample per measurement are also provided in Figure 5.9-4. Because the concentrations by themselves cannot indicate the significance of the investigated sources, the emission mass flows were calculated or estimated from available data. These indicate that the highest values were contributed by the leakage gas drawn off by the exhaust system. The measurements were performed in the collected leakage gas; this, however, is not emitted but used in the undergrate firing. The efficiency of collecting the leakage gas from the doors amounts to 95 % according to an optimistic estimate and 30 % according to a pessimistic estimate. In a first approximation a collection efficiency of 70 % was assumed. Table 5.9-2 lists all emission mass flows:

Table 5.9-2: Comparison of the different sources

source	emission concentration ng I-TEQ/m^3	emission mg I-TEQ/h	specific emission ng I-TEQ/t coke
battery I, mixed gas	0.006	0.0014	6.9
battery 2, mixed gas / coke gas	0.003	0.0007	3.5
dust removal from the coke	0.006	0.0011	5.4
dry cooling of the coke	0.006	0.0003	2.2
after cooling of the coke	0.014	0.0013	6.9
quenching tower	0.012	0.00015	0.2
gas main	0.009	< 0.00000	0.02
leakage gas	0.05	0.0018	9
charging opening	0.012	0.005	2.6

Figure 5.9-2: Concentration in the cleaned gas in the flues of the coke oven batteries for different fuel gas compositions

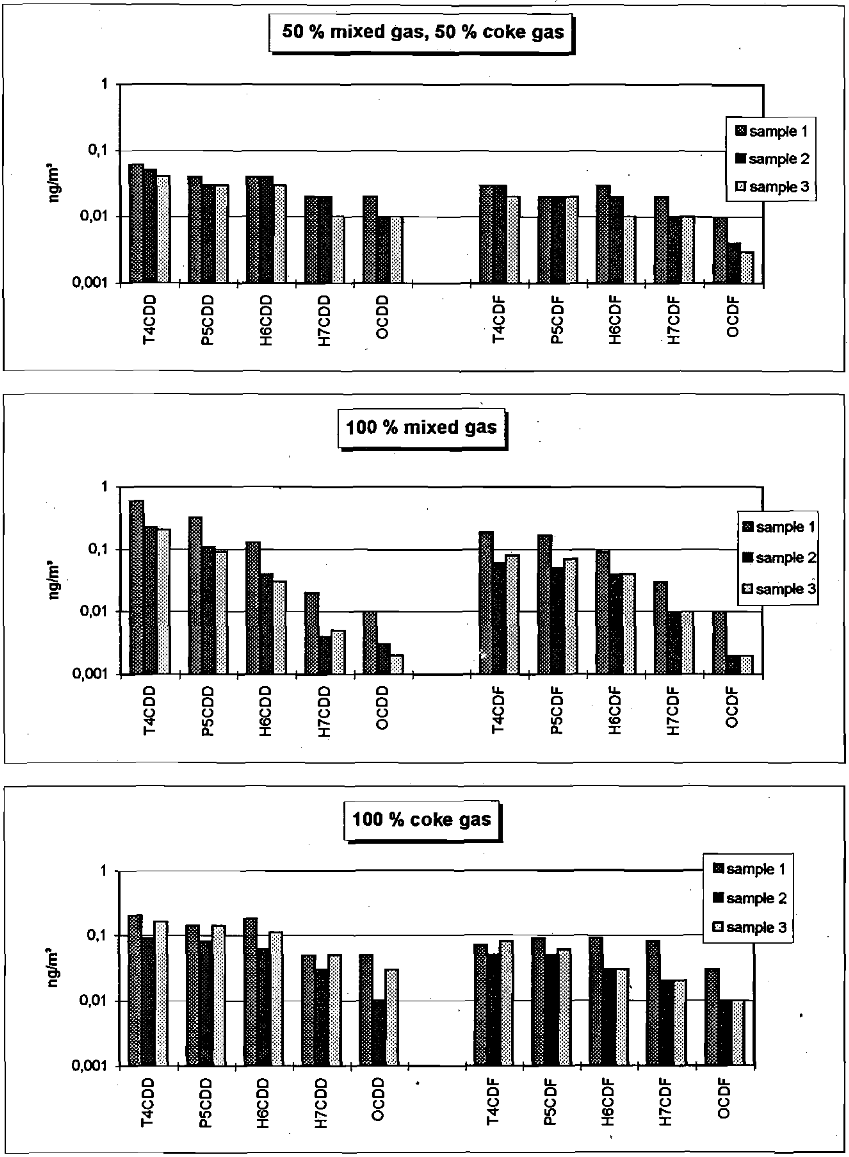


Figure 5.9-3: Comparsion of the different sources

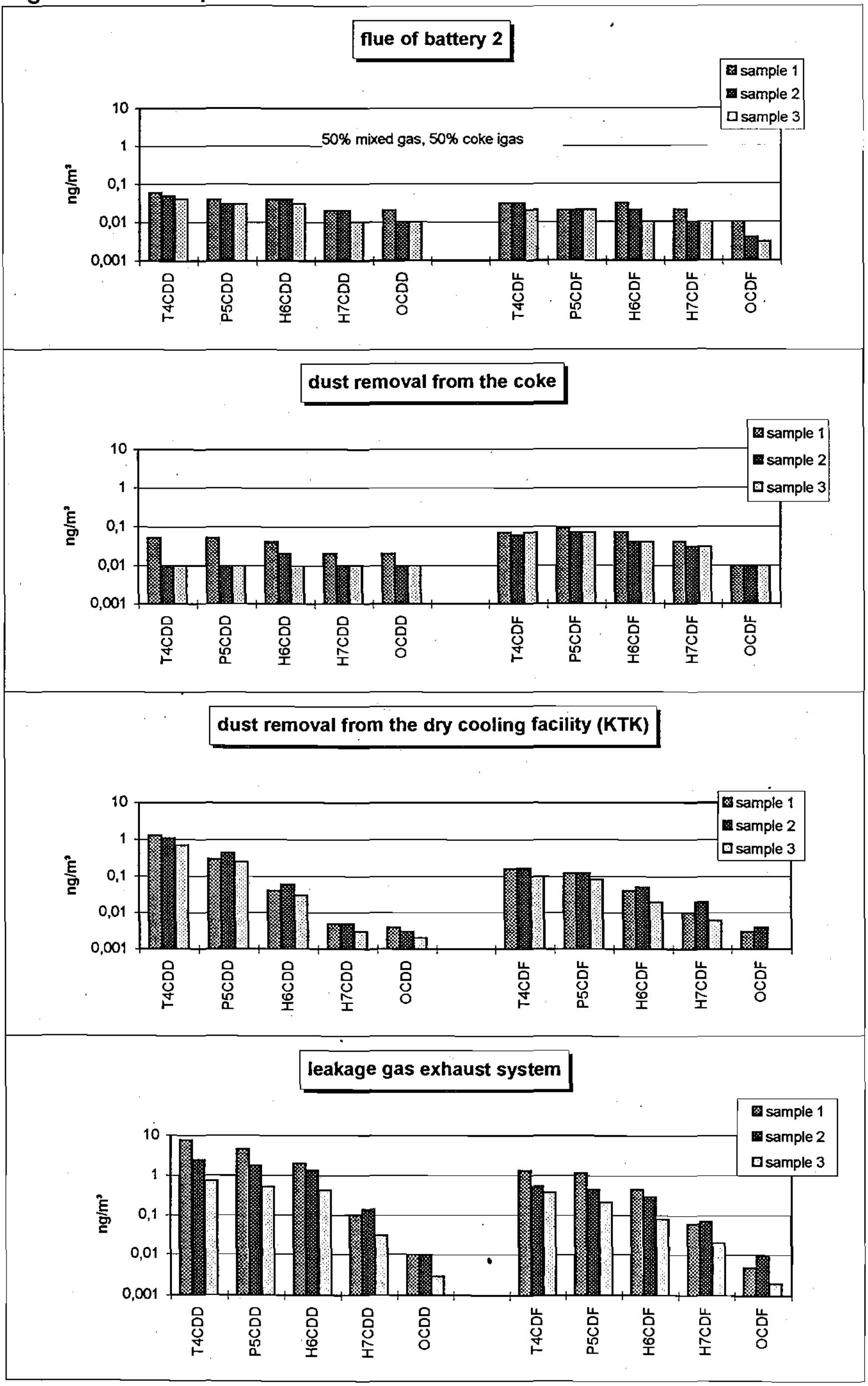
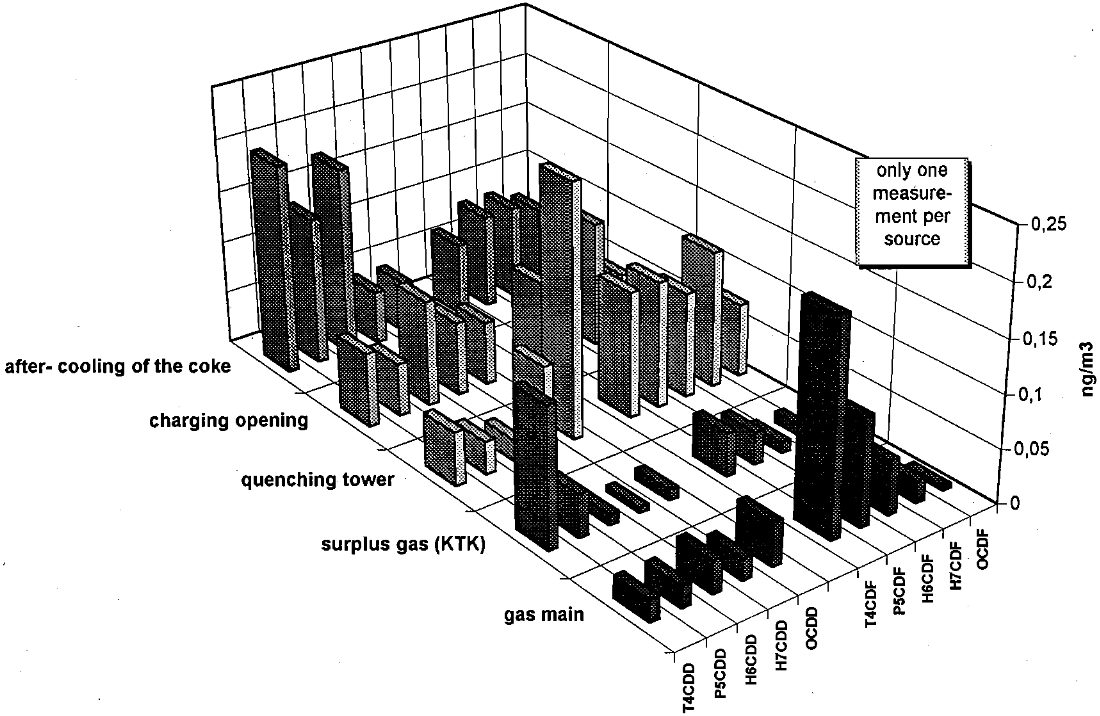


