Deposition of solid MSW incinerator ashes and sewage sludge as a source of PCDD/F and PCB in the environment?

Franz Schuler, Peter Schmid and Christian Schlatter
Institute of Toxicology, Swiss Federal Institute of Technology and University of Zurich, Schorenstrasse 16, CH-8603 Schwerzenbach

1. Introduction

The incineration of municipal solid waste is known to be an important source for PCDD/Fs in the environment. Most of the PCDD/Fs formed in the combustion process are retained in the slag, fly ash and electrostatic percipitator dust. These components are usually deposited in incinerator waste disposal sites either solidified with cement or without further treatment.
In laboratory experiments PCDD/Fs showed very little leachability with distilled water from these matrices due to their physico-chemical properties[1)2)]. Nevertheless organic substances in the leaching water, such as humic acids, can increase the solubility of the PCDD/Fs[3)].
Sewage sludge contains total PCB concentrations up to 10 mg/kg dry matter (d.m.)[4)] and PCDD/F concentrations up to 180 ng I-TEq/kg d.m.[5)]. Besides application as fertiliser on pasture land and incineration significant amounts of dehydrated and solidified sewage sludge are deposited in landfills.
It was the objective of this study to assess the leachability of single congeners from such matrices under ambient conditions into the aquatic environment. Deposited material and the effluents of an incinerator waste and sewage sludge disposal site (site A) were analysed for PCDD/Fs and PCBs and compared to the effluents of a similar disposal site for unburned municipal solid waste (site B).

2. Methods

Sample Extraction:
The aqueous phases of filtered effluent were extracted with toluene for PCDD/F and with dichloromethane for PCB analysis. Particulate matter of the filtrate was leached with 1M hydrochloric acid and Soxhlet extracted for 30 h. Incinerator ashes and sewage sludge samples were leached with 1M HCl, dried by lyophilisation and ground. The powders were Soxhlet-extracted for 30 h.
Clean-up Procedure:
The clean-up procedure for PCDD/F analysis included chromatography on pre-rinsed activated silica, caesium silicate and acidified silica and final purification on alumina for all extracts. Prior to this clean-up the raw sewage sludge extract was purified on alumina[6)].
For PCB analysis the raw extracts were purified on previously percolated activated silica, acidified silica and caesium silicate. The samples were then fractionated on activated carbon to obtain three fractions for di- to tetra-ortho PCBs, mono-ortho PCBs and coplanar non-ortho PCBs[7)]. PCDD/Fs and PCBs were analysed by HRMS.

Blanks: Clean-up procedures were tested by analysing blank samples. OCDD was detected at a level of 1 pg/sample. The other PCDD/F congeners could not be detected in blank samples.
Blank level of PCBs was 0.6 ng ΣPCB/Clean-up and below 10% for each congener compared to the lowest levels in the investigated samples.

3. Results and Discussion

The quantitative composition of the two investigated sites is given in **Table 1**. The bottoms of the disposal sites are sealed, and leaching water is collected in drainage tubes which lead into sedimentation chambers. Both sites emit an average leachate of 50'000 m^3/y which is pumped into the municipal sewerage.
In the sedimentation chambers of the disposal sites most of the particles are retained. Thus PCDD/Fs and PCBs show a higher mobility when dissolved than adsorbed to particles. Therefore effluent samples were filtered. PCB congeners to be analysed were selected for their occurrence in the environment and their toxic potential expressed as TCDD I-TEF. For the calculation of I-TEq eight congeners (77, 105, 114, 118, 126, 156, 169 and 180) were used[8].
In site A MSW incinerator ashes, sewage sludge and construction rubble are the main components. It was supposed that the latter does not remarkably contribute to the overall content of PCDD/Fs and PCBs. Therefore MSW incinerator ashes and sewage sludge were analysed. Due to the inhomogeneity of the components in site B no representative samples could be taken.

Table 1: Composition of the two investigated disposal sites.

Deposited material	Site A	Site B
Municipal solid waste	10'700 m^3	524'344 tons
MSW incinerator ashes, 75% d.m.	224'000 tons	-
Sewage sludge/lime 2:1, 40% d.m.	113'000 m^3	-
Sewage sludge 27% d.m.	-	31'480 tons
Sewage sludge liquid	-	7'040 tons
Construction rubble	107'000 m^3	116'050 tons
Industrial wastes	-	150'000 tons
Sand from waste water treatment plant	17'000 m^3	-
Soil from construction sites	46'000 m^3	-

In **Table 2** the concentrations of the 2,3,7,8-chlorosubstituted PCDD/F and selected PCB congeners in the analysed matrices are given.
Total concentrations:
In site A deposited incinerator wastes contained 191 pg I-TEq PCDD/F/g d.m. which is quite moderate compared to the concentrations reported for fly ash and for slag (13 ng I-TEq/g and 80 pg I-TEq/g respectively)[9]. This might be due to the low content of filter dust and a relatively high amount of low-contaminated slag in this material.
Sewage sludge contained 38 pg I-TEq PCDD/F /g d.m. and the total PCB concentration was more than twice as high as in the incinerator waste.
The total PCDD/F concentrations in the effluents of both sites were similar to those reported for city garbage dumps[10]. An investigation on leaching water from incinerator waste disposal sites also reported PCDD/F levels below 50 pg I-TEq/l[11]. When expressed as I-TEq concentrations of PCBs were clearly lower than of PCDD/Fs in the effluents of both sites.

