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THEME II: MONITORING AND ASSESSMENT OF CONTAMINATION BY OBSOLETE PESTICIDES AND NGO'S POINTS OF VIEW

PCDD/PCDF CONTAMINATION FROM HISTORICAL PESTICIDE USE AND PRODUCTION – A CASE STUDY USING DATA FROM JAPAN AND GERMANY

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ABSTRACT

Pesticide use and deposition of pesticide production residues contribute to environmental PCDD/PCDF contamination, in particular on a historical scale. Despite potentially substantial quantities of PCDD/PCDF emission, and remaining depositions via this route, only limited information is available on the resulting environmental contamination load or pathways. The total dioxin emission from the use of pesticides in Japan during the past 40 years (1955-1995) was estimated to 540 tonnes of PCDD/PCDF or 250 kg of TEQ from PCP (with predominant OCDD/OCDF and other highly chlorinated congeners), and 380 tonnes of PCDD/PCDF or 210 kg TEQ from 2,4,6-trichlorophenyl-4'-nitrophenyl ether (CNP) (with 1,3,6,8/1,3,7,9-TCDD as dominant congeners).

The PCDD/PCDF impurities from PCP and CNP pesticides still contribute a large part of today's PCDD/PCDF contamination in Japanese soil and sediments. A comparison of PCDD/PCDF loads derived from PCP/CNP application and their deposition in sediments of the Tokyo bay showed that only a small portion of PCDD/PCDF agrochemical impurities have been deposited in the Tokyo Bay sediment during the past 45 years. This indicates that a large part of the PCDD/PCDF load still exists in the terrestrial soil or river sediments of this area, which results in future runoff into Tokyo Bay. This highlights the pertinence of assessing pesticide contamination and application history for the understanding of environmental PCDD/PCDF loads and risk assessment.

Information from former pesticide production sites and associated landfills present another example for emissions of large quantities of PCDD/PCDFs to the environment in the past and future. In particular, the residues from produc-

tion of various chlorinated pesticides (e.g. 2,4,5-T, PCP, PCP-Na, HCH¹) were contaminated with high concentrations of PCDD/PCDFs and were found to leach from deposits together with pesticides, other chlorinated aromatics and aliphatics. This highlights the necessity of monitoring, containment and possibly remediation of such hotspots.

The present paper summarises and discusses available data and estimates from two case studies in Japan and Germany on pesticide application and production-derived PCDD/PCDF contamination in order to highlight the potential significance of such, predominantly past actions, to environmental PCDD/PCDF loads of the future.

Key words: PCDD, PCDF, pesticide, PCP, 2,4-D, 2,4,5-T, HCH, CNP, chloralkali electrolysis, remediation.

INTRODUCTION

The Stockholm Convention is a global treaty aimed to protect environmental and human health from contamination with persistent organic pollutants (POPs (Stockholm Convention (SC) 2001). At present the most notorious 12 POPs are included in the list of the Stockholm convention, 8 of which represent pesticides (SC 2001). Polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) are also included in the Stockholm Convention as unintentionally formed POPs (Article 5/Annex C) (SC 2001). Today the scientific discussion on PCDD/PCDF sources focuses mainly on thermal emissions (e.g. waste incineration, sinter plants, secondary metal production), however, the history of PCDD/PCDF contamination is closely related to the chlorine industry and the production and use of chlorine and chlorinated organics including chlorinated pesticides² (Weidenbach et al. 1984, UNEP 2005). "Highlights" of the "PCDD/PCDF history include contamination from pesticide production and use (in particular from 2,4,5-T/2,4,5-T₃CP production).

Pesticide production was found to result in high exposure and contamination of workers (Degler and Uentzelmann 1984, Weidenbach et al. 1984, Dohmeier and Janson 1983, Schecter 1994). In addition, the application of PCDD/PCDF containing 2,4,5-T agents in the Vietnam war (Stellmann et al. 2003) contaminated large areas in South East Asia, including local populations and spraying personnel ((Degler and Uentzelmann 1984, Dohmeier and Janson 1983, Weidenbach et al. 1984, Stellmann et al. 2003). Also the

¹ High concentration of PCDD/PCDF (46 g/kg) were present in residues from HCH degradation for chlorobenzene production of the factory in Hamburg (Degler and Uentzelmann 1984).

² Some emission factors for relevant pesticides are listed in the "Standardized toolkit for identification and quantification of dioxin and furan release" (UNEP 2005).