Figure 5.9-4: Cleaned gas concentrations determined by the pilot measurements



Based on all these data a specific emission of 0.037 µg I-TEQ/t coke was obtained.

5.10 Company Krupp-Hoesch Stahl AG

The necessary raw materials for producing sinter such as ore, circulating material, additives and fuel are prepared in the ore pre-processing section and are transported to the bins for raw materials. The sintering charge is evenly spread over the whole width of the sintering belts and ignited at is surface. The active areas of the sintering belts amount to

sintering belt 3	444 m^2
sintering belt 4	250 m^2.

The process air is supplied to the sintering belt 3 and sintering belt 4 by two blowers each. Dust is removed from both sintering belts via electrostatic precipitators. After sintering the raw sinter is crushed and subsequently graded to separate the return material from the sinter. The hot sinter is passed via a hopper to the sinter cooler. All hoppers and transfer points of the sintering plant are enclosed. The dust in the enclosures is removed by an exhaust system. Each sintering belt has its own electrostatic precipitator with blower and stack for cleaning the waste gas. At sintering belt 4 the exhaust system takes up also the waste gas from the dust removal system of the cooling facility. The crushed and cooled sinter is conveyed to the grading and loading stations. These units are enclosed and connected to a fabric-filter for dust collection.

At the company Krupp-Hoesch Stahl AG three dioxins measurement programmes were conducted :

• measurement programme I	measurements at two experimental fabric-filters;
• measurement programme II	measurements at sintering belt 3,
• measurement programme III	measurements at sintering belt 4.

At the beginning of the measurements at Hoesch results of measurements were already available which had been taken at other sintering installations. Therefore emission concentrations below 5 ng I-TEQ/m^3 in the cleaned gas coming from the dust removal system of the sintering belts were expected here at Hoesch as well. The measurements at Hoesch were planned to cover besides the emissions from the dust removal system of sintering belts also those of the air filtering systems at the sinter loading stations. The measurements at the experimental filters were expected to yield information on the retention of PCDD/PCDF in fabric-filters. The experimental filters were fed by a portion of the cleaned waste gas from the dust removal system of both sintering belts. Four samples were drawn for all emission flows investigated in measurement programme II. Two samples were taken when used sand had been added to the sinter charge and two samples when no used sand was present. In all other cases the plant was operated under standard conditions.

During the measurement programme III samples were taken in the area of sintering belt 4. At each investigated source and material flow three samples were taken in parallel.

Results

Due to the large waste gas volume flow the dioxin concentrations measured at the dust removal unit of sintering belt 4 produced the highest emission mass flow known for a single installation.

In Table 5.10-1 all mean values are listed for each unit. Because no difference was noticeable between operations with or without used sand, only one mean value was computed for the sources of sintering belt 3.

Comparison with a domestic waste incinerator which must observe a limit value of 0.1 ng I-TEQ/m³ (17. BImSchV) shows that its dioxin emission would be lower by a factor of more than 1000 than the dioxin emissions of the dust removal system of sintering belt 4 at the time of the measurement.

Also the dioxin emissions of the dust removal system treating the fumes collected by the exhaust system in the area of this sintering belt were 50 times higher than the emissions through the stack of a modern waste incinerator with a capacity of e.g. 16 t waste per hour and an emission mass flow of usually under 5 µg I-TEQ/h.

The results of the measurement programme I revealed that the experimental fabric-filters fed by a portion of the waste gas flow achieved collection efficiencies of 36 to 73 % for dioxin equivalents TE according to NATO/CCMS. The higher chlorinated PCDD/PCDF were better retained (89 %) than the lower chlorinated ones. The results motivated Hoesch to modify the operation of the equipment. Numerous subsequent measurements performed outside the dioxins measurement project described here confirmed that the values were lowered to the usual range of dust removal systems of sintering belts.

Figure 5.10-1: Synopsis of all measurement results obtained at the dust removal systems of sintering belts 3 and 4