Table 2: Concentrations of 2,3,7,8-chlorosubstituted PCDD/F and selected PCB congeners in effluent samples, deposited incinerator waste and sewage sludge.

	Site A				Site B	
	Effluent		Deposited material		Effluent	
Congener	Filtrate pg/l	Particulate pg/l	Inc. waste pg/g	Sewage sl pg/g	Filtrate pg/l	Particulate pg/l
2378-TCDD	2.8	1.1	38	8.0	3.3	1.4
12378-PeCDD	<0.7	<0.7	28	2.8	2.0	<0.7
123478-HxCDD	<1.0	<0.9	32	4.9	2.4	<1.0
123678-HxCDD	<0.9	1.6	76	52	9.0	2.3
123789-HxCDD	<1	1.8	97	32	6.3	2.1
1234678-HpCDD	4.4	27	853	1051	155	63
OCDD	42	231	3149	3883	1348	594
2378-TCDF	1.9	2.3	67	5.4	4.6	2.1
12378-PeCDF	1.1	3.9	86	4.2	2.1	8.4
23478-PeCDF	<0.6	<0.5	70	3.1	0.7	0.6
123478-HxCDF	<0.8	2.4	243	10	2.4	<1.1
123678-HxCDF	<0.6	1.2	96	3.6	0.9	<0.8
234678-HxCDF	<0.8	2.3	165	13	<0.8	<1.1
123789-HxCDF	<1.2	0.5	16	1.7	<1.2	<1.4
1234678-HpCDF	1.5	11	708	43	13	6.9
1234789-HpCDF	<1.2	0.8	133	3.9	<2.0	<1.4
OCDF	3.4	13	700	27	31	18
PCB 28	1500	5500	1100	1600	16000	4200
PCB 37	300	1400	190	770	2400	890
PCB 52	2700	3800	11000	5500	12000	3500
PCB 70	970	4700	3800	2000	12000	4200
PCB 81	<1	16	9	12	26	9
PCB 77	53	280	180	270	460	220
PCB 101	3800	8400	10000	19000	13000	4300
PCB 118	1200	5500	7600	8800	11000	5000
PCB 114	20	140	180	130	310	130
PCB 105	450	3400	6500	4700	5300	2800
PCB 126	<2	17	26	55	18	12
PCB 153	5500	9500	3900	30000	19000	5700
PCB 138	5200	11000	9200	32000	19000	6700
PCB 156	210	1300	1100	5000	1800	950
PCB 169	<3	<3	7	6	<3	10
PCB 180	4500	5600	2100	24000	13000	4900
Σ PCB	26000	60000	57000	134000	125000	44000
I-TEq PCDD/F*	3.6	3.4	191	38	10	4.4
I-TEq PCB*	0.4	3.5	3.2	9.9	4.9	2.8

*For the calculation of Σ I-TEq half the detection limit was used for congeners below the detection limit.

Pattern comparison:
Sewage sludge showed a higher concentration of chlorinated dioxins than furans; HpCDD and OCDD were by far the most abundant congeners. The PCB profiles were dominated by congeners no.138, 153 and 180 in the sewage sludge whereas congeners no.52 and 101 were the principal PCBs in the incinerator waste sample.
Solubility:

The mobility of a congener is given by the ratio between the dissolved and the adsorbed fractions. In site A the mobility decreased with increasing chlorination of the PCDD/Fs whereas in site B the mobility remained constant for all congeners. For PCBs the degree of chlorination seemed not to have an important influence on the partition between aqueous and particulate phases of the effluents of both sites. Inspection of the congener profiles shows a relatively high adsorption to particulate material of the planar mono- and non-ortho PCBs.
The leachabilities of the single PCDD/F congeners were assessed at site A under the conservative assumption that deposited incinerator wastes and sewage sludge are the dominant sources for PCDD/Fs in the effluent. The congener specific values are given in **Table 3**.
Although the data basis for the calculation of these factors is small, clear differences in the solubility of single congeners can be observed. Thus, tetra-chloro congeners show the highest mobility. However no significant decrease can be observed from hexa- through octa-chloro congeners.