Table 1. PCDD/PCDF concentration in Japanese agrochemical pentachlorophenol samples (concentration calculated to gram active ingredient)

Sample (Ref.)	Expiry date year	Estimated production year	PCDDs (mg/g)	PCDFs (mg/g)	PCDDs	PCDFs	Total TEQ (ND = 0) (ngTEQ/g)
					TEQ	TEQ	
					(ng/g)	(ng/g)	
PCP herbicide/particle formulation (a)	1967	1964	24.000	290	5.000	330	5.400
PCP herbicide/particle formulation (a)	1970	1967	260	59	52	180	230
PCP herbicide/particle formulation (a)	1971	1968	120	75	340	200	540
PCP herbicide/particle formulation (a)	not known		12	1,7	130	18	140
PCP herbicide/particle formulation (b)	1969	1966	110	62	280	170	440
PCP herbicide/particle formulation (b)	1970	1967	730	96	170	160	330
PCP herbicide/particle formulation (b)	1971	1968	3,0	0,33	32	4,8	37
PCP herbicide/particle formulation (b)	1973	1970	15.000	400	7.200	340	7.500
PCP particle for solution (b)	1975	1972	64	0,32	17	1,7	19
PCP herbicide (b)	1978	1975	660	57	710	110	810
PCP solution (b)	1980	1977	1.000	1.400	430	1.000	1.500
PCP solution (b)	1982	1979	860	77	2.800	550	3.300
PCP particle for solution (b)	1985	1982	1.600	490	380	250	630
PCP solution (b)	1988	1985	3,6	0,071	4,1	0,41	4,5
Arithmetic Mean			3.173	215	1.300	240	1.500
Geometrical mean			261	27	250	72	370

(a) Masunaga et al. 2001; (b) Seike et al., 2003

public discussion and awareness on PCDD/PCDF was finally initiated by a heavy accident at a 2,4,5-T₃CP production site 1976 in Seveso (Mocarelli 2001). The actual release of PCDD/PCDF to land via waste from pesticide production, however, is not clear. Wenborn et al. (1999) estimated the release of PCDD/PCDF from pesticide production to 160 to 26500 g/year (Wenborn et al. 1999)³. The wide range of the estimation is indicative for the lack of data required for a clear determination of emission factors.

Since pesticides were a major PCDD/PCDF source in the past, PCDD/PCDF emissions from these sources have already been distributed and disposed of. Due to the persistency of PCDD/PCDF, however, the burden of “historical” pesticides use and production may still represent a key source to the environment and humans today and into the future through runoff from soil and sediments, leaching from deposits (landfills, dumps, unsecured stockpiles), existing contamination/exposure in contaminated regions and former and potentially present application of contaminated pesticide stockpiles in developing countries.

There remains little research focus on these topics and, consequently, only limited information is available to date that would allow an estimate on the total share of pesticides to the global PCDD/PCDF burden and contamination flux. Hence it is not possible to evaluate their actual impact on environmental contamination and their fate with respect to wildlife and human exposure at present and in the future.

In recent years, the total historic release of PCDD/PCDF from pesticide use was investigated and assessed for Japan (Masunaga 2004, Masunaga 2001a, Ogura et al. 2001). In addition, the relevance of PCDD/PCDF contamination from

former pesticide production sites was revealed during an investigation and remediation attempt of former pesticide production sites and associated landfills/areas in Germany (Universtät Bayreuth 1995, Degler and Uentzelmann 1984, Schnittger 2001, Otto 2005). These “case studies” provide an overview on the subject and the current paper aims to illustrate the relevance of (predominantly) historical pesticide contamination for PCDD/PCDF emissions to the environment through their application and production. Experiences with remediation of pesticide production and disposal sites are presented and the challenges involved with this past legacy are discussed.

RESULTS AND DISCUSSION

1. Dimension of PCDD/PCDF release from historic pesticide production

1.1 Concentration of PCDD/PCDF in pesticides

The fingerprint and amount of PCDD and PCDF impurities in agrochemicals were studied by trace analysis of historic Japanese pesticide formulations in order to evaluate the contribution of historical pesticide use to environmental PCDD/PCDF contamination (Masunaga et al. 2001, Seike et al. 2003). The chemicals analysed include pentachlorophenol (PCP) (Table 1), 2,4,6-trichlorophenyl-4'-nitrophenyl ether (chloronitrofen CNP), 2,4-dichlorophenyl-4'-nitrophenyl ether (nitrofen, NIP), tetrachloro-isophthalonitrile (chlorothalonil, TPN), and 2-methyl-4-chlorophenoxyacetic acid (MCP) and recently produced 2,4-dichlorophenoxyacetic acid (2,4-D). Two herbicides, PCP and CNP, produced during the 1960s and 1970s, contained elevated concentrations of PCDD/PCDF and TEQ.