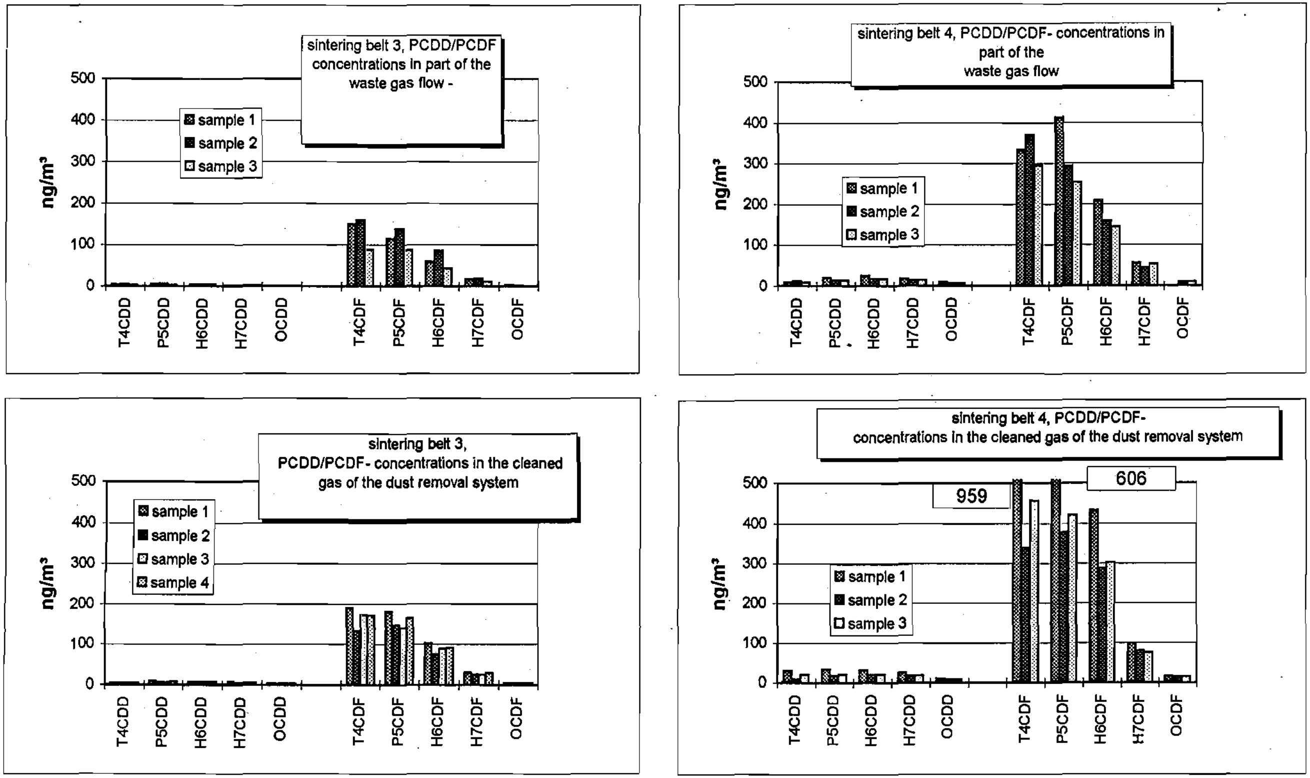
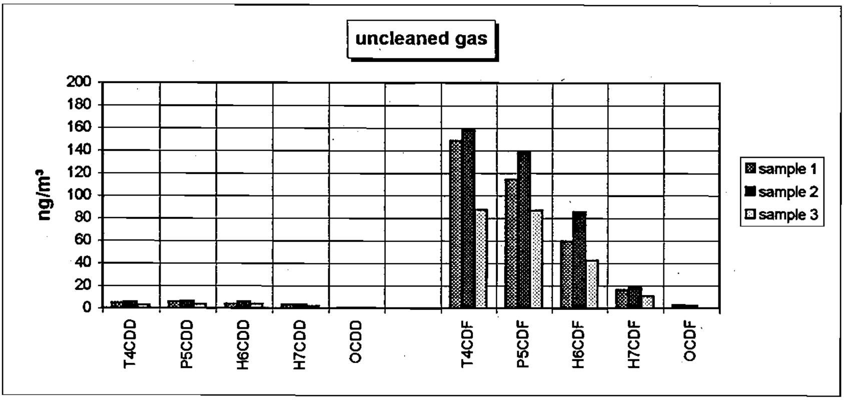
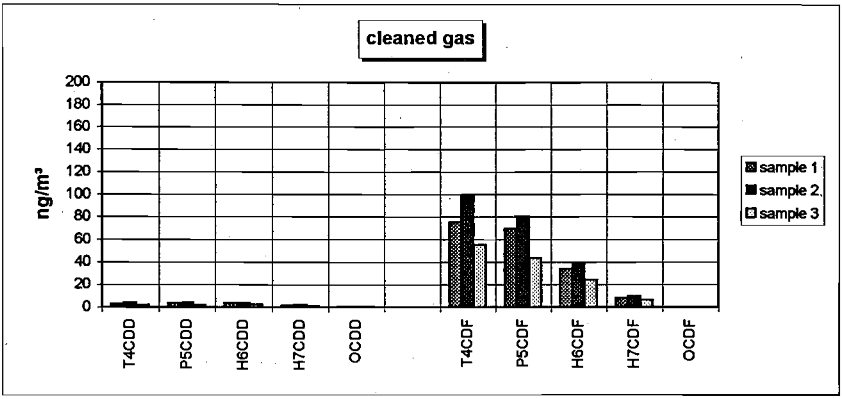


Figure 5.10-2: PCDD/PCDF- concentrations, experimental filter 2

(dust removal from the sintering belt)





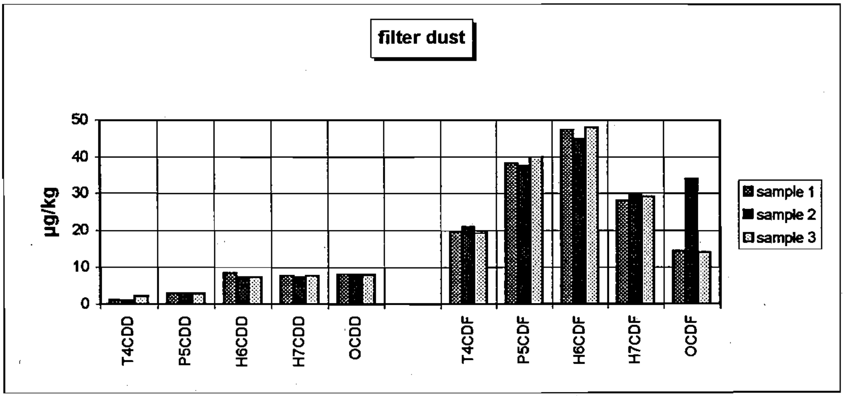
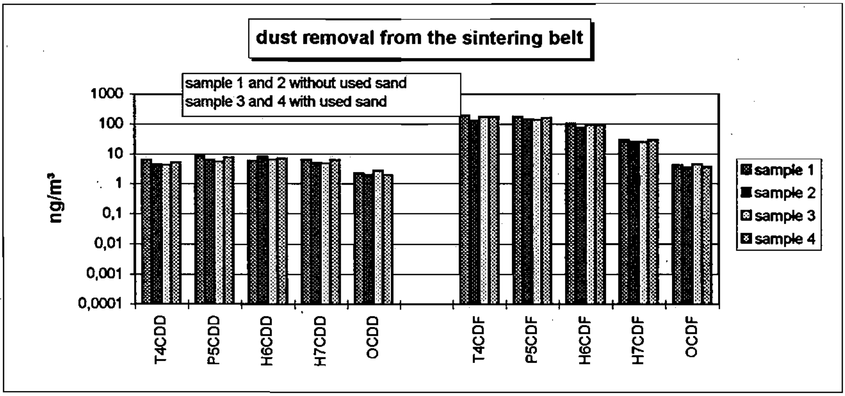
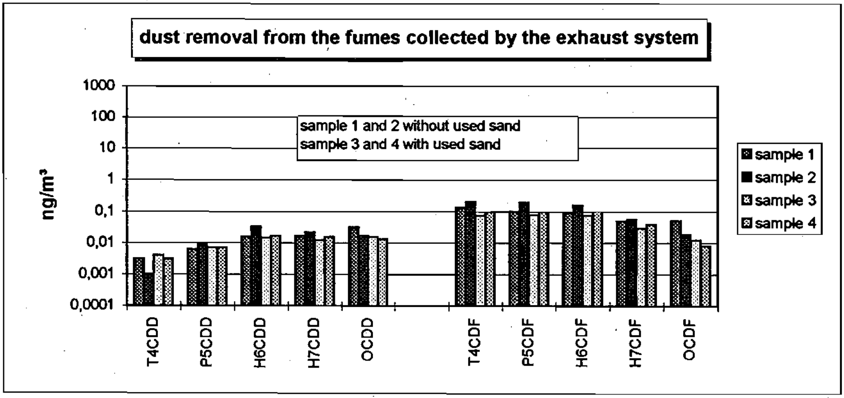


