

EPA DIOXIN-Reassessment: Implications for Germany

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1 INTRODUCTION

On September 13, 1994, the US-EPA released a „public review draft“ of its Dioxin Reassessment. For more than three years, EPA and outside scientists had collected information on polychlorinated dibenzo-*p*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), and dioxin-like polychlorinated biphenyls (PCB) to conduct a scientific reassessment of the health risks of exposure to these compounds. The reassessment is considered to be a scientific document and does not address policy or regulatory issues. The preparation of the draft document was accompanied by public meetings and workshops. After its presentation in September 1994, the document was open for discussions and comments. Moreover, there was a call-in for additional data to fill the gaps in the understanding of dioxin exposure. Thus, EPA was calling on all parties - industry, public interest groups, state and local governments, academia, and hospital facilities (note: was identified as the major dioxin emitter) to voluntarily submit any data that can help. Finally, the draft document was peer-reviewed by EPA's Science Advisory Board and following review, comments, and revisions, the final document will be released by approximately the end of 1995.

Such procedure to compile a large database for one group of chemical compounds and start open participatory scientific discussions about exposure and risks caused by dioxins as performed for the DIOXIN Reassessment by US-EPA is unknown in Germany or Europe. However, as for US citizens and scientists, there was and still is a chance to make individual inputs into EPA's DIOXIN Reassessment. This chance was taken by many individuals and has started discussions in various countries and organisations. Results of such efforts are given below, *e.g.* national inventories.

This paper will deal with the Exposure part of the Dioxin Reassessment (which included sources, environmental levels, and background exposures) and not address the Health chapter. Moreover, the site-specific assessment procedures are not addressed specifically in terms of the appropriateness of the models used.

2 NATIONAL INVENTORIES

Since the late 1980s, several authors from various countries did estimate annual emissions of PCDD/PCDF into the environment. Maybe as a result of EPA's efforts to make a dioxin emission estimate from US sources, new mass balances were calculated for many countries.

Most authors used the same approach to calculate the annual emission from a given source:

$$\text{Emission of source} = \text{Emission factor} \cdot \text{"Production" term}$$

In other words, the PCDD/PCDF emission per year of a given source in (e.g. mg I-TEQ/yr.) was calculated by multiplying the release of PCDD/PCDF (in e.g. mg I-TEQ) per unit of feed material processed or produced (e.g. ton or liter) with the amount of feed material processed or produced (ton per year). In order to make a source emission estimate, information is required for

- a) representative dioxin measurements for a given source. In many cases, these estimates are very uncertain as emissions are deduced from a few test results to a nation-wide basis or not existing and thus, either numbers from the literature were taken or emissions derived from similar processes.
- b) the total amount of feed material processed or produced. Very often, there is a high degree of certainty for such information, e.g. all fields of waste disposal, paper and pulp production, fuel consumed, etc.

Very often, the results obtained from emissions from known sources are compared with deposition measurements. So far, all comparisons gave relatively large discrepancies between emitted amounts and loads received on the countries surface. Interestingly, in all cases the total amount calculation for deposition is much higher than the amount emitted to the air. Moreover, it is thought that processes such as revolatilization and photolytical transformation as well as erosion do not account for the „missing dioxins“. For discussion of ambient air concentrations see Fiedler (this volume) and Chapters 3 and 4.3.

The latest information on nation-wide inventories available for Sweden, the Netherlands, the United States of America, the United Kingdom, and Germany are given in this chapter. To my knowledge, no update was made for Austria or Japan within the last three years.

Most countries performed mass balances for emissions to the air and did not consider PCDD/PCDF in technical products, such as residues from thermal and industrial processes e.g. (fly) ashes, stillbottoms, paper products (e.g. 1 million ton of recycling paper contains approx. 5 g I-TEQ) or PCDD/PCDF-containing intermediates in industrial processes and dioxin-containing waste in landfills. This potential seems to be negligible in terms of environmental impact and human exposure and risk.

Moreover, no inventory includes PCDD/PCDF in „natural“ products such as food-stuffs of animal origin, vegetation, etc., and the dioxin potential present in sediments, soils, and reservoirs such as sewage sludge and compost. The last mentioned are not completely immobile or restricted to the technosphere and thus, can have a potential to enter the environment and the human food-chain.

An interesting discussion is related to the use of the term „background“. The US-EPA Dioxin Reassessment document defines „background“ to areas which are not exposed to readily identifiable point sources of dioxin-like compounds. During the SAB meeting however, it was mentioned that „background“ should only be used on a nation-wide basis and not when describing site-specific situations. In such case, the term „baseline“ would be more appropriate.

2.1 Sweden

Within the Swedish Dioxin Study, emission estimates were made for the years 1990 and 1993 (Table 1) (de Wit 1995). Whereas no change was postulated for the amounts of PCDD/PCDF emitted to water and found in products and wastes, a decrease was calculated for the total emissions to air: the air emissions of 31.8-115 g N-TEQ -from 1990 would have been reduced to 21.6-88 g N-TEQ in the year 1993. The categories with the largest reductions were primary lime production, municipal waste incineration, and wood burning stoves. However, small increases due to larger amounts of material or fuel processed were found, too (natural and biogas burning as well as use of diesel and unleaded gasoline; cremation). In Table 1 decreases are indicated by bold numbers and increases by an asterisk.