In the case of CNP, the average dioxin content in formulations produced pre-1982 was 6000 µg PCDD/PCDF/g and 3.60 vg WHO-TEQ/g active ingredient (N= 39 samples). In

³The estimated contemporary release from 55 countries (national inventories for emission to air from 22 countries (10370 g) and total release from 23 countries using the toolkit approach (9770g)) amounted to 20140 g (Fiedler 2005).

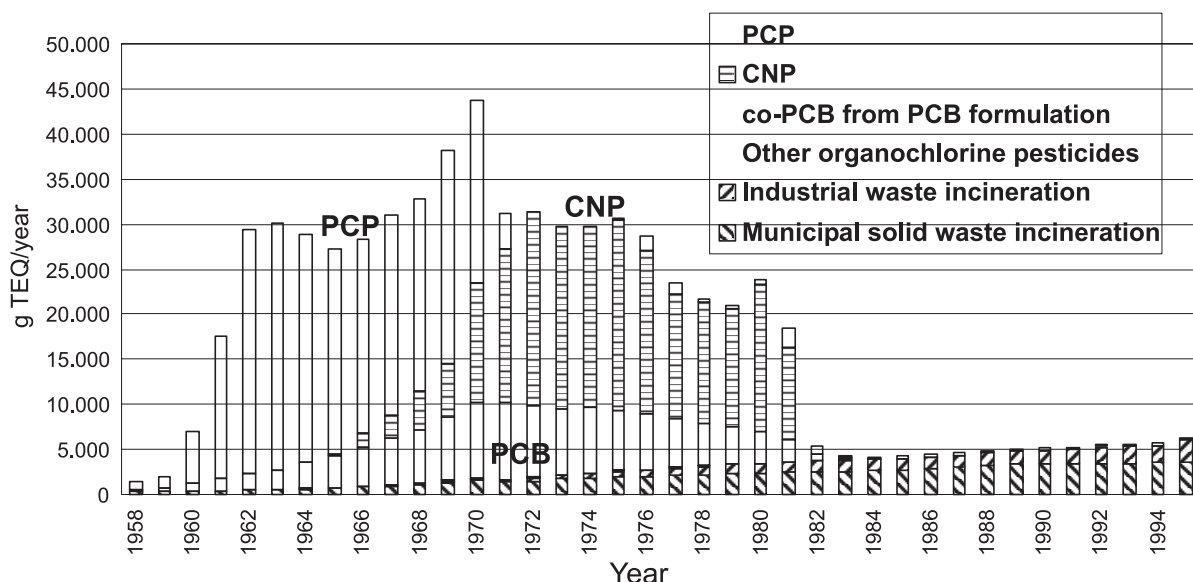


Figure 1. Historic Japanese PCDD/PCDF (TEQ) inventory and release to the Japanese environment

1982 the Dioxin content of CNP decreased due to the change of production processes resulting in an average concentration of $710 \mu\text{g PCDD/PCDFs/g}$ and $0.022 \mu\text{g WHO-TEQ/g}$ active ingredient for post-1982 produced formulations (N= 23 samples) (Masunaga et al. 2001, Seike et al 2003, Yamagishi et al. 1981, Morita 1991, Mitsui Chemicals 2002). In contrast to CNP, no specific time trend could be observed for PCP and high PCDD/PCDF concentration were still detected in samples produced during the end of the 1970s (Table 1). The average dioxin content in PCP (N= 14 samples) was $3,300 \mu\text{g PCDD/PCDF/g}$ and $1.50 \mu\text{g WHO-TEQ/g}^1$ active ingredient (Table 1) (Masunaga et al. 2001, Seike et al. 2003, Mitsui Chemicals 2002). The remaining pesticide formulations investigated contained comparatively low concentrations of PCDD/PCDF (Masunaga et al. 2001).