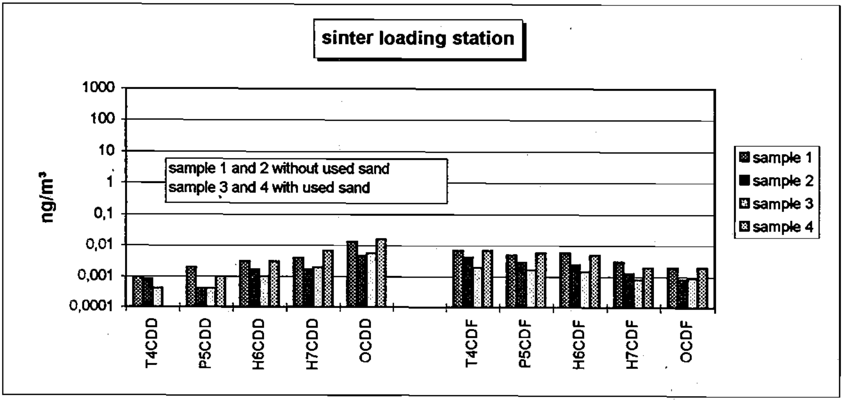
Figure 5.10-3: Emission concentrations at the sources of the sintering belt 3



dust removal from the sintering belt



dust removal from the fumes collected by the exhaust system



sinter loading station

Figure 5.10-4: Emission concentrations at the sources of the sintering belt 4

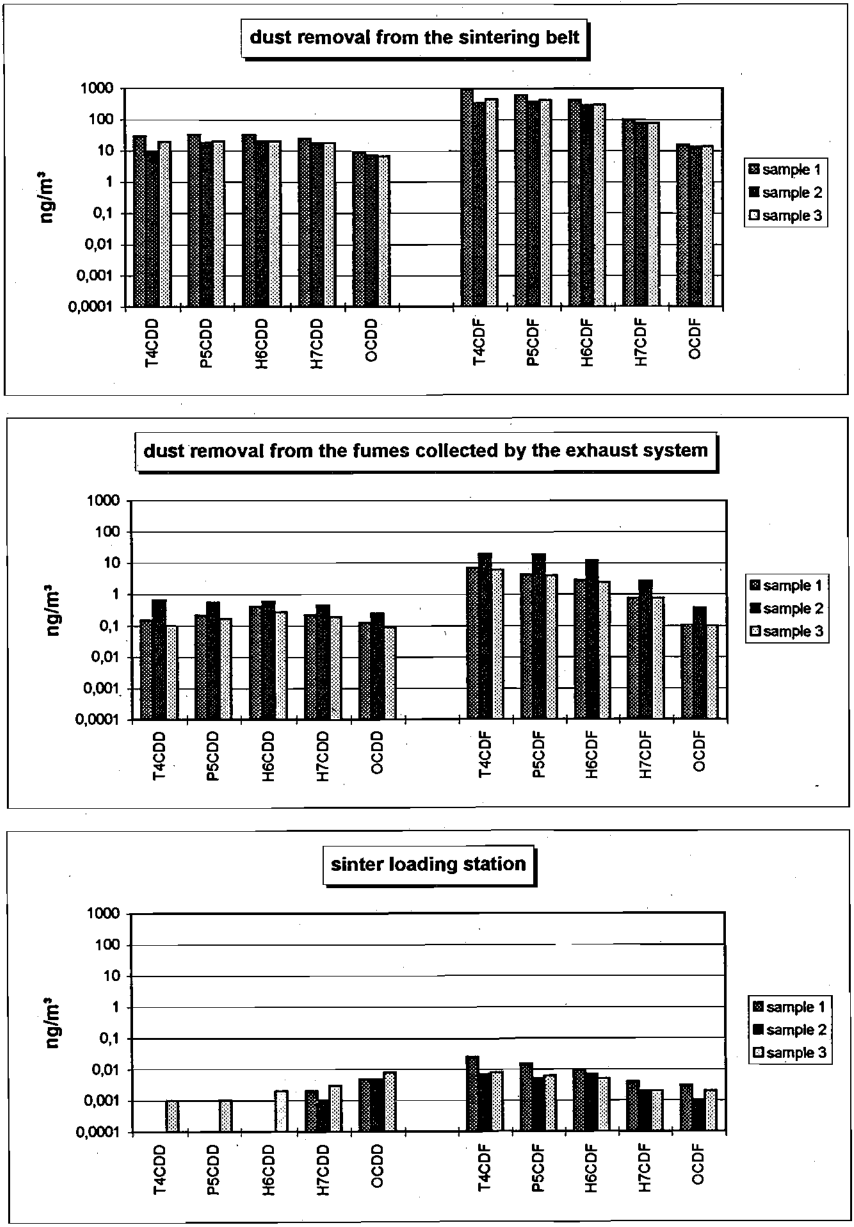


Figure 5.10-5: PCDD/PCDF concentrations, experimental filter 1

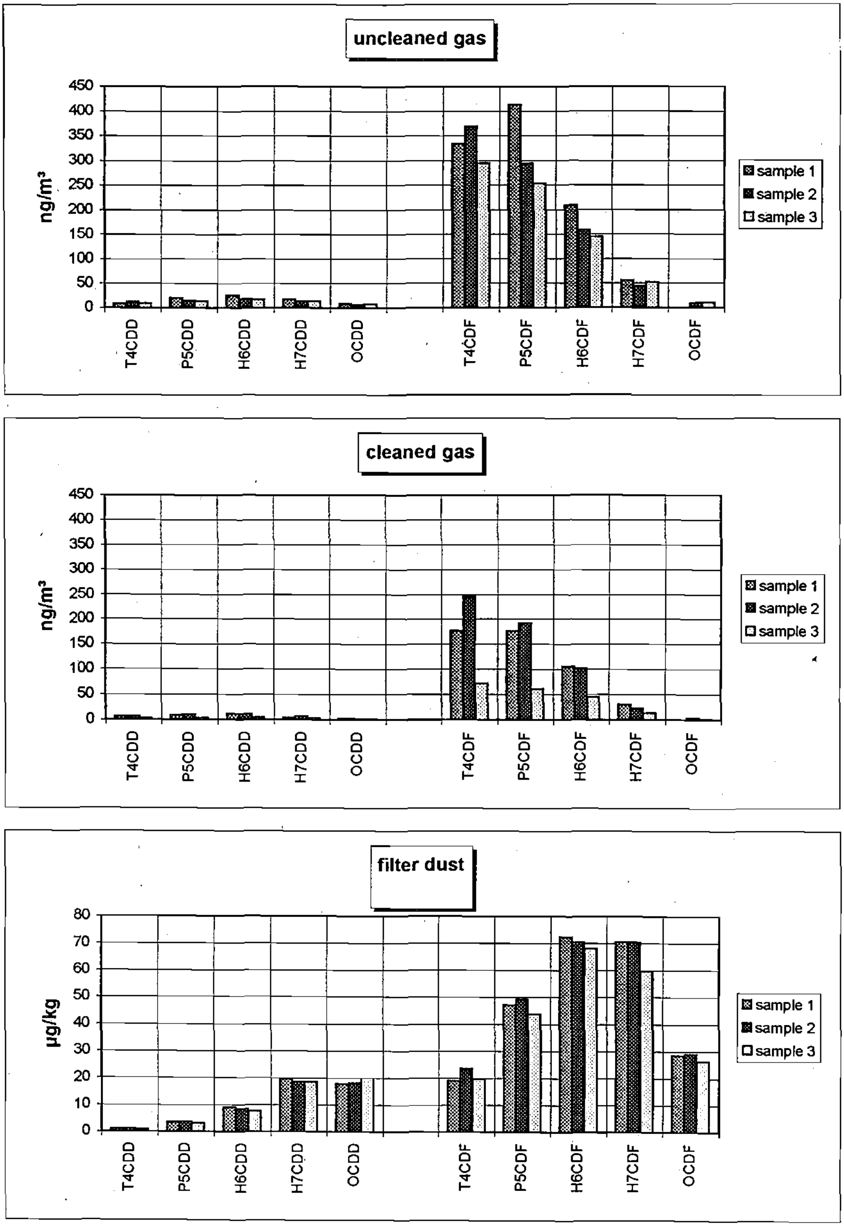
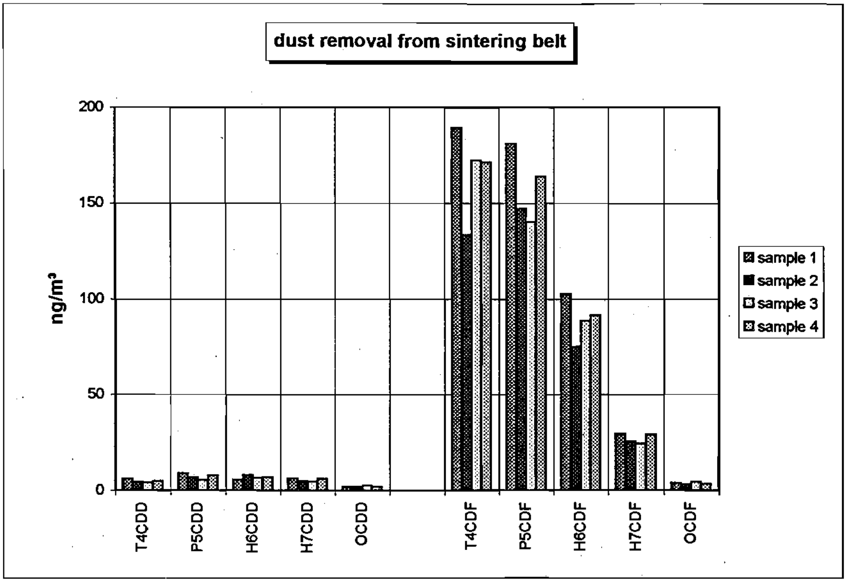