Sweden is aware of additional sources, such as textile production, dry cleaners, and forest fires; however, no estimate was made. Sweden and the USA (see Chapter 2.3) are the only countries that try to differentiate between the emission streams to air, water, and sinks such as products and wastes.

2.2 The Netherlands

Annual PCDD/PCDF emissions have been estimated for the Netherlands (Table 2) (de Koning *et al.* 1994). For the year 1989, the total flux to the air were much higher (960 g I-TEQ). The decrease to 1991 is due to the fact that some municipal waste incinerators with high emissions (up to 92 ng I-TEQ/m³) were either shut-down or retrofitted.

In 1991, with 79 % municipal waste incineration was still the largest contributor. The residual 21 % were split on 16 process categories. High uncertainty is with the emission estimates from cable processing, wood combustion, and the former use of wood preservatives. No data were available for accidental fires. Thus, this category was not quantified.

Table 1: Preliminary estimates of PCDD/PCDF emissions from various sources in Sweden during 1990 and 1993 given in g Nordic-TEQ (N-TEQ)/yr. (de Wit 1995).

Source	To Air 1990	To Air 1993	To Water	In Wastes	In Products
Industry					
Bleached kraft pulp	1	1	1.5-5		0.3-6.6
Recycling paper pulp					2.8
Chloralkali plants			0.28-0.6	0.25	
Mercury distillation	0.000005	0.000005	0.003	0.004	
Sewage sludge			0.11	2.9	1.5
Steel mills	1.6-4	1.6-4		8.2	
Scrap steel mills	0.4-15	0.4-15		20	
Prim. non-ferrous smelters	0.13-0.27	0.13-0.27		0.38	
Sec. non-ferrous smelters	4.3	4.3		2.1	
Foundries	0.007-0.49	0.007-0.49		0.82-15	
Cement kiln - gases	0.07-1.3	0.07-1.3			
Cement kilns - dust	0.35	0.28			
Lime burning, prim. prod.	9.8-18	2-2.5			
Lime burning - industrial use	0.5-6.3	0.5-6.3			
Ceramic salt glazing	0.01	0.01			
Incineration					
Glassfiber waste incineration	0.00004	0.00006 *			
Municipal waste incineration	4.5	3.0		0.6-2.4	
Hazardous waste incineration	0.01	0.007			
Hospital waste incineration	0.001	0.001			
Cremation	0.34-0.68	0.37-0.73*			
Uncontrolled landfill fires	2.8-30	2.8-30			
Illegal metal reclamation	?	?		0.02-0.04	
Heating/Energy					
Oil	0.1-2.6	0.1-2.5			
Coal	0.75	0.61			
Natural gas	0.03	0.04 *			
Wood burning stoves	3-13.8	2.1-9.8			
Other biofuel	1.2-6.4	1.4-7.7 *			
Traffic					
Ferries (gas oil, heavy oil)	0.7	0.63			
Planes (aviation fuel)	0.03-0.93	0.02-0.86			
Vehicles - diesel	0.067-0.14	0.73-0.15*			
gasoline - leaded	0.026-2.9	0.009-0.97			
gasoline - unleaded	0.08-0.16	0.14-0.27*			
Totals	31.8-115	21.6-88	1.6-5.1	35-52	4.6-10.9

Table 2: Estimated annual PCDD/PCDF emissions into the air for the Netherlands (de Koning *et al.* 1994)

Source	Emission for 1991	Emission for 2000 ¹⁾
Municipal waste incineration	382	2-4
Hazardous waste incineration	16	1.7
Landfill, biogas, and sludge incineration	0.3	1.5
Cable and electromotor burning	1.5	1.5
Hospital waste incineration	2.1	0
Asphalt mixing plants ²⁾	0.3	0.3
Combustion of oil	1.0	1.0
Combustion of coal	3.7	3.7
Combustion of wood ³⁾	12	9
Crematories	0.2	0.2
Traffic	7.0	0.2-5
Sintering plants	26	3
NE-Non-ferrous metal industry	4.0	4.0
Chemical production processes	0.5	0.5
Use of wood preservatives	25	20
Other high temperature processes ⁴⁾	2.7	2.7
Accidental fires	?	?
Total (without fires)	484	max. 58

- 1) The emission estimate for 2000, with the exemption of MWI, does not account for growth or decrease in the total mass processed
- 2) Emission as a result of heat generation is mentioned by the energy generators concerned
- 3) Highly uncertain; further research recommended
- 4) Thermal soil treatment, drying of fly-ash, cement and glass/mineral wool production, etc.