1.2 Estimation on total PCDD/PCDF emissions from Pesticide use in Japan

The total dioxin emission from the application of pesticides in Japan during the past 40 years (1955-1995) was estimated based on the arithmetic average concentration of PCDD/PCF in historical pesticides and amount of pesticides used (see 1.1). The total emission from PCP use was estimated to 540 tonnes of PCDD/PCDF (with predominant OCDD/OCDF and other highly chlorinated congeners) or 250 kg of TEQ³. The total emission from CNP use was estimated to 380 tonnes of PCDD/PCDF (with 1,3,6,8/1,3,7,9-TCDD as dominant congeners) or 210 kg TEQ³. These loads contribute a large part of today's PCDD/PCDF contamination in Japanese soil and sediments. In comparison to the total release of PCDD/PCDFs from waste incineration, today's key PCDD/PCDF emission source representing approximately 90% of PCDD/PCDF emissions in Japan, the estimated total release of PCDD/PCDFs from pesticide use is considerably higher (Figure 1). This highlights that his-

torical pesticide use represents a key contributor of PCDD/PCDF contamination in Japan.

1.3. Mobility of PCDD/PCDFs from former pesticide use - trend and sources of dioxin pollution in Tokyo Bay

One key question, currently still unresolved, with regards to assessing the past and future environmental PCDD/PCDF contamination (and hence food web cycling and human exposure) is the mobility of POPs and pesticides deposited in landfills, dumps, uncontained storages and soils and sediments (Figure 2). A comprehensive study on historical PCDD/PCDF load and their transport to rivers and ocean sediments has been performed for the Tokyo Bay basin (Masunaga 2004). For this task, the dioxin load to Tokyo Bay basin was estimated from the annual quantities of agrochemical shipments to Tokyo, Saitama, Chiba and Kanagawa Prefectures (Ministry of Agriculture, Forestry and Fishery, 1959-1996), the percentage of prefecture area belonging to the basin, and the dioxin contamination of the agrochemicals.

The total PCDD/PCDF load to Tokyo Bay basin during the past 45 years from PCP was estimated to be approximately 31,000 kg PCDD/PCDFs and 14 kg TEQ. Those from CNP were estimated at 9,300 kg PCDD/PCDFs and 5 kg TEQ. Assuming that annual PCDD/PCDF deposition from combustion sources did not vary much during the past 45 years, the estimated recent average deposition in the Kanto region (Ogura et al. 2001) was used to as the average deposition of past years to calculate the basin-wide load from

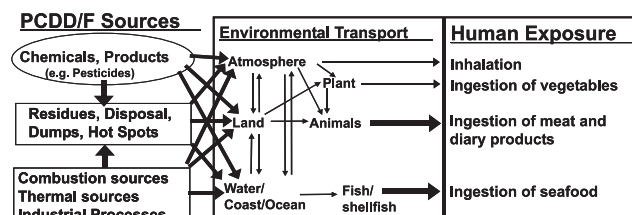


Figure 2. Sources, environmental transport and major human exposure pathways of PCDD/PCDF

⁴ The average TEQ value is in good agreement with the emission factor of $2,000,000 \mu\text{g TEQ/t}$ listed in the "Standardized toolkit for identification and quantification of dioxin and furan release" (UNEP 2005).

