SOUR II

INDUSTRIAL EMISSIONS OF PCDD/F AND OF DIOXIN-LIKE PCB'S IN SAXONY-ANHALT

Ehrlich, Chr. , Kalkoff, W.-D. , Albrecht, W.
Saxony-Anhalt State Environmental Protection Agency, Reideburger Str. 47-49,
D - 06116 Halle (Saale), Germany

Abstract
The estimation of annual PCDD/F -emission in Saxony-Anhalt on the basis of 58 results of emission measurements (with 3 single-measurements each) for 28 sources prove the absolute dominance of the PCDD/F-emissions from secondary smelters (copper and aluminium). Industrial emissions of PCDD/F amount to 91% of the annual PCDD/F emission, in contrast to that domestic heating emission amount to 6% and traffic emissions to 3%.
Additional environmental impacts are due to the dioxin-like PCBs in the flue gas. The ratios of dioxin-like PCBs in TEQ (WHO[1]) versus PCDD/F in I-TEQ are 2-4% for crematories, combustion installations of waste wood and of lignite; 20-40% for secondary smelters (copper and iron), brick works and others; 50% for domestic combustion of lignite briquettes.

Objectives
To find out the major sources of dioxins, furans and dioxin-like PCB's in the Federal State Saxony-Anhalt (Germany), to estimate the annual emission of PCDD/F and to make a decision basis for reducing the dioxin emissions as far as possible.

Introduction
To reduce the PCDD/F- and dioxin-like PCB-input into the environment, an exact knowledge of all relevant sources is necessary. The emissions of municipal waste incinerators (MWI) are well known, but in the German New Länder such incinerators do not exist. There were nearly no data from other industrial installations 4 years ago. Studies in North Rhine -Westphalia and other states of Germany [2), 3)] help to improve the data basis. To detect the different emissions in a former Comecon-State, a dioxin monitoring programme of industrial emissions was started in Saxony-Anhalt in 1993. The first results of this programme are presented in this article. 44 out of several hundred industrial installations were selected, because of a relevant potential of dioxin emissions.

Experimental
The flue gases were sampled according to the German Guideline VDI 3499. The used special probe, made of titanium, contained a water-cooled quartz tube. A defined part of flue gas was sampled in form of an isokinetic network measurement including the whole cross-section of the chimney. The sample, which had left the water-cooled quartz tube, passed a vessel where the condensate was accumulated and then a XAD-2 sorbens tube. The sample consists of an extract from the titanium probe, quartz insert (cut), condensate from the vessel, XAD-2-adsorbent and the glassware of the

sampler. In preparation for the GC/MS analysis all samples were extracted and cleaned up according to the VDI-method 3499. Samples include the gas and particulate phase with a detection limit for dioxins or furans to homologue state of 0.005 ng/standard cubic meter or less and for biphenyls of 0.005 ng/standard cubic meter or less. Sampling of dioxins and furans as well as biphenyls was realized simultaneously. Characteristic flue gas components such as CO, TOC, NO_X, SO_2 and HCl were measured parallel to PCDD/F sampling.