2.3 United States of America

Nation-wide emission estimates for the United States have not previously been compiled. As part of the Reassessment document, the annual PCDD/PCDF emissions into the atmosphere were estimated by the US-EPA (US-EPA 1994). A summary is given in Table 3 (Schaum *et al.* 1994). Moreover, a confidence rating for the production and emission estimate as well as the ratio of the number of plants investigated towards the number of existing plants is shown in Table 3. The data from Table 3 were generated for the EPA's Dioxin Reassessment. Since the official release of the draft document on September 14, 1994, many comments have been submitted. Consequently, the emission estimates may go up or down. Although it was found that the inventory covered major sources of PCDD/PCDF some were either not mentioned or quantified, such as accidental fires, smelters, etc. Resuspension from

existing reservoirs, esp. PCP and PVC production as well as from chloralkali electrodes, and natural formation of PCDD/PCDF from chlorophenols were not included. Thus, the final document may present either a higher or lower numbers.

Table 3: Estimated PCDD/PCDF emission rates for the USA in g I-TEQ/yr.
(Schaum *et al.* 1994)

Source	Annual Emissions	Confidence Rating	Ratio of Facilities Tested towards Facilities Existing
Medical waste incinerators	1600-16000	M/L	6/6700
Municipal waste incinerators	1800-9000	H/M	30/171
Cement kilns	110-1100	H/L	17/212
Industrial wood burning	100-1000	H/L	2/?
Sec. copper smelting	74-7400	H/L	1/24
Forest fires	27-270	M/L	1 study
Diesel fuelled vehicles	27-270	H/L	See *
hazardous waste incineration	11-110	M/L	6/190
Residential wood burning	13-63	H/L	2 studies
Sewage sludge combustion	10-52	H/M	3/199
Drum and barrel reclaimers	0.5-5	L/L	1/?
Kraft black liquor boilers	0.9-4.3	H/M	3/104
Secondary lead smelters	0.7-3.5	M/M	3/23
Total	3,774-34,278		

H = High; M = Medium; L = Low. The first letter represents the confidence rating for production estimate and the second letter is the confidence rating for the emission estimate

* Lower emission estimate is based on test of one Swedish truck and upper estimate on a tunnel study in Norway

The Reassessment document includes an estimate of PCDD/PCDF emissions to other media, too (EPA 1994). However, there is not much information available and EPA is aware of a large gaps of knowledge. For example, many products * - although mentioned - were not analysed for PCDD/PCDF, e.g. products from municipal, hazardous, and medical waste incineration, kraft black liquor boilers, sewage sludge incineration, and carbon reactivation furnaces. Moreover, all „products“ from vehicle fuel combustion, wood, coal, and oil combustion and forest fires were not analysed. Only a few emissions to water and landfills were quantified (see Table 4). The releases associated with chemical manufacturing could not be quantified due to

* product is defined to include substances or articles, e.g. paper pulp or sewage sludge that is distributed/marketed commercially.

lack of test data. Potentially releases were though to occur *via* all media (air, water, land) and in the product itself.

Table 4: Current PCDD/PCDF emissions to various media (g I-TEQ/yr.) (EPA 1994)

NEG = Expected to be negligible or non-existent

Blank = Insufficient data available upon which to base an estimate

Emission Source	Water	Land/Landfill	Product
Bleached chemical pulp and paper mills	74-150	71-140	110-210
Publicly owned treatment works (sewer plants)		150-290	2.5-5.0
Chemical manufacture and processing	NEG	NEG	
Municipal waste incineration	NEG	810-4000	NA
Cement kilns		7.6-76	
Total (approx.)	74-150	1000-4500	110-220

2.4 United Kingdom

An inventory of PCDD/PCDF releases into the atmosphere of the United Kingdom was performed in 1995 (ERM 1995). The numbers given in Table 5 were derived from emission factors (μg I-TEQ/tonne of material produced or treated) and the amount of material treated or produced by each of the processes. In the case of crematoria and traffic, the emission factors were expressed in terms of the quantity of PCDD/PCDF emitted per cremation and per kilometer travelled, respectively. In the majority of cases, emission factors were obtained from the literature. Same as for the USA, a confidence rating was included. As industrial practices in the UK is currently undergoing significant changes, the present estimates as shown in Table 5 should not be taken as definitive, rather they should be regarded as indicative of the current situation in the UK using the best data currently available. In addition, future emissions were projected, too.

As can be seen from Table 5, industrial processes account for approximately 90 % of the total inventory which ranges from 560 to 1,100 g I-TEQ per year. Municipal waste incineration (MWI) was identified as today's major source of PCDD/PCDF emissions to the atmosphere. However, as these emissions are subject to stringent control from 1995/96, the contribution of this source will reduce significantly. The non-industrial sources contribute emissions of 24-145 g I-TEQ/yr., approximately 4-15 % of the inventory.

Emissions to the atmosphere from combustion sources such as thermal waste disposal and thermal metallurgical processes, will undergo significant changes over the next few years as a result of the implementation of Integrated Pollution Control.