Figure 5.10-6: PCDD/PCDF concentrations, dust removal from belt 3



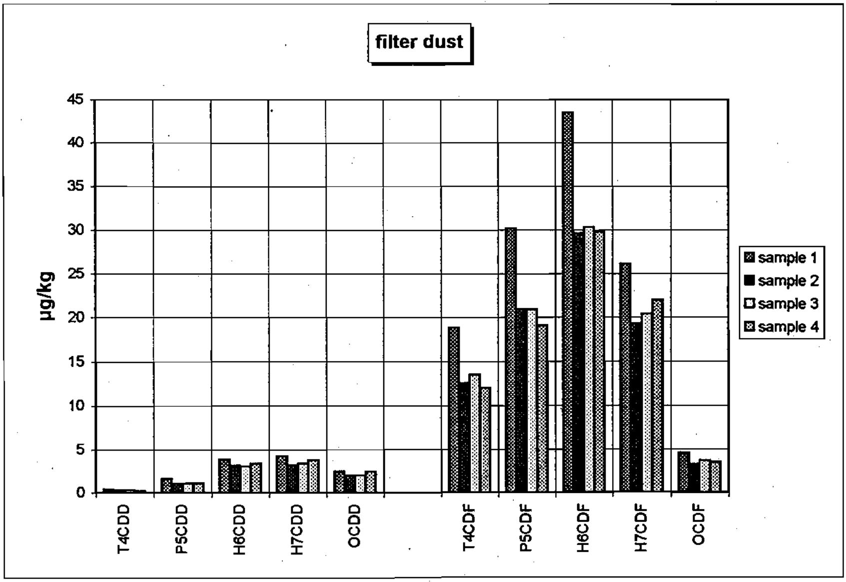
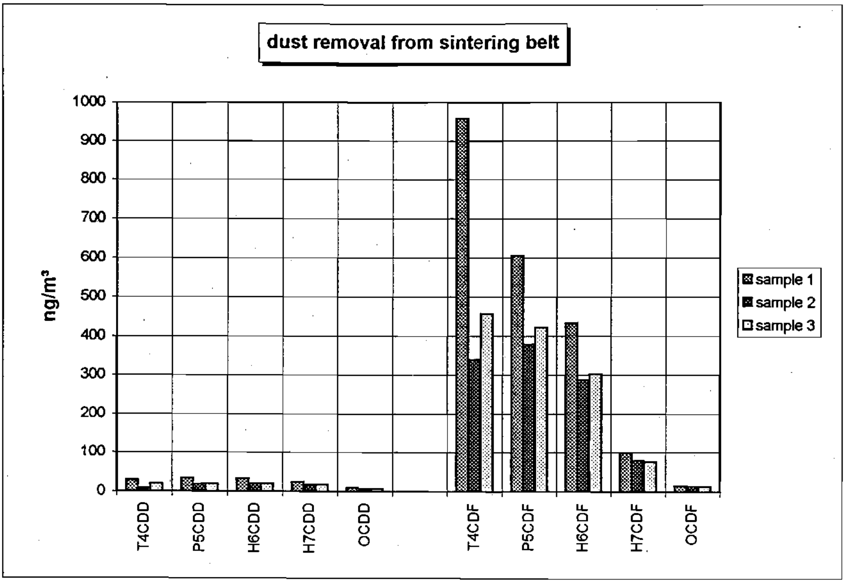


Figure 5.10-7: PCDD/PCDF concentrations, dust removal from belt 4



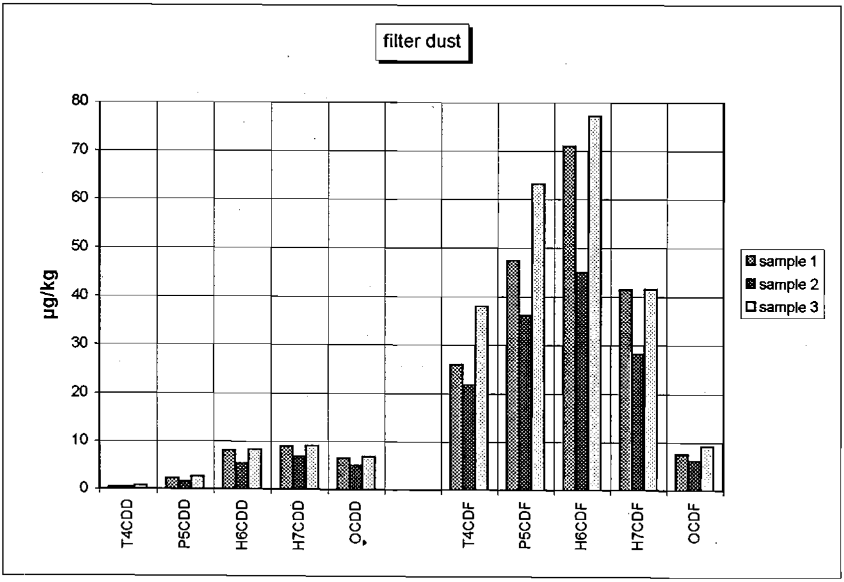


Table 5.10-1: PCDD/PCDF emissions of the sintering plant mean values at standard operation

unit	sintering belt no.	concentration, ng I-TEQ/m³	waste gas volume flow, m³/h	mass flow, mg I-TEQ/h
dust removal from the belt	3	11.5	501,854	5.78
dust removal from fumes collected by the exhaust system	3	0.011	217,000	0.0024
loading station	3	0.0007	131,000	0.00009
dust removal from the belt	4	43.2	680,000	29.4
dust removal from fumes collected by the exhaust system	4	0.619	439,000	0.272
loading station	4	0.0016	152,000	0.002

The Figures 5.10-1 to 5.10-7 show the distribution of the concentrations of congeners in the waste gas and filter dust samples.

5.11 Contribution of the different components to the toxicity equivalent

The measurement results presented in Section 4 of this report are mostly quoted as equivalent values. They were calculated in accordance with a recommendation by NATO/CCMS which is reproduced in Table 5.11-1. These weighting factors were also employed in the appendix to 17. BImSchV for calculating the limit value of PCDD/PCDF. In order to gain information whether the use of dust collectors changes the distribution of those congener groups which are relevant for the calculation of the I-TEQ, the contributions of these components was determined in some measurement series.