Results

A. Emissions for PCDD/PCDF

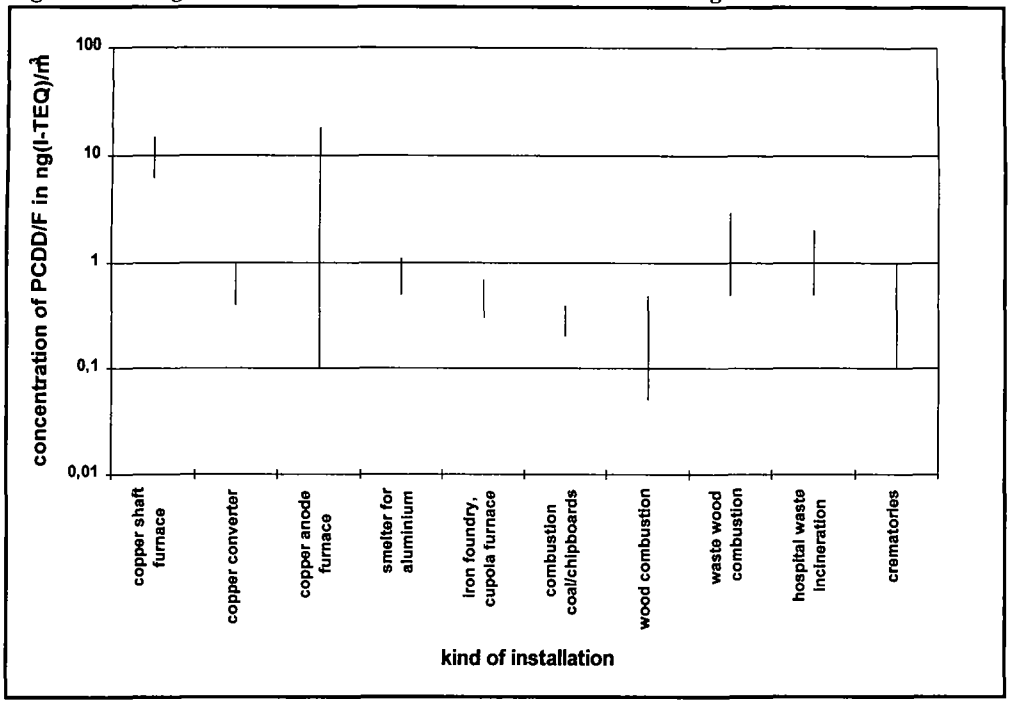
In the years from 1994 to 1995 a comprehensive measuring programme has been carried out to estimate industrial sources for PCDD/F. At first industrial installations with a theoretical relevant emission potential for PCDD/F were selected.

These are smelters and foundries for non ferrous metals (especially with secondary materials) and for iron, installations for combustion of lignite coal, wood and waste, crematories, chemical processes for PVC-production, installations for the production of building materials, smoked installations and domestic coal combustion. In addition to it dioxin emissions per year in Saxony-Anhalt in the sectors industry, traffic and domestic combustion were estimated. The following Table 1 shows the results of measurements :

Table 1 : Dioxin-emissions of different installations

installation	**flue gas concentration of PCDD/F in ng(I-TEQ)/m^3**
smelter for secondary copper	
- shaft furnace	6 ... 15
- converter	0,4 ... 1
- copper anode furnace	0,1 ... 18
smelter for secondary aluminium	0,5 ... 1,1
iron foundry, cupola furnace	0,3 ... 1
installation for combustion of	
- coal (lignite)	0,002 ... 0,05
with liquid waste products	0,0001 ... 0,01
with chipboards	0,2 ... 0,4
- wood (furniture industry)	0,05 ... 0,5
- waste wood	0,5 ... 3
- hospital waste incineration	0,5 ... 2
- liquid and gaseous waste products of PVC-process	0,004 ... 0,01
production of building materials	
- cement (Fuel : coal and waste oil)	0,001 ... 0,06
- brick-works	0,002 ... 0,01
- asphalt mixing plants	0,001 ... 0,003
crematories	0,1 ... 1
smoked installations for meat and sausage	0,004 ... 0,03
domestic combustion of coal	0,01 ... 0,05

Figure 1 : Flue-gas concentration of PCDD/F for some of the investigated installations