Table 5: Estimated emissions of PCDD/PCDF (g I-TEQ/yr.) to the atmosphere for the United Kingdom (ERM 1995)

Process	Emissions to Atmosphere		Estimate Quality *)
	Present	Future	
Coke production	2	2	H/M
Coal combustion (industrial)	5-67	5-67	H/M
Waste oil combustion	0.8-2.4	0.8-2.4	M/M
Wood combustion (industrial)	1.4-2.9	1.4-2.9	M/L
Straw combustion	3.4-10	3.4-10	L/L
Tires combustion	1.7	1.7	H/H
Landfill gas combustion	1.6-5.5	1.6-5.5	M/M
Sinter plants	29-54	29-47	M/L
Iron and steel	3-41	14	M/L
Non-ferrous metals	5-35	10	M/L
Cement manufacture	0.2-11	0.2-11	H/M
Lime manufacture	0.04-2.2	0.04-2.2	H/M
Glass manufacture	0.005-0.01	0.05-0.31	H/M
Ceramic production	0.02-0.06	0.02-0.06	H/M
Halogenated chemicals	0.02	0.02	L/M
Pesticide production	0.1-0.3	0.3	L/M
MSW combustion	460-580	15	H/M
Chemical waste combustion	1.5-8.7	0.3 ²⁾	M/M
Clinical waste combustion	18-88	5	H/M
Sewage sludge combustion	0.7-6	0.9	H/H
Carbon regeneration	0.006	0.003	H/M
Asphalt mixing	1.6	1.6	H/M
PCP in timber processes	0.8	0.8	L/L
Crematoria	1-35	1-35	H/L
Domestic wood combustion	2-18	2-18	L/L
Domestic coal combustion	20-34	20-34	L/L
Traffic	1-45	1-45	H/L
Natural fires	0.4-12 ¹⁾	0.4-12	L/L
Total	559-1,099	112-345	

*) The values are assigned a rating for estimate quality. The first letter for quality of data relates to UK production and the second to the emission data (H = High, M = Medium, L = Low)

¹⁾ Based on open fires data. Soot-based approach not used.

²⁾ Assumed to comply with EU Directive COM(92)9 Final -SYN 406 (= emission limit value of 0.1 ng I-TEQ/m³).

2.5 Germany

Lahl and Zeschmar-Lahl (1995) presented an inventory of sources with relevant PCDD/PCDF emissions to the atmosphere (Table 6). As can be seen from Table 6 and as was concluded in the EPA Reassessment, there is not much information available on the concentrations of PCDD/PCDF in chemicals and products (except for pulp and paper products). Some data were summarised by Fiedler (1995, this volume); however, older analyses of chlorinated chemicals as summarised in the NATO/CCMS Report (1988) were not performed congener-specific.

Table 6: Estimated PCDD/PCDF emissions to the atmosphere for Germany (Lahl and Zeschmar-Lahl 1995). Concentrations in g I-TEQ/yr.

Source	Dioxin Emissions	
	1985-1990	1993/1995
Chemical production	?	?
Waste incineration		
Municipal waste	400	50-100
Hazardous waste	30	<1
Hospital waste	5-6	-
Other combustion processes	30-90	25-65
Fossil fuel power plants	0.1-15	0.1-15
Combustion of wood	<1	<1
Automobiles (gasoline)	10-30	<5
Automobiles (diesel without trucks)	<1	<1
Automobiles (trucks)	?	?
Private home heating	20-45	20-45
Metal generation and processing	570-1010	276-381
Paper manufacture	<1	<1
Contaminated areas	100	100
PVC fires (including residues)	1-10	1-10
Total	1,166-1,646	452-656

2.6 Comparison of National Inventories

Table 7 summarises the national emission estimates. Although there are large differences between the PCDD/PCDF amounts released from all known sources for the various countries, it can be seen that the total masses roughly correlate with anthropogenic activities. Thus, in the less populated countries such as Sweden and the Netherlands, the dioxin emissions are smaller than in the USA where a population of 240 million Americans seems to produce higher amounts of PCDD/PCDF. The high degree of industrialisation can be seen for the Netherlands, the United Kingdom, and Germany: technological improvements for purification of off-gases have resulted or will result in a sharp decrease of the PCDD/PCDF emissions to the air.

Table 7: Summary of PCDD/PCDF national emission inventories (g TEQ/yr.)

Sweden		The Netherlands		USA	United Kingdom		Germany	
1990	1993	1991	2000		Present	Future	1985-1990	1993/95
31.8-115	21.6-88	484	<58	3774-34278	559-1099	112-345	1166-1646	452-656

Mainly, the same sources were considered in all mass balances. However, some differences can be observed as well:

- Lime burning for primary production was considered to be the major source of atmospheric emissions in Sweden. However, Sweden is the only country to include this type of industry.
- Although aware of the fact that crematories are known dioxin sources, such emissions were not included in the inventories of Germany and the USA.
- The Netherlands are the only country to attribute significant emissions to chemical production processes (25 g I-TEQ/yr.).
- Only the USA estimate has a high number for diesel truck-derived PCDD/PCDF emissions (27-270 g I-TEQ/yr.). However, this estimate has got a low confidence rating.