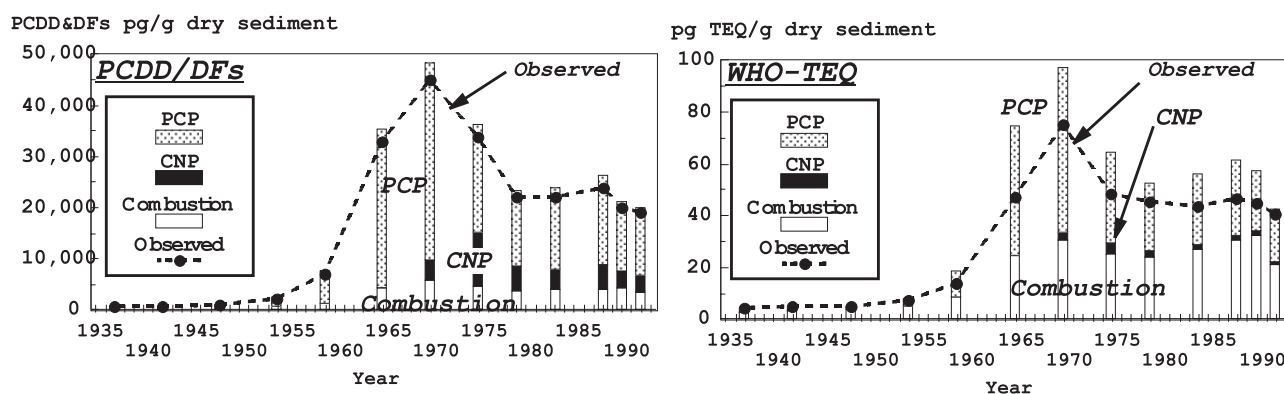


Figure 3. Estimated dioxin source contributions in Tokyo Bay sediment core in terms of total amounts [left] and toxic equivalents (TEQ) [right] (Masunaga 2004)

Table 2. Mass balance of dioxins in Tokyo Bay basin between 1951 and 1995

Source	PCDD/PCDF			WHO-TEQ		
	Load to basin kg	Amount existed in sediment kg	Run-off rate %	Load to basin g TEQ	Amount existed in sediment g TEQ	Run-off rate %
PCP	31,000	760	2.5	14,000	1,200	8.6
CNP	9,300	140	1.5	5,000	65	1.3
Combustion	42* 340**	150	39 (32)***	460* 3,600**	950	23 (14)***

* Direct deposition to seawater surface in Tokyo Bay; ** Deposition to terrestrial basin; *** Run-off rate for load to terrestrial basin.

combustion sources. The total PCDD/PCDF input to the basin from these three key sources are listed in Table 2 for the past 45 years (1951-1995).

The total amount of PCDD/PCDFs deposited in sediments of Tokyo Bay during the same period was estimated from sediment core data with horizontal corrections based on surface sediment data (Masunaga 2004) (Table 2). A comparison between the total PCDD/PCDF emissions and sediment load in Tokyo Bay shows that only a few % of PCDD/PCDFs applied to paddy fields as agrochemical impurities have been deposited in Tokyo Bay to date.

Due to the persistency of these compounds, the remaining PCDD/PCDF portion still exists in the terrestrial soil or river sediments, providing an input source to Tokyo Bay into the future). Similarly, a relatively long time lag has been observed in Tokyo Bay sediment cores, where sediment PCDD/PCDF concentrations (derived from PCP and CNP) peaked during the mid 1960s and the beginning of 1970s, but in particular PCP derived PCDD/PCDFs still contributed a large proportion to the total TEQ in most recent sediment layers (Figure 3). According to the concentration of PCDD/PCDFs in Tokyo Bay sediments, the flux from PCP originating PCDD/PCDFs remained constant over the past 20 years (Figure 4). This indicates that PCDD/PCDF transport processes in the environment may last for decades (and most likely centuries), and will impact on the environment of future generations.

2. PCDD/PCDF IN RESIDUES FROM PESTICIDE PRODUCTION

2.1 PCDD/PCDF in residues of pesticide production

Residues from production of various chlorinated pesticides (e.g. 2,4,5-T, PCP, PCP-Na, HCH¹) represent another

source of release of large PCDD/PCDF quantities. While these pesticides have been produced around the world, not many cases are documented on total PCDD/PCDF contamination of disposed residues. However, two cases in Germany which gained public and political attention (and therefore detailed investigations) demonstrated that considerable amounts of PCDD/PCDF were released in residues from pesticide production (Degler and Uentzelmann 1984, Universität Bayreuth 1995, Lutz 1991, Thater 1996, Otto 2005). The total contamination from pesticide production residues (predominantly 2,4,5-T and HCH¹ and other chlorinated organics) from one German factory in Hamburg during ca. 30 years was estimated to 377 kg TEQ³ (Universität Bayreuth 1995); these residues were deposited on nearby landfills and the production area.

In the second case, contamination from residues of a PCP and PCP-Na production in Rheinfelden (South Germany) was estimated to 7 tons of PCDD/PCDF (preliminarily OCDD) and 7.7 kg TEQ mainly from PCP-Na production (Otto 2005, Schönberger 2005). In addition, the area was heavily contaminated with PCDD/PCDF from deposited residues of a chloralkali electrolysis facility⁵ (8.5 kg TEQ) (sludge from electrolysis cells resulting mainly from reaction of chlorine with the pitch binder of graphite anodes – Lutz et al. 1991). The total PCDD/PCDF amount deposited from PCP/PCP-Na production and chloralkali electrolysis amounted to 16.2 kg TEQ³ (Otto 2005).