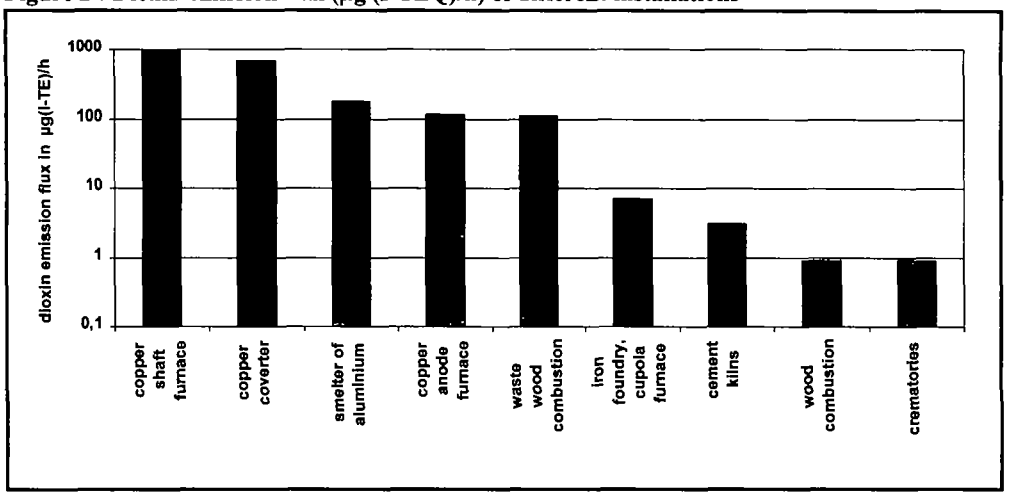


Besides the concentration of PCDD/F the emission flux of installations have to be considered. Figure 2 presents results of emission flux for the estimated sources.
Nowadays the annual dioxin emissions in Saxony-Anhalt amount to approximately 20 gram (I-TEQ). The most important sources are installations for smelting secondary non ferrous metals.

Table 2 : The annual emissions of PCDD/F in Saxony-Anhalt

kind of industrial installation, domestic combustion, traffic	annual dioxin flux in mg (I-TEQ)	annual dioxin flux in %
copper and aluminium smelter with secondary materials	15500	88
industrial combustion	430	2,4
cement kilns	35	0,2
crematories	30	0,2
iron foundry, cupola furnace	40	0,2
production of PVC	0,1	<0,1
domestic combustion	1100	6
traffic	500	3

Figure 2 : Dioxin emission flux (µg (I-TEQ)/h) of different installations



In result of the investigations different steps for the reduction of dioxin sources have to be derived. With redevelopment of old installations in future dioxin emissions in Saxony-Anhalt will be decreased. For traffic an emission reduction is expected as a result of the increasing use of unleaded petrol.

B. Emissions of dioxin-like PCBs

Flue gas samples were collected from 13 industrial installations and one domestic heating installation in order to evaluate the emission of dioxin-like PCBs and to evaluate the magnitude of environmental impact in relation to the emission of PCDD/F.