There seem still to be large difficulties to do a profound estimate on PCDD/PCDF emissions from residential homes. Based on the information by LIS (LIS 1992) and Schatowitz (Schatowitz *et al.* 1993) heating with gas, oil, coal, and wood does not produce high concentrations of dioxins. However, as private waste disposal in ovens, stoves, and chimneys can generate high PCDD/PCDF emissions, there is a high uncertainty on both, the number of such events per year and the concentration in the off-gases. Moreover, the amount of fossil fuel, esp. wood, used in residential heating seems to be unclear.

No sound information is available on the contribution from accidental and uncontrolled fires, such as burning homes (Germany: 1-10 g I-TEQ/yr.), forest fires (USA: 27-270 g I-TEQ/yr.), landfill fires (Sweden: 2.8-30 g n-TEQ/yr.), burning of straw, volcanic eruptions, etc. and on diffuse losses from manufacturing processes. Lahl's estimate for Germany included 100 g I-TEQ/yr. emitted from Kieselrot-contaminated areas.

3 NATIONAL MASS BALANCES

In the USA, there exist deposition data from just two places (Koester and Hites 1992). Total fluxes of wet and dry deposition - given as sum of PCDD and PCDF - were determined for the cities of Indianapolis and Bloomington, IN, USA (see Table 8). Due to the lack of congener-specific deposition data, no I-TEQ could be calculated. However, due to the difference in physical-chemical properties, congener-specific information is necessary to correctly estimate such fluxes. The US data do not consider gaseous PCDD/PCDF. - For Germany, there is a much better database on air concentrations of PCDD/PCDF available (e.g. see Fiedler 1995). A mass balance for PCDD/PCDF on a TEQ basis was performed by Wintermeyer and Rotard (1994). The authors used a tiered approach and divided the country into regions of low and higher deposition; the results are shown in Table 9. Inclusion of the gaseous part of the aerial PCDD/PCDF would result in a total atmospheric deposition of 2,000-10,000 g TEQ/yr.

Table 8: Deposition estimates for the USA

	Wet deposition ng/(m ² -yr.)	Dry deposition ng/(m ² -yr.)	Total ng/(m ² -yr.)
Indianapolis (Koester&Hites)	220	320	540
Bloomington (Koester&Hites)	210	160	370
	Remote Areas ng I-TEQ/(m ² -yr.)	Populated Areas ng I-TEQ/(m ² -yr.)	Total g TEQ/yr.
US-EPA	1	2-6	20000-50000

Table 9: Annual deposition in Germany - former FRG (Wintermeyer and Rotard 1994)
All concentrations refer to deposition measurements (dust) and do not include PCDD/PCDF in the gas-phase

Region	Deposition pg TEQ/(m ² -d)	Deposition ng TEQ/(m ² -yr.)	Total Area (km ²)	Input g TEQ/yr.
Agricultural and forestry use	5-20	1.8-7.3	218000 (87.2 %)	400-1600
Residential/industrial	20-100	7.3-36.5	3000 (12.2 %)	200-1000
	100-500	36.5-183	540 (1.8 %)	200-800
	500-3000	183-1100	120 (0.4 %)	200-1100
Total				1000-4500

As for all other countries, e.g. Sweden (Rappe 1991) and the United Kingdom (Harrad and Jones 1992), the estimated deposition for the USA and Germany exceed the estimated emissions by a factor of ten or more. Thus, presently all mass balances - independent of the quality of data used to calculate emissions and deposition (including gaseous deposition as the gas-phase PCDD/PCDF are included in all emission estimates!) enface the same unsolved problem:

$$\text{Annual deposition PCDD/PCDF} \gg \text{Annual emissions PCDD/PCDF}$$

Several reasons were mentioned to explain these discrepancies, e.g.:

- Emission data are not representative for the known sources (in general, the emissions are underestimated for several sources)
- Deposition data are not representative
- There are additional unidentified sources (esp. diffuse emissions)
- Additional deposition from emissions generated outside the country (long-range transport)
- Resuspension and deposition from reservoirs
- Atmospheric transformation processes.

4 LESS WELL-KNOWN SOURCES

4.1 Thermal

The generation of energy in fossil-fuelled power plants contributes only minor amounts of PCDD/PCDF. Measurements at coal-fired power plants were much below 0,1 ng I-TEQ/m³ (0.02-0.0001 ng I-TEQ/m³).

In Germany, there exist approx. 100 crematories; many are equipped with an after-burning chamber, cyclone, bag-house or electrostatic filter. However, measures to control the input-material, e.g. low content of halogens (chlorine and bromine) in the coffin, as well as better firing conditions will help to reduce the emissions of crematories. Known concentrations were in the range 1-14 ng TEQ/m³. Using gas- or oil-fuelled facilities the volume emitted is about 1,200 m³/h.