There are vast numbers of former production sites of 2,4,5-T, PCP, other chlorinated aromatic pesticides and HCH¹ around the globe (often associated with chlorine production via chloralkali electrolysis). Similar high PCDD/PCDF contamination for these sites are probable and similar burdens in (typically nearby) landfills and the production sites can be expected. However, the deposited PCDD/PCDF quantity depends in addition to the products itself also on the production process of the respective pesticide and some other key factors. For example, the key factors determining the amount and environmental emission of PCDD/PCDF from

⁵ The bulk production of chlorinated pesticides are often associated with a chloralkali electrolysis process providing the basic material for chlorination of organics (chlorine). The experiences in Germany, Sweden and the USA demonstrated that the chloralkali process can generate large amounts of PCDD/PCDF (mainly PCDF) contaminated residues and can contaminate associated land, landfills and water sheets (Lutz et al. 1991, Rappe et al. 1991, Kannan et al. 1998).

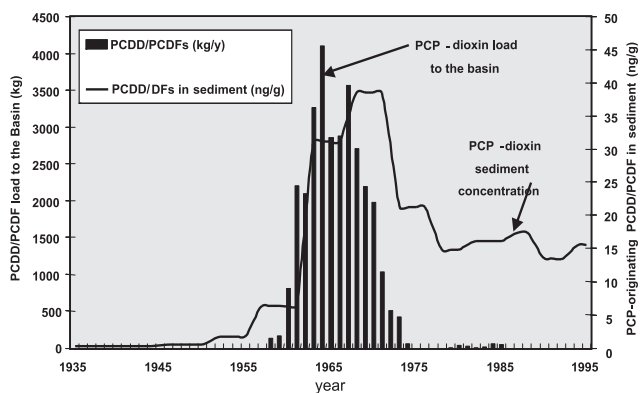


Figure 4. PCP-originating annual PCDD/PCDF load to the Tokyo Basin and PCP-originating sediment concentration in Tokyo Bay

2,4,5-T production include the synthesis methods and production temperature, whether PCDD/PCDFs are separated from the pesticide product (resulting in contaminated residues which may be reused) and finally, whether residues are destroyed in hazardous waste incinerators or placed into landfills. Therefore, the (former) production processes and waste management practice have to be considered for evaluating the potential relevance of PCDD/PCDF contaminations from respective production site and associated landfills. In addition, PCDD/PCDF loads from such activities have to be assessed for the evaluation of their contribution to environmental PCDD/PCDF burdens. Finally, the assessment of PCDD/PCDF loads and the environmental relevance from such sites requires evaluation based on actual measurements.

2.2. Leaching of PCDD/PCDF and pesticide/pesticide residues from landfills and deposits

To date, only limited information exists on the potential of residue contaminant leaching from landfills to ground water over extended periods of time. While PCDD/PCDFs are typically considered the least mobile of contaminants, due to physico-chemical properties, experiences from the former pesticide production site and related landfills in Hamburg revealed that PCDD/PCDF, the pesticides residues and other chlorinated aromatics and aliphatics can leach readily from such sites depending e.g. on the quality of the landfill, the geological conditions and other wastes co-deposited with the PCDD/PCDF and pesticide residues. The high concentrations of (chlorinated) organics in leachates from these type of landfills support the leaching of PCDD/PCDF from the landfill and concentrations of 2,3,7,8-TCDD up to 75000 ng/kg were detected in oily leachates from one landfill (Schnittger 2001). This case highlights that leachates and ground water around landfills/dumps and hot spots of former pesticide production sites have to be monitored for contaminants including PCDD/PCDFs.

2.3 Remediation of contaminated production sites and associated landfills

The remediation of soils and sediments impacted from use of pesticides (and PCDD/PCDF contaminants) seems impossible due to the wide distribution and dilution in the

environmental compartments and will therefore continue to impact environment and humans (Figure 2). However, the remediation or containment of former production areas and associated landfills (pesticide production and other chemical production) is a contemporary issue e.g. in Germany (see below, Schnittger 2001) and Switzerland⁶ (BCI 2005; Forter and Walther 2004) and will remain an important global task in the future. The remediation and containment of the above discussed pesticide production areas and associated landfills in Hamburg and Rheinfelden are ongoing to date and can be viewed as one of worldwide precedent cases^{6,7}.