Table 3: Concentration of single PCDD/F congeners dissolved in the effluent relative to the concentration in the disposal site A; the factors are calculated relative to 2378-TCDD.

PCDDs	Relative Leachability	PCDFs	Relative Leachability
2378-TCDD	1	2378-TCDF	0.4
12378-PeCDD	<0.3	12378-PeCDF	0.2
		23478-PeCDF	<0.1
123478-HxCDD	<0.4	123478-HxCDF	<0.05
123678-HxCDD	<0.2	123678-HxCDF	<0.1
		234678-HxCDF	<0.
123789-HxCDD	<0.2	123789-HxCDF	<1
1234678-HpCDD	0.05	1234678-HpCDF	0.05
		1234789-HpCDF	<0.1
OCDD	0.1	OCDF	0.1
		Σ I-TEq	0.25

The output of PCDD/Fs and PCBs was calculated for whole leachate (dissolved and particulate) and for the filtrate alone, as a high portion of particles is retained in the sedimentation chamber. In **Table 4** the annual emissions are given in terms of I-TEq.

Table 4: PCDD/F and PCB emissions from the two sites in terms of I-TEq.

I-TEq	Site A		Site B	
	PCDD/F	PCB	PCDD/F	PCB
Concentration in effluent (pg/l)	7.0	3.9	14	7.6
Calculated emission per year (mg/y)	0.35	0.20	0.70	0.38
Percentage in aqueous fraction (%)	51	10	71	63

4. Conclusions

Effluents and deposited material of an incinerator waste/sewage sludge disposal site were analysed for their PCDD/F and PCB content. The study design and the results allow the following conclusions:

1. The effluents from the mixed waste disposal site and the incinerator waste/sewage sludge disposal site were similar. The 224'000 tons of stored incinerator wastes at site A correspond to about 670'000 tons of unburned solid waste. A similar amount of industrial and municipal solid wastes is deposited at site B. Thus the combustion of waste will not lead to higher aqueous PCDD/F and PCB emissions at the final disposal site than the deposition of unburned waste.
2. In terms of I-TEq PCDD/F emissions exceeded the PCB emissions at both sites by a factor of two based on eight PCB congeners included for I-TEq calculation.
3. The solubility of single PCDD/F congeners decreased with increasing chlorination and varied up to a factor 30 between TCDD and HpCDF.
4. It can not be excluded that the emissions lead to an increase in PCDD/F content in sediments of the recipient rivers. This should be further investigated.

5. Acknowledgement

The financial support of this work by the "Amt für Umweltschutz des Kt. Luzern" is gratefully acknowledged.

6. References

1) Carsch, S., Thoma, H. and Hutzinger, O. (1986) *Chemosphere*, **15**, 1927-1930.
2) Fischer, J., Lorenz, B. and Bahadir, M. (1992) *Chemosphere*, **25**, 543-552.
3) Webster, G.R.B., Muldrew, D.H., Graham, J.J., Sarna, L.P. and Muir, D.C.G. (1986) *Chemosphere*, **15**, 1379-1386.
4) Alcock, R.E. and Jones, K.C. (1993). *Chemosphere*, **26**, 2199-2207.
5) Hagenmaier, H., She, J., Benz, T., Dawidowsky, N., Düsterhöft, L. and Lindig, C. (1992) *Chemosphere*, **25**, 1457-1462.
6) Hagenmaier, H., Brunner, H., Haag, R., and Berchtold, A. (1986) *Chemosphere*, **15**, 1421-1428.
7) Schmid, P. and Zimmermann, G. (1995) *in preparation*,
8) Ahlborg, U.G., Becking, G.C., Birnbaum, L.S., Brouwer, A., Derks, H.J.G.M., Feeley, M., Golor, G., Hanberg, A., Larsen, J.C., Liem, A.K.D., Safe, S.H., Schlatter, C., Waern, F., Younes, M. and Yrjänheikki, E. (1994) *Chemosphere*, **28**, 1049-1067.
9) Fiedler, H. and Hutzinger, O. (1992) *Chemosphere*, **25**, 1487-1491.
10) de Wit, C., Jansson, B., Strandell, M., Jonsson, P., Bergqvist, P.-A., Bergek, S., Kjeller, L.-O., Rappe, C., Olsson, M. and Slorach, S. (1990) *Chemosphere*, **20**, 1473-1480.
11) Hiraoka, M., Tanaka, M., Matsuzawa, Y., Miyaji, K., Kawanishi, T., Matumoto, S., Horii, Y. and Ihara, H. (1993) in *"Dioxin'93"* Conference Proceeding.
12) Näf, C., Broman, D., Ishaq, R. and Zebühr, Y. (1990) *Chemosphere*, **20**, 1503- 1510.