Table 3: Dioxin-like PCB-emissions of different installations

PCB	77	105	114	118	123	126	156	157	167	169	170	180	189
TEF	0,0005	0,0001	0,0005	0,0001	0,0001	0.1	0,0005	0,0005	0,00001	0,01	0,0001	0,00001	0,0001
installation	average PCB-concentration in ng/m³												
secondary smelter (Cu converter)	1.393	3.270	0.747	7.086	0.846	1.188	1.647	0.606	1.941	0.472	4.308	3.384	1.287
brick works	0.248	0.309	0.023	1.831	0.185	0.012	0.061	0.023	0.177	0.013	0.514	1.319	<0,023
iron foundry (induction)	0.110	0.156	<0,011	0.571	0.040	0.015	0.042	<0,011	0.052	0.005	0.167	0.467	0.034
iron foundry (arc)	0.052	0.123	<0,012	0.724	0.070	0.010	0.069	<0,012	0.052	<0,006	0.255	0.590	<0,016
hot-dip zinc galvanizing plant	0.248	0.081	<0,020	0.600	0.083	0.021	0.089	<0,020	0.089	<0,010	0.231	0.551	<0,020
asphalt mixing plant	0.133	0.804	0.128	5.053	0.743	0.013	0.292	0.060	0.222	<0,007	0.953	2.079	0.053
crematorium 1	0.428	0.279	0.059	0.649	0.074	0.142	0.166	0.066	0.174	0.029	0.390	0.608	<0,017
crematorium 2	0.556	0.251	0.061	0.948	0.225	0.261	0.244	0.120	0.314	0.072	0.711	0.946	<0,062
crematorium 3	0.069	0.050	0.012	0.176	0.019	0.025	0.041	0.012	0.046	0.007	0.093	0.165	<0,01
hospital waste incinerator	0.579	0.290	0.093	0.806	0.135	0.337	0.593	0.041	0.260	0.071	1.460	2.585	0.116
combustion install. for waste wood	0.009	n.d.	n.d.	n.d.	n.d.	0.07	n.d.	n.d.	n.d.	0.01	n.d.	4.140	n.d.
comb. install. for lignite and chipboards	2.013	3.496	0.369	7.513	0.414	0.052	0.382	0.054	0.473	0.011	1.731	2.363	0.105
combustion install. for lignite	<0,015	n.d.	0.079	0.223	<0,016	<0,014	0.043	<0,019	0.022	<0,020	0.127	0.248	<0,030
domestic comb. of lignite briquettes	0.400	n.d.	n.d.	n.d.	n.d.	0.070	n.d.	n.d.	n.d.	0.180	n.d.	0.550	n.d.

For estimating the risks associated with complex mixtures of PCDD/F and dioxin-like PCBs, the 2,3,7,8- TCDD Toxicity Equivalence Factor (TEF) method by WHO [1)] is used.

Table 4: PCDD/F emissions in comparison with dioxin-like PCBs on the basis of the I-TEQ and TEQ(WHO) concept for different industrial installations

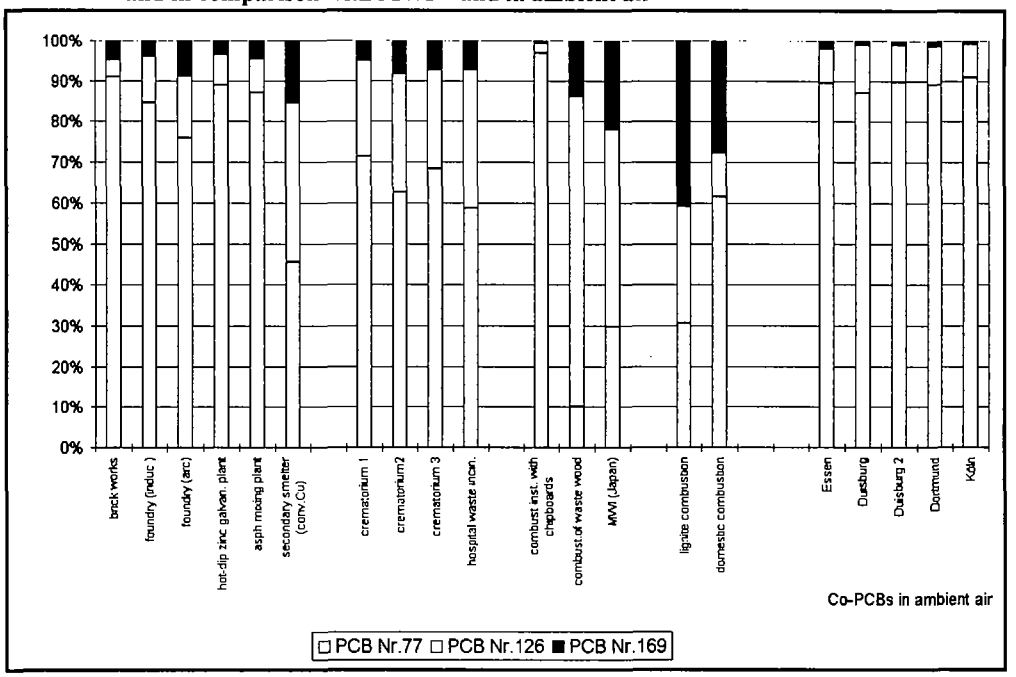
installation	PCB pg TEQ(WHO)/m³ excl.detect.limit	PCDD/F pg I-TEQ/m³ excl.det.limit	PCB/ PCDD/F %
secondary smelter (Cu converter)	127.4	571.0	22
brick works	1.8	8.2	22
iron foundry (induction)	1.7	4.3	40
iron foundry (arc)	1.2	6.3	19
hot-dip zinc galvanizing plant	2.4	33.7	7
asphalt mixing plant	2.4	2.2	107
crematorium 1	15.0	564.0	3
crematorium 2	27.5	1818.0	2
crematorium 3	2.7	122.7	2
hospital waste incinerator	35.5	970.0	4
combustion install. for waste wood	7.1	1330.0	1
combust. install. for lignite and chipboards	8.1	296.0	3
combustion install. for lignite	0.1	2.8	3
domestic combustion of lignite briquettes	9.0	17.6	51