One key conclusion that can be drawn is that it remains difficult and cost extensive to completely remediate contaminated areas due to the large volume of contaminated soils and landfilled materials. In Hamburg a complete remediation of the contaminated areas was considered relatively unfeasible due to the estimated costs (although the sites are inside the city) resulting in primarily containing the contaminated areas. Even the remediation of some hot spot areas in this case, the break down of production buildings, containment of the production area and related landfills and the measures for minimization of contamination of ground water resulted in expenditures in the order of several hundred million EURO⁴ by the responsible company.

Similarly, in Rheinfelden (South Germany), several landfill sites were heavily contaminated by PCDD/PCDF⁵. In addition wide areas of the city were/are impacted by PCDD/PCDF since contaminated solid residues were filled in gravel-pits, which arose at many individual estates to gain construction material⁸. Therefore, the entire inner city of Rheinfelden (ca. 290 ha) had to be evaluated (1916 estates) including the analysis of soil samples from 729 estates and the establishment of a detailed "soil map" of the city (Thater et al. 1996). Heavy contaminated soil (> 1000 ng TEQ/kg) was substituted and removed or, in some cases was contained by removing of the top soil, fitting a geo textile and cover the bottom soil again with non-contaminated soil. A total of 36 estates/contaminated sites have been remediated. However, still an assessment has to be carried out for any new construction activity within the town today and in future (Otto 2005).

All 36 "hot spot estates" with a PCDD/PCDF-contamination of more than 1000 ng TEQ/kg have been remediated, whereas estates with a contamination below this value remain without actions, however, agricultural use of estates with a PCDD/PCDF-contamination of more than 40 ng TEQ/kg is not allowed. Against this background, also for Rheinfelden a complete remediation of the contaminated areas (landfills, production site and lower impacted estates) was considered not feasible due to the high cost. However,

⁶ Switzerland exemplifies the requirement of total remediation of chemical waste landfills (based on a polluter pays principle). Two large scale remediation projects are currently undertaken in K lliken (estimated remediation cost 500.000.000 SFr) and Bonfol (estimated remediation cost 300.000.000 SFr). (Forter and Walther 2004, BCI 2005).

⁷ Other cases are e.g. treated in the US in the frame of the Superfund site (US EPA 2005) and the above mentioned cases in Switzerland.

⁸ In several cases, highly PCDD/PCDF-contaminated sludge from chloralkali cells has been dumped in such gravel-pits also.

the containment of the former landfills and soil contamination on the production site could minimize the risk of further environmental contamination in Rheinfelden (and Hamburg). Furthermore, responsible and rational management of the contaminated estates inside the town could minimize the risk of health impact on the population of Rheinfelden (Otto 2005, Schönberger 2005, Thater et al. 1996).

Some conclusions and experiences with remediation and secure containment of former chlorinated pesticide production sites and associated landfills in Germany are:

- Detailed documentation of former production processes of the facility and transparency of type, amount and location of waste residues from these productions are important.
- Landfills and contaminated areas (based on detailed data from historic documentation) need to be localised.
- Assessment of the landfills and contaminated area:
 - Extent of contamination,
 - Geological conditions and frame of the sites,
 - Actual contamination/contamination risk of ground water;
 - Mobility of contaminants.
- Close cooperation of the pesticide/chemical company and state/local authorities is required; open communication with impacted public and NGOs is required.
- Extent and type of PCDD/PCDF contaminants in production residues and therefore at production sites (including buildings) and associated landfills need to be evaluated
- Experienced engineering offices qualified in the field of remediation of contaminated areas of similar type should be consulted. The planning needs high creativity since the solutions applied are normally not the standard engineering techniques but might be rather unique.
- Priority setting after comprehensive environmental impact assessment, overview on contamination and available remediation funds.
- Specific safety guidelines for worker protection are inevitable. The supervision of the building/remediation site needs special care.
- Comprehensive evaluation of remediation technologies – wrong choice of technologies can lead to enormous costs and project delay.
- Secured landfills and secured production sites are constructions not made for “eternity” but built for a limited time which need to be controlled, supervised and potentially repaired/renewed⁹. Furthermore the leachats and the ground water need possibly continuous remediation and supervision. These activities result in high maintenance costs, which have to be paid for decades, most likely centuries (millennia?) to come.
- Assessment if total remediation of the area is possible and necessary⁹.
- Timely environmental impact assessments and then prompt remedial and securing actions can minimize total damage and costs.
- Evaluate how and to which extent the “polluter pays principle” can be applied.