4.2 Reservoirs

So far, hardly any country did a reservoir inventory for PCDD/PCDF. In other words, there is almost no knowledge about the total amounts of PCDD/PCDF present in sinks such as sediments of harbours, rivers, lakes, and oceans, landfills (including residues of accidental fires, fly ash, residues and sludges from chemical manufacture), contaminated soils from (chemical) production sites. It is thought that these reservoirs contain large amounts of PCDD/PCDF. Although these reservoirs may be highly contaminated with PCDD/PCDF, the chemical-physical properties of these compounds imply that dioxins and furans will stay absorbed to organic carbon of soils or other particles. On the other hand, mobilisation can occur in the presence of lipophilic solvents (⇒ leaching into deeper layers of soils and/or groundwater) or in cases of erosion or run-off by rain from topsoil (⇒ translocation into the neighbourhood). Although there is little information available, experience has shown that PCDD/PCDF transport due to soil erosion and run-off does not play a major role for environmental contamination and human exposure. However, considerable impact to the neighbourhood was proven in cases of Kieselrot contamination.

Volatilisation of gaseous PCDD/PCDF from contaminated soils was proven by plant-uptake (Prinz *et al.* 1993). Contamination of leafy plants via a soil→plant transfer was studied in open field, greenhouse, and chamber experiments. A transfer of PCDD/PCDF from soil to plant was detected under these micro-climate conditions; however, due to open air turbulence an influence of the soil could not be detected in the plants (carrot leaves). As shown in greenhouse experiments, this pathway may become important for vegetation growing closely to topsoil (Prinz *et al.* 1993, DECHEMA 1995).

A major translocation of PCDD/PCDF can occur in cases of excavating dioxin-contaminated landfills for remedial action or dredging of harbour and river sediments. Such action can lead to human exposure when the sediments are brought to areas with farming or horticultural use (⇒ relevance for terrestrial food-chain).

Other reservoirs include the former use of PCDD/PCDF-contaminated products such as 2,4,5-T, polychlorinated biphenyls (PCB), and pentachlorophenol/pentachlorophenate (PCP/PCP-Na). Although there are estimates of the total amount of these compounds produced for various purposes it seems to be impossible to deduce from these numbers a quantitative impact of PCDD/PCDF to the environment or humans.

4.3 Biological

Biological formation of PCDD/PCDF from chlorinated precursors was discussed for compost and sewage sludge and questions on the possibility of a biogenic formation did arise for sediments and soils (esp. forest soils). Based on the results of Öberg *et al.* (1992) the turnover to convert pentachlorophenol (PCP, the most suitable precursor) to PCDD is in the low ppm-range (see Table 10). Consequently, a chlorinated precursor present in an environmental matrix, such as soil or sediment, at ppm-concentrations should be converted to not more than ppt-levels of high chlorinated PCDD (Cl₇DD and Cl₈DD). In other words, ppm-concentrations of chlorophenols would generate ppt-levels Cl₇DD and Cl₈DD or ppq-concentrations in TEQ. Thus, based on present knowledge, biological formation of PCDD from chlorinated phenols under environmental conditions are negligible.

Table 10: ¹³C-PCDD (total pg) found in sludge samples after spiked with ¹³C-PCP and proportion of ¹³C-PCP converted to ¹³C-PCDD (Öberg *et al.* 1992)
Incubation temperature was 22 °C for * samples and 10 °C for ** samples

Sample	¹³ C-1234679 Cl ₇ DD	¹³ C-1234678 Cl ₇ DD	¹³ C-Cl ₈ DD	Total ¹³ C-PCDD	¹³ C-PCDD ¹³ C-PCP
Activated sludge *	274	3726	2188	6187	3.5 ppm
Sedimented sludge *	310	1395	2597	4302	2.4 ppm
Sedimented sludge **	403	2494	3017	5913	3.4 ppm

5 EXPOSURE DATA

EPA's Dioxin Reassessment document revealed that for some media there is hardly any information available for the United States (EPA 1994). As an example, there are no deposition data and more data is needed for environmental levels in air, soil, sediments, and water. Although, the daily intake of PCDD/PCDF is estimated to be about 90 % *via* food ingestion, there is not enough food data available (e.g. milk intake is based on two analyses).

Understanding of the environmental fate of PCDD/PCDF is fundamental to evaluating human exposure. Empirical measurements of inter-media transfers, environmental degradation and clearance rates, as well as bioaccumulation factors are fundamental to apply mathematical models to simulate such events. Although the TEQ-approach was developed and proven as a helpful tools for risk assessment, input data for models and exposure assessment have to be congener-specific. For further information on terrestrial models (air→grass→cow milk) see McLachlan *et al.* (1995).

Most information is available on congener-specific transfer data were determined for fodder → cow (milk) transfer in three studies (Fürst *et al.* 1992, McLachlan 1992, and Blüthgen *et al.* 1994). The results are presented in Table 11.