The Figures 5.11-1 and 5.11-2 display distributions found in the waste gas of a wood-fired furnace. In spite of the broad range of the concentrations in both the uncleaned and the cleaned gas - the I-TEQ values cover the range from 0.46 to 12 ng I-TEQ/m³ -, the fractional contributions of the individual congeners to the equivalent values obtained by all measurements agree well. The dioxins 2,3,7,8-TCDD and 1,2,3,7,8-PCDD and the furan 2,3,4,7,8-PCDF constitute more than 50 % of the TEQ-value. The amount of the dioxins is about the same as that of the furan. The upper part of Figure 5.11-4 shows the general agreement between the fractional contributions of the congeners from the waste gas and the dust from prefilters and the fabric-filters.

A totally different picture is presented by the distributions obtained from the measurements of the cleaned gas of the dust removal systems of the two sintering belts of

Krupp-Hoesch Stahl AG. In each case more than 50 % of the I-TEQ-value must be attributed to 2,3,4,7,8-PeCDF. This is followed with about 10 % by 1,2,3,4,7,8-HxCDF. The contribution of the dioxins to the I-TEQ-value is insignificant. This is also true for the dust of an experimental fabric-filter, which follows an electrostatic precipitator in the dust removal system of the sintering belt, cf. lower part of Figure 5.14-4. Of the furans, the contribution of 2,3,4,7,8-PCDF with about 35 % in all three measurements is significantly lower than in the cleaned gas samples mentioned above. This is made up by three further furans which contribute more than 10 % to the I-TEQ value.

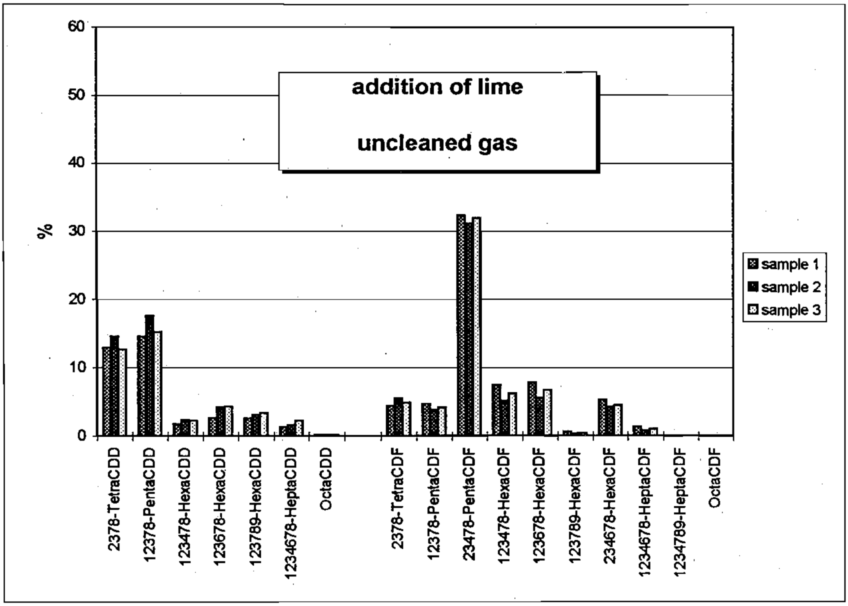
The distributions shown in the Figures 5.11-1 to 5.11-4 demonstrate that the relative frequencies of the congeners may differ significantly from one to the other industrial sector. Moreover, the selectivity of some waste gas cleaning installations must be taken into account because it can influence the distribution of the congeners. On the other hand, independently of the I-TEQ concentration, a good agreement between different measurement series and also between comparable types of installations is discernible.

Table 5.11-1: Toxicity equivalent factors of 2,3,7,8-tetraCDD

	NATO/CCMS-1988
2,3,7,8-TetraCDD	1
1,2,3,7,8-PentaCDD	0,5
1,2,3,4,7,8-HexaCDD	0,1
1,2,3,6,7,8-Hexa CDD	0,1
1,2,3,7,8,9-HexaCDD	0,1
1,2,3,4,6,7,8-HeptaCDD	0,01
OctaCDD	0,001
2,3,7,8-TetraCDF	0,1
1,2,3,7,8-PentaCDF	0,05
2,3,4,7,8-PentaCDF	0,5
1,2,3,4,7,8-HexaCDF	0,1
1,2,3,6,7,8-HexaCDF	0,1
1,2,3,7,8,9-HexaCDF	0,1
2,3,4,6,7,8-HexaCDF	0,1
1,2,3,4,6,7,8-HeptaCDF	0,01
1,2,3,4,7,8,9-HeptaCDF	0,01
OctaCDF	0,001

Figure 5.11-1: Contribution of the PCDD/PCDF to the equivalent values

(wood-burning furnace with fabric filter and addition of lime)



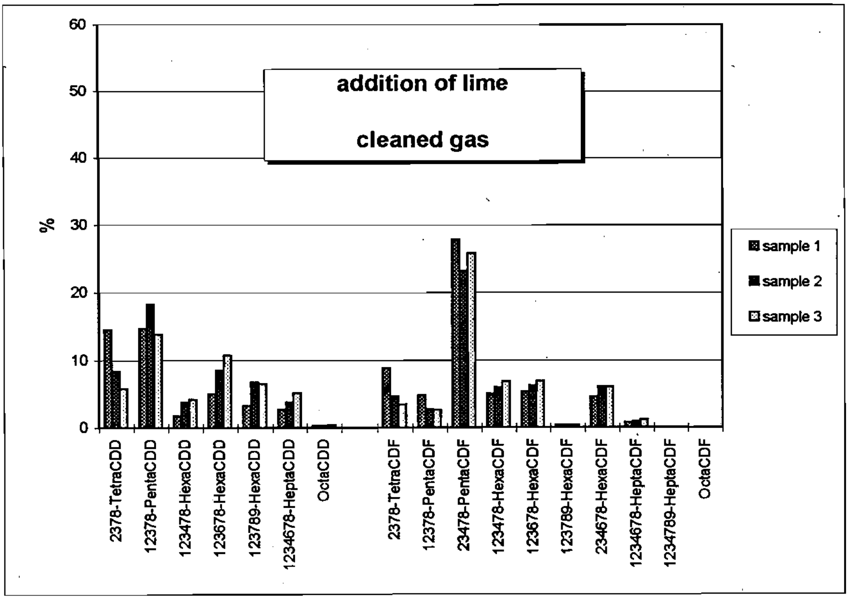
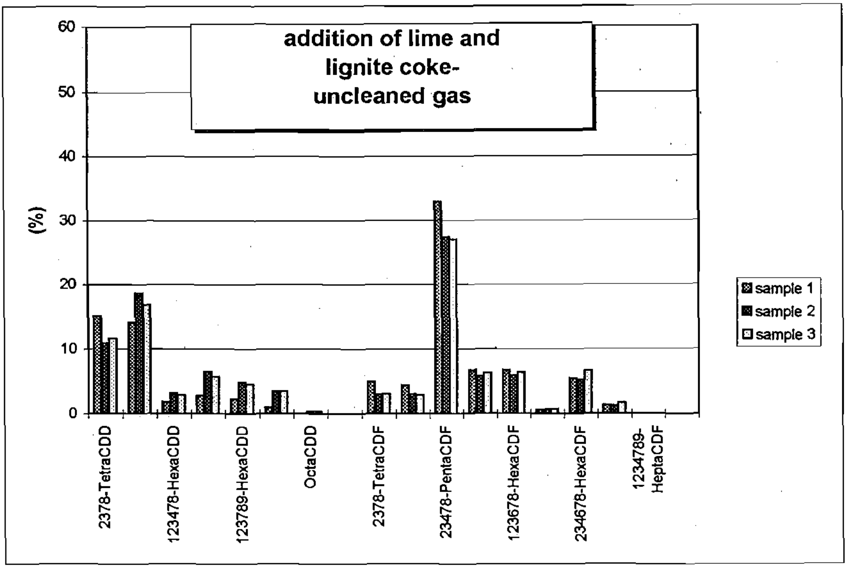


Figure 5.11-2: Contribution of the PCDD/PCDF to the equivalent values
(wood-burning furnace with fabric filter and addition of lime and lignite coke)