⁹ The question arises if the securing constructions are more persistent or the chlorinated organic pollutants.

CONCLUSIONS

A large percentage of today's PCDD/PCDF loads in the environment (soil, sediments, former production sites, associated landfills and other hot spots) originate from pesticide use and pesticide production. For Japan, the largest source of PCDD/PCDF release into the environment resulted from historical pesticide use (Figure 1). The contamination of the same type of pesticide varied depending on the time of production and the production process. It was discovered that not only well known key pesticides like PCP can contain high PCDD/PCDF concentrations but that also lower chlorinated pesticides like 2,4,6-trichlorophenyl-4'-nitrophenyl ether (CNP) can contribute high levels of PCDD/PCDF to total environmental burden.

While the information on CNP use is limited to Japan, it is known that PCP and other potentially PCDD/PCDF contaminated pesticides (e.g. 2,4-D, 2,4,5-T, other chlorinated aromatic pesticides) were used worldwide. Therefore the assessment of impurities in former chlorinated pesticides and the amount and pattern of pesticide use is one key of understanding PCDD/PCDF contamination of soils and sediments in a country and for global contamination. In this respect the relevance of PCDD/PCDF contamination of pesticide stockpiles may additionally be considered/evaluated. Further, for the final destruction of pesticide stockpiles the risk of PCDD/PCDF formation and emission have to be considered, evaluated and monitored (Weber 2005).

A further significant PCDD/PCDF burden to the environment associated to chlorinated pesticide production stem from land filling of production residues and the contamination of the production area and buildings. The contaminations from production residues are normally restricted to hot spots at production sites and associated landfills but can possibly impact extensive local regions including residential areas (such as Rheinfelden). From experiences in Germany these former pesticide production sites, related landfills and other impacted areas can be contaminated with tons of PCDD/PCDF and hundreds of kg of TEQ¹ if specific chlorinated aromatics (e.g. PCP-Na, 2,4,5-T or HCH¹) were in the production portfolio.

The remediation and/or securing of this type of area remain a difficult but important task and should be considered as one priority in the action planning of national implementation plans of the Stockholm Convention. The current impossibility of comprehensive remediation of contaminated areas and landfills, the possibility for leaching of the contaminant, the difficulties of containing these sites and the tremendous costs of these projects demonstrate that land filling of hazardous waste creates large burdens for environment and society (in the future) which can not be accepted for the sake of future generations and when acknowledging the principle of sustainable development.

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HCH RESIDUES IN SOME FRESH WATER, SEDIMENT AND IN SOME AQUATIC ORGANISMS IN TURKEY

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ABSTRACT

The widespread use of synthetic organic pesticides over the past half-century has led to their detection in many hydrologic systems of the countries. Pesticides, as well as agricultural and industrial toxic chemicals are complex mixtures of isomers and congeners, which have been detected in air, water, and in biota all over the world. Pesticide's contamination of surface water, sediments and groundwater from agricultural use has been well documented around the world. The widespread use of pesticides for agricultural and non-agricultural purposes has resulted in the presence

of their residues in various environmental matrices. Organochlorinated Pesticides such as HCH and its isomers are known to resist biodegradation and they can be recycled through food chains and produce a significant magnification of the original concentration at the end of the chain. Due to long residence time of these substances in the environment, there is a great interest in examining the pollution they cause.

Their use has been prohibited in Turkey as well as in other countries, after evidence of their toxicity, persistence and bioaccumulation in the environment became known. The determination of pesticide residue in water sediment and fish samples is necessary.

HCH was analysed in

- water, sediment, blue carp, two fish species (carp and grey mullet) and water birds (*Fluca atra*, *Anas platyrhynchos* and *Egretta garzetta*) in the Göksu delta,
- water and sediment in Manyas Bird Lake,
- water, sediment and fish (*Cyprinus carpio*) in Upper Sakarya basin,
- water, sediment and fish species (bleak, carp and wells) in Sariyer Dam Lake,
- water, sediment, blue carp and fish species (*Capoeta capoeta*, *Oreochromis mosambica*, *Liza ramada*, *Chelon labrosus* and *Anguilla anguilla*) in the Köycegiz Lagoon system,