Table 11: Congener-specific migration rates for transfer grass (fodder)→cow milk (%)

	Fürst <i>et al.</i> (1992)	McLachlan (1992)	Blüthgen <i>et al.</i> (1994)
2,3,7,8-Cl ₄ DD	35	36	36
1,2,3,7,8-Cl ₅ DD	19	32	15
1,2,3,4,7,8-Cl ₆ DD	13	16	8
1,2,3,6,7,8-Cl ₆ DD	13	15	
1,2,3,7,8,9-Cl ₆ DD	4.5	15	
1,2,3,4,6,7,8-Cl ₇ DD	1.5	3	
Cl ₈ DD	0.8	4	
2,3,7,8-Cl ₄ DF	1.5	7	<1
1,2,3,7,8-Cl ₅ DF	1	5	
2,3,4,7,8-Cl ₅ DF	15	33	27
1,2,3,4,7,8-Cl ₆ DF	6	15	10
1,2,3,6,7,8-Cl ₆ DF	6	15	
1,2,3,7,8,9-Cl ₆ DF			
2,3,4,6,7,8-Cl ₆ DF	7	14	
1,2,3,4,6,7,8-Cl ₇ DF	2	3	<1
1,2,3,4,7,8,9-Cl ₇ DF		8	
Cl ₈ DF	0.5	2	
I-TEQ	11.5	21	19.2

LaFleur *et al.* (1992) studied the migration of 2,3,7,8-Cl₄DD and 2,3,7,8-Cl₄DF from paper products into liquids. After 288 hours about 8 % of 2,3,7,8-Cl₄DD and 16 % of 2,3,7,8-Cl₄DF were transferred from the paper carton into the milk. Further experiments did not show any correlation between the migration rate and the fat content of

the milk product. The migration rate from coffee filters into coffee was $10.3\% \pm 7.0$ for 2,3,7,8-Cl₄DD and $16.3\% \pm 7.9\%$ for 2,3,7,8-Cl₄DF. Thus, both experiments showed a higher mobility for the tetrafuran than for the tetradioxin.

6 ENVIRONMENTAL TRANSFORMATION PROCESSES

The EPA Dioxin-Reassessment could not give any answer on degradation or formation processes of PCDD/PCDF under environmental conditions. The Exposure Panel at the Science Advisory Board Dioxin Reassessment Review Committee (Washington, DC, May 15-16, 1995) concluded that, there are major gaps on environmental transformation processes:

- There are no photolysis data at all.
- There are gaps between emissions and sinks - nobody has any idea what causes the changes in profiles and patterns of PCDD/PCDF.

More specifically, the discussions at the Science Advisory Board Dioxin Reassessment Review Committee and the results of a DECHEMA, Germany, workshop (DECHEMA 1995), can be summarised as follows:

- Background samples show differences between the homologue and congener profiles and pattern between sources and environmental sinks. For example: the most abundant homologues emitted from combustion sources are Cl₄/Cl₅DF; however, in sinks such as soil, Cl₈DD is dominating. Moreover, the profiles in ambient air samples are different from those of emission samples. These findings are taken as indirect evidence that photolysis occurs in the vapour phase.
- There is hardly any information available on photolytic degradation of PCDD/PCDF in air and soil. Photolysis is either direct or via hydroxy radicals. Particle-phase photolysis does not seem to occur (Koester and Hites 1992b); however, there is only one experiment and no congener-specific data are available. In one poor paper it has been shown that the TCDD half-life is only a few seconds (\leftarrow direct photolysis). More important are OH radicals; however, there are no experiments to address this question. Atkinson (1987) determined a half-life time of 1-40 days for Cl₄-Cl₈DD. Thus, reaction rates for OH radical induced photodegradation are much slower than for direct photolysis. Moreover, the photolytic degradation products of PCDD/PCDF are unknown.
- In contrast, Rappe (1992) and Vollmuth et al (1994) report on the photolytic formation of PCDD/PCDF.
- There is no information available on the microbial degradation of PCDD/PCDF under environmental conditions. There are indications for reductive dechlorination of higher chlorinated PCDD under methanogenic conditions in sediments and sewage sludge. So far, degradation under aerobic conditions was only proven for mono- and di- but not for higher chlorinated dibenzo-*p*-dioxins.
- On the other hand, it has been shown that peroxidases are capable to synthesise PCDD/PCDF from precursors such as chlorophenols (Öberg *et al.* 1993 and

1992, Öberg and Rappe 1992, Öberg *et al.* 1990, Wagner *et al.* 1992). The formation of esp. Cl₇DD and Cl₈DD during the composting process has been proven in many experiments (for summary, see Fiedler 1994). The overall effect found was that the I-TEQ increases by about 1-2 ppt during the composting process (when comparing the I-TEQ of the input material with the final compost and after correction for the loss of organic matter during composting). The increase seems to be independent of the PCDD/PCDF level in the input material; thus, first results reporting a 3- to 8-fold increase of the I-TEQ during composting could not be verified when performing experiments in higher contamination ranges.