As shown in Table 4 there are additional environmental impacts because of the dioxin-like PCBs in flue gas. The tendency that dioxin-like PCBs gave smaller TEQ values than did PCDD/F was observed in all tested installations, with the exception of the results of an asphalt mixing plant. In this case very low emissions were detected.

The ratios of dioxin-like PCBs (in TEQ(WHO)) versus PCDD/F (in I-TEQ) are 2-4% for crematories, combustion installations of waste wood and of lignite; 20-40% for secondary smelters (copper and iron), brick works and others; 50% for domestic combustion of lignite briquettes and 100% for an asphalt mixing plant.

The congeneric pattern of coplanar PCBs in the flue gas of the investigated installations are different from those of ambient air [4] (0,003..0,005 ng/m³ absolute, summarized).

Figure 3 : Congeneric pattern of coplanar PCBs in flue gas of different installations and in comparison with MWI [5] and in ambient air [4]



Acknowledgements

This work is financially supported by Saxony-Anhalt Ministry of Environment, Nature Conservation and Regional Planing.

We would like to thank Dr. Rauhut, U. et.al. and Dr. Schumann, H. et.al. for analytical works and Mr. Reifert, A., Dr. Noll, G., Mr. Maiwald, B., Mr. Lux, R. as well as Mr. Pohle, A. for technical assistance.

References

[1]Ahlborg U.G., G.C. Becking, L.S. Birnbaum, A. Brouwer, H.J.G.M. Derks, M. Feeley, G. Golor, A. Hanberg, J.C. Larsen, A.K.D. Liem, S.H. Safe, C. Schlatter, F. Waern, M. Younes, E. Yrjänheikki (1994): Toxic Equivalency Factors for Dioxin-like PCBs, Chemosphere 28, pp.1049-1067.

[2]Ergebnisse und Maßnahmen des Dioxinmeß- und Minderungsprogrammes (1994): Seminarbeiträge, Ministerium für Umwelt, Raumordnung und Landwirtschaft Nordrhein-Westfalen, Düsseldorf.

[3]Erarbeitung von Anforderungen zur Emissionsbegrenzung von Dioxinen und Furanen (1995): Schriftenreihe des LAI, Nr.9, Erich Schmidt Verlag, Berlin.

[4]Hiester E., P. Bruckmann, R. Böhm, P. Eynck, A. Gerlach, W. Mülder, H. Ristow (1996): Pronounced decrease of PCDD/PCDF Burden in Ambient Air, to be published in Chemosphere.

[5]Miyata H., O. Aozasa, Y. Mase, S. Ohta, S. Khono, S.Asada (1993): Real situation on emission of PCDDs, PCDFs and non ortho chlorine substituted coplanar PCBs via flue gas from urban waste incinerators in Japan in DIOXIN '93,13th International Symposium on Chlorinated Dioxins and Related Compounds, Vienna, Volume: Analytical Methods, Formation and Sources pp. 253-256.