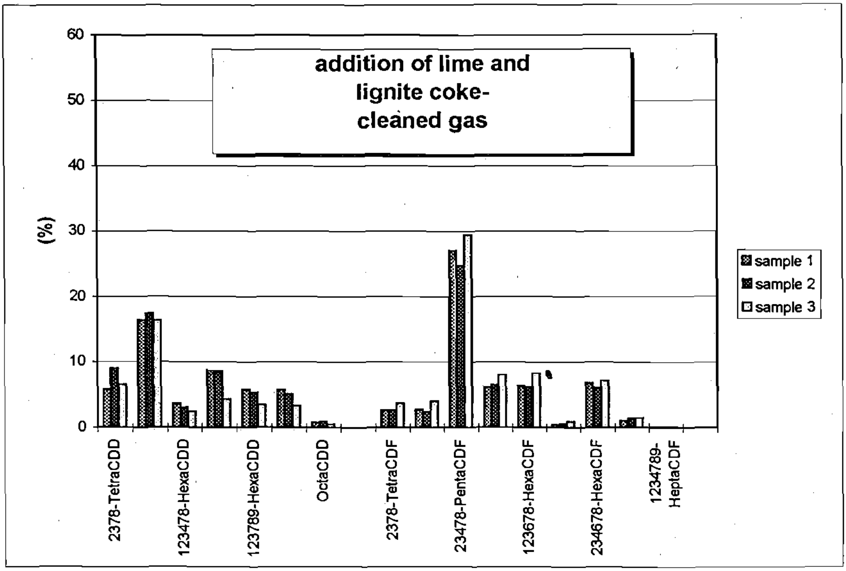


Figure 5.11-3:Contribution of the PCDD/PCDF to the equivalent values (sintering plant)

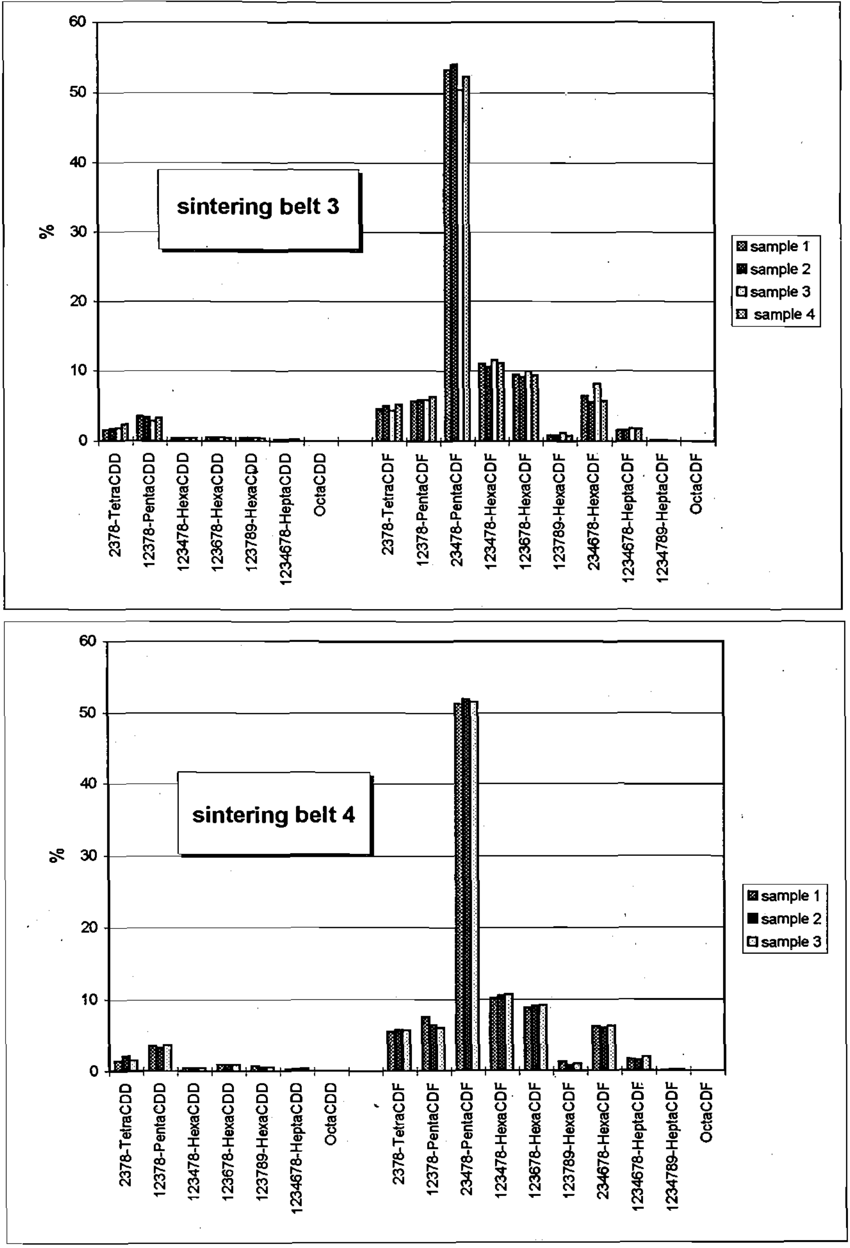
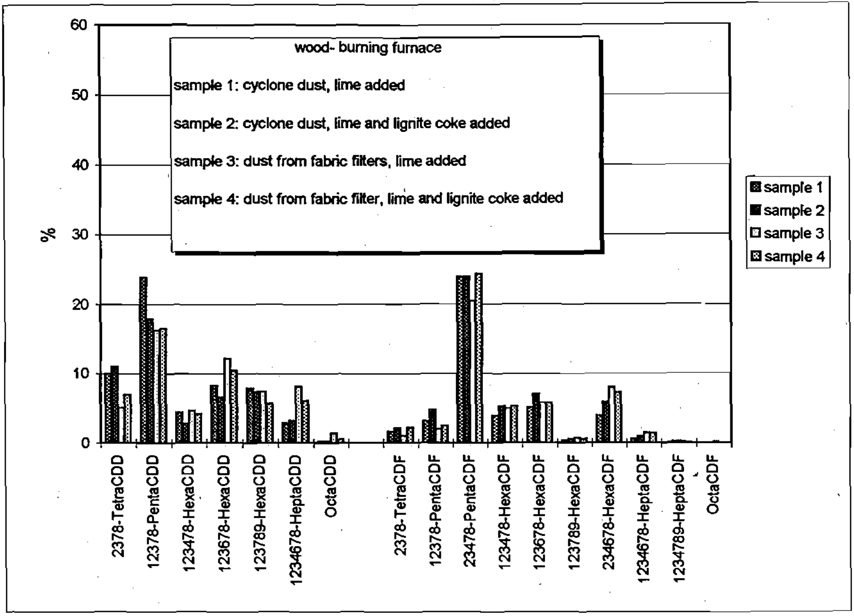
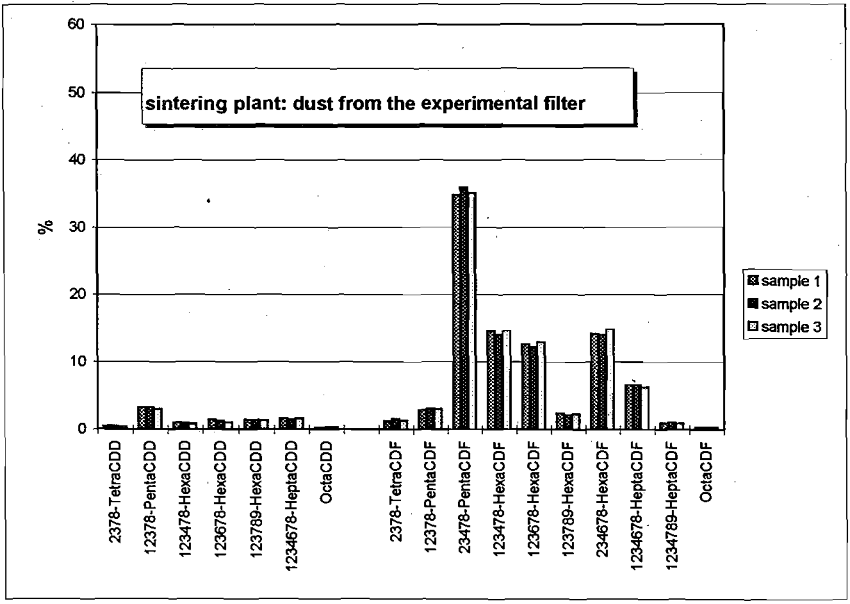