- The decrease of 2,3,7,8-Cl₄DD in the topsoil of Seveso (DECHEMA 1995, Bertazzi *et al.* 1994) which was observed during the first approx. six months after the accident was explained by photodegradation and volatilisation. It was not possible to differentiate between these two degradation pathways. Over the next five years, the disappearance of 2,3,7,8-Cl₄DD was much slower; thus, a half-life of 9.1 years was calculated for this compound. The decrease was attributed to translocation processes rather than to biodegradation.

7 DIOXIN-LIKE PCB

The US-EPA Dioxin Reassessment includes few data on the chemical-physical properties of PCB and qualitative information of potential sources as well as some environmental levels. However, nothing is documented on background exposures to coplanar and *mono-ortho*-substituted PCB (dioxin-like PCB). In Germany, due to legislation and guideline concentrations, there exists only information on six non-dioxin-like PCB (namely, 2,4,4'-trichlorobiphenyl (PCB 28), 2,2',5,5'-tetrachlorobiphenyl (PCB 52), 2,2',4,5,5'-pentachlorobiphenyl (PCB 101), 2,2',3,4,4',5'-hexachlorobiphenyl (PCB 138), 2,2',4,4',5,5'-hexachlorobiphenyl (PCB 153), and 2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB 180)). It was estimated that worldwide about 1.5 million tons of PCB were produced commercially (Rantanen 1992). Other sources are not well known and there are only a few measurements on environmental levels of coplanar and *mono-ortho*-substituted PCB available. To my knowledge, no compilation of such data has been performed.

8 CONCLUSIONS

8.1 Procedure

The effort undertaken by EPA to compile all available scientific information on one group of compounds is unique and started many activities in the own country and throughout the world. Inherent to the process is that EPA asked for additional information and comments during the reassessment process. So far, the Dioxin Reas-

assessment is pure science and it is unknown if the findings of the Dioxin Reassessment will have an impact on legislation and policy.

In Germany, the situation is quite different: there are several laws to directly (Ordinance on Emissions from Waste Combustion Plants = 17th BImSchV, Sewage Sludge Ordinance, Ordinance of the Prohibition of Certain Chemicals = limit values for PCDD/PCDF in products, preparations, articles) or indirectly (Ban of Pentachlorophenol, Ban of Polychlorinated Biphenyls, Ban of Scavengers in Leaded Petrol) regulate PCDD/PCDF. Moreover, there are guideline values and recommendations for PCDD/PCDF levels in soil (for agricultural and horticultural use and soil exchange) and cow milk. The State of Baden-Württemberg has incorporated the recommendations of the Bund/Länder-Arbeitsgruppe into an ordinance (EPA-BW 1992) and established guideline levels for PCDD/PCDF in bio- and green compost (= 17 ng I-TEQ/kg d.m., EPA-BW 1994).

Two „Toxicology Forums“ were held in 1990 (Karlsruhe) and 1992 (Berlin) to present the present state-of-knowledge on PCDD/PCDF each of them followed by a two days public meeting with discussions. The results of both were published as final documents The Toxicology Forum 1990, 1993, Lukassowitz 1990, BGA/UBA 1993).

8.2 Open Questions

- Lack of data for PCDD/PCDF contents in chemicals, products, and residues from *manufacture and production*.
- Insufficient knowledge on amounts of materials processed or volumes emitted from thermal processes except waste incineration.
- So far, no adequate surrogate could be identified to predict PCDD/PCDF concentrations by measuring a simpler parameter.
- There is a need for better understanding the seasonal trends in ambient air concentrations (higher PCDD/PCDF concentrations in winter than in summer) - due to seasonal emitting sources, such as residential heating, additional traffic, or meteorological influence (slower or reduced air exchange, long-range transport, *etc.*).
- Remobilisation of PCDD/PCDF from contaminated surfaces (revolatilization, evaporation, leakage).
- Significance of reservoirs, *e.g.* contaminated areas, sediments, old products. Is there a possibility, that releases from such reservoirs become more important when „actively“ emitting PCDD/PCDF sources will be reduced in the future?
- There are many open questions in terms of environmental fate of PCDD/PCDF, *e.g.* understanding transformation processes; here, congener-specific research is needed to see if transformation under environmental conditions does increase or

decrease the overall toxicity of the compounds. There are contradictory results for photolytic degradation/formation, biological formation/biodegradation.

- Importance of particle-bound and gas-phase PCDD/PCDF to impact on terrestrial food-chain.
- Mechanisms and significance of long-range transport; e.g. contamination of the Arctic and Antarctic environment with PCDD/PCDF. Results have shown that 2,3,7,8-Cl₄DF is found in higher concentrations in Arctic seals than in animals closer to the source. Thus, due to air-water exchange processes during transport a global distillation will enrich the more volatile PCDD/PCDF.
- Biomagnification processes were modelled, esp. for the aqueous environment; however, PCDD/PCDF levels in fish show large varieties and seem to be dependent on the species, sex, age, time of the season, etc.
- PCB data for coplanar and mono-ortho-substituted congeners are insufficient.

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