Figure 5.11-4: Contribution of PCDD/PCDF to the equivalent values
(dusts from fabrik filters from sintering plant and wood- burning furnaces)





6. Summary

In the year 1991 a list of 340 industrial plants subject to licensing was compiled in co-operation with the industrial inspection agencies of North Rhine-Westphalia. The list contained those industrial plants which were thought to produce dioxins and furans because of the prevailing conditions (such as temperatures > 200 °C, O_2 containing atmosphere), the employed method of flue gas cleaning, the use of chlorine containing input materials and because of existing reports of measurements taken in similar plants. The list formed the starting point of the measurement programme which was initiated at the end of 1991. The list was not a static tool but was continuously updated. A project group that was in charge of the entire measurement programme continuously updated the list of plants and integrated available results. The measurements were taken over a period of three years. A total of 50 industrial plants were covered. Up to 11 individual sources per plant were included in the measurements. The State Environment Agency LUA and all participating laboratories analysed more than 400 samples containing dioxins. The results considerably expanded the present knowledge of the importance of the various sources emitting dioxins and furans. The contributions of some emission sources have been underestimated in the past. This is primarily true for the iron and steel industry.

Figure 6-1 shows the ranges of dioxins emitted by various kinds of plants. Almost 70 % of the plants emitted less than 0.1 ng I-TEQ/m³. Nearly 10 % of the plants fell into the group with emissions ranging from 0.1 to 0.5 ng I-TEQ/m³ and somewhat more than 20 % of the plants emitted more than 0.5 ng I-TEQ/m³. In view of the fact that only plants were studied which were expected to emit important quantities of PCDD/PCDF the emissions of PCDD/PCDF, with few exceptions, turned out to be considerably more favourable than initially expected.

Taking a mass flow of 0.005 mg I-TEQ/h which corresponds to that of a modern garbage incinerator with a capacity of 16 t/h as threshold to being an important emission source, 22 sources from various industrial sectors were above this value. For all industrial plants which were included in the measurement programme a mass flow of PCDD/PCDF of almost 60 mg I-TEQ/h was obtained. The 22 sources accounted for nearly 100% of that amount. The contribution by the various sources of a sintering plant amounted to 60 % of the total emission. When these high values became apparent changes in the operation of the plants were initiated and some input materials were eliminated so that a 90 % reduction of the emissions could be achieved immediately. Through further primary measures the level of emission was further reduced. In other plants, too, measures which reduced the emissions were initiated by the inspection authorities. Therefore, the above mentioned value of 60 mg I-TEQ/h no longer reflects the actual situation.

The programme for the measurement of dioxins was intended to identify important sources emitting dioxins which have been unknown in the past or for which not enough information has been available. Originally it was not a goal of the programme to obtain specific emissions factors. Nevertheless, it has been attempted to convert the available data in a first approximation into emission factors.

Table 6-1 lists those sources for which specific emission factors could be derived and whose emissions were found to be > 0.005 mg I-TEQ/h. Individual sources of one industrial complex are listed separately so that the contributions by the various types of equipment to the emissions of an industrial plant become obvious. As is revealed sintering plant 4 emits a total of 3.7 µg I-TEQ/t of sintered material which includes the emissions by the sintering belt and the dust collector for the exhaust system. The contribution by the dust collector installed in the exhaust system amounts to 24 %. The results presented in Table 6-1 are based on the averages obtained from three individual values.

In conducting the measurements great emphasis was placed on quality control. The importance of setting quality standards prior to the measurements for evaluating the results of the measurements became clear. Had the programme been carried out without those standards being handed out with the contracts a large fraction of false results would have been obtained.

Figure 6-1: Distribution of the concentrations of dioxins measured in the flue gases over various concentration ranges

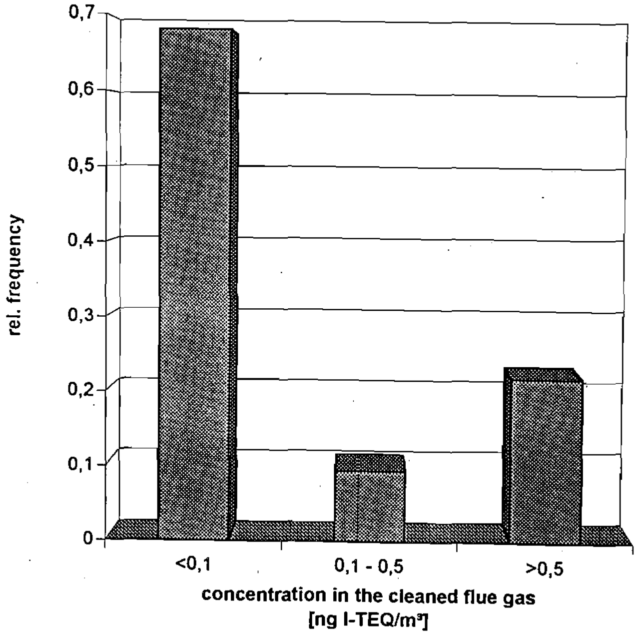


Table 6-1: **Specific emission factors**
(emission > 0.005 mg I-TEQ/h)

type of plant	**emission mg I-TEQ/h**	**material on which emission rate is based**	**capacity**	**emission rate**
iron ore sintering plant, dust removal from sintering belt	29.4	sintered material	310 t/h	94 µg I-TEQ/t sintered material
sintering plant (recycling material)	13.2	sintered material	39 t/h	338 µg I-TEQ/t sintered material
iron ore sintering plant, dust removal from sintering belt	5.8	sintered material	209 t/h	28 µg I-TEQ/t sintered material
hot-briquetting plant	3.69	hot briquettes	387 t/h	9.5 µg I-TEQ/t hot briquettes
iron ore sintering plant, dust removal from sintering belt	1.95	sintered material	549 t/h	3.6 µg I-TEQ/t sintered material
iron ore sintering plant, dust removal from sintering belt	1.62	sintered material	358 t/h	2.8 µg I-TEQ/t sintered material
rotating cylinder	1.04	oxides	3.1 t/h	335 µg I-TEQ/t oxides
secondary aluminium smelter	0.6	aluminium alloy	4.6 t/h	130 µg I-TEQ/t aluminium alloy
iron ore sintering plant, dust removal from air inside enclosures	0.317	sintered material	358 t/h	0.89 µg I-TEQ/t sintered material
iron ore sintering plant, dust removal from air inside enclosures	0.272	sintered material	310 t/h	0.88 µg I-TEQ/t sintered material
tin smelter, short rotary kiln	0.092	tin alloy	0.8 t/h	113 µg I-TEQ/t tin alloy
secondary non-ferrous metal smelter	0.064	non-ferrous metals	10 t/h	6.2 µg I-TEQ/t non-ferrous metals
lead and tin smelter	0.038	tin alloy	0.6 t/h	63 µg I-TEQ/t tin alloy
metal chips processing unit	0.038	input chips	2.6 t/h	15 µg I-TEQ/t input chips
secondary aluminium smelter	0.031	secondary aluminium	5.2 t/h	5.9 µg I-TEQ/t aluminium
Bessemer steel works	0.02	crude iron	279 t/h	0.07 µg I-TEQ/t crude iron
fibre board production plant, rotary drier	0.019	dried material	5.2 t/h	3.7 µg I-TEQ/t dried material
blast furnace, recuperator	0.01	crude iron	329 t/h	0.03 µg I-TEQ/t crude iron
cowper/recuperator	0.009	raw lead	4.3 t/h	2.1 µg I-TEQ/t raw lead
furnace fired with wood working residues, (0.97MW	0.0086	thermal capacity	1 MW	8.6 µg I-TEQ/MW

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