WASTE CHARACTERIZATION: OCCURRENCE AND CONCENTRATION OF PCDD/Fs, PCBs, PBDEs AND HCB

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Introduction

Increase in quality of life of developed countries, has resulted in a rampant appearance of wastes, as unwanted or undesired materials. Waste, could have toxic properties, which could be due to the presence of some Persistent Bioaccumulable and Toxic Pollutants (PBTs).

Over the past several years, the risk posed by wastes has become of increasing concern in many countries, resulting in actions, at the national, regional and international levels, to protect human health and the environment. In this sense, The European Waste List (2001/118/EC (EC 2001)) is a harmonized list of about 850 different waste types. This list replaces the 97/3/EC List of Waste and the 94/904Ç/E List of Hazardous Waste and forms a consistent waste classification system across the EU. It includes 850 waste six-digit-codes in 20 chapters, defining 405 waste types as hazardous waste material and 200 waste types in so called "mirror entries". A mirror entry is defined as follows: Waste with potential to be either hazardous or non-hazardous depending on their composition and the concentration on dangerous substances [2]. In this list, 14 hazard criteria are defined: H1 explosive, H2 oxidizing, H3 flammable, H4 irritant, H5 harmful, H6 toxic, H7 carcinogenic, H8 corrosive, H9 infectious, H10 teratogenic, H11 mutagenic, H12 substances which release toxic gases, H13 substances capable of yielding any of the characteristic listed above, and H14 ecotoxic [3]. H7 criterion, carcinogenic, should be evaluated through the analysis of persistent organic pollutants, POPs, which have toxic equivalence factors (TEF) relatives to the 2,3,7,8 TCDD, that is consider by the International Agency for Research on Cancer (IARC) as carcinogenic group 1[4].

This paper, evaluates some wastes for chemicals with TEF (PCDD/F and dl-PCBs), besides others compounds, which toxicological potential are presently being studied (i-PCBs, HCB and PBDEs).

Materials and Methods

Sample collection:

Samples were obtained from a interlaboratory study organized by: Umweltbundesamt (UBA) Desssau, Germany, Federal Institute for Materials Research and Testing (BAM) Berlin, Germany, University of Applied Science Fachhochschule (FH) Giessen-Friedberg, Giessen, Germany and ECT Oekotoxicilogie GmbH Flörsheim, Germany. It was performed with three representative waste types: i) an ash from a Dutch municipal incineration plant (INC), ii) a polluted sandy soil from a former gasworks site in Berlin, Germany, (SOI), and iii) a wood sample (WOO) mixture of treated and untreated woods from a commercial timber processing plant, which were treated with cooper-based wood preservatives according to the regulations of different European countries [2]. Although the ring test was focused in the ecotoxicological characterization, the same samples were analysed for PCDD, PCDFs, dl-PCBs, i-PCBs, HCB and PBDEs.

Sample Extraction and Clean up:

Samples were dried at 40^{o}C until constant weight to avoid lack of volatile congeners. Prior to extraction all samples were spiked with a known amount of LCS 1613, WP-LCS and MBDE-MXE for PCDD/Fs, dl-PCBs and PBDEs determination. Standard solutions were obtained form Wellington Laboratories Inc., Canada. INC sample was treated with HCl 3 M for 2 h prior to extraction, as described elsewhere[5].

Samples were extracted using an ASE 100 system (Accelerated Solvent Extraction), in three static cycles. Resulting extracts were subjected to different clean up stages depending on the type of waste analysed, including: liquid-extraction with concentrated sulphuric acid, multilayer silica column and an automated purification method, performed in a Power Prep™ System (FMS, Inc., USA) with acidic silica gel, basic alumina and carbon columns. An outline of extraction and clean up is shown in Table 1.

The extracts obtained were concentrated to incipient dryness and spiked with the recovery standard 1613 ISS for PCDD/Fs, WP-ISS for dl-PCBs, i-PCBs and HCB, and BDE-CVS-EISS for PBDEs analysis (Wellington Laboratories Inc., Canada) previously to be analyzed by GC-MS.

Sample Analysis:
Analyses of PCDD/Fs, PCBs and HCB were performed on an Agilent GC 6890, fitted with a 60m x 0.25mm x 0.25 µm film thickness chromatographic capillary column (DB-5MS from J&W) connected to a Micromass Ultima NT HRMS, at 10,000 resolving power.

Analyses of PBDEs were carried out by GC-qEI-MS in a Agilent 6890 Gas Chromatograph equipped with a 7683 Autosampler, and a temperature programmable injector (PTV) working in pulsed splitless, connected to a Low Resolution Mass Spectrometer (LRMS) detector, Agilent 5973 MSD Network. A J&W Scientific DB-5MS (15 m x 0.25 mm x 0.10 µm film thickness) capillary column was used.

Complete details about the analysis methods were published elsewhere [6,7]. Identification and quantification was carried out using isotopic dilution for PCDD/Fs, dl-PCBs and PBDEs, which allows high accuracy in the calculation of final results. Thus, data were corrected for recoveries. On the other hand, HCB and i-PCBs quantification were performed using WP-ISS as internal standard.

Procedural Blanks were processed and analyzed under the same conditions as samples. Concentrations obtained were used to correct those for the wastes analysed. In this way, the final result of each sample is obtained by subtracting the blank values.

Results and Discussion
Corrected concentration levels for all analytes are listed in Table 2. Limits of detection, LODs, were defined as the smaller concentration giving a signal with S/N>3, were: i) 0.02 - 12.60 pg g^{-1} d.w. for PCDD/Fs, ii) 0.04 - 4.00 pg g^{-1} d.w. for dl-PCBs, iii) 0.02-18.04 pg g^{-1} d.w for i-PCBs and HCB, iv) 9 - 897 pg g^{-1} d.w. for Tri to Nona-BDE and 4.01 ng g^{-1} d.w. for Deca-BDE. Recoveries for PCDD/Fs and dl-PCBs were 42 -118 % and 59-118 % respectively, while for PBDEs were in the range of 48 to 92 %.

PCDD/Fs and dl-PCBs
Total WHO-TEQ (pg g^{-1}), including PCDD/Fs and dl-PCBs were calculated in order to elucidate their potential toxicity. The major contribution to the total WHO-TEQ level corresponded to the PCDD/Fs, as can be shown in Table 2. Analyzing the profiles, it can be noticed that, the highest concentration corresponded to the OCDD for all samples, with a contribution to the total PCDD/Fs above 40, 65 and 75 %, for INC, SOI and WOO respectively.

Results obtained in this study reported the highest TEQ value for the INC sample. On contrast, ecotoxicological result obtained in the ring test, conclude that SOI caused the lowest effects and WOO was most toxic, while INC shown an intermediate toxicity [2]. A reason for this toxicological difference between result obtained in this study and those reported in the interlaboratory study, may be due the presence of fungicides such as pentachlorophenol in the WOO sample. This compound, as a dioxin precursor, could explain the high concentration of OCDD found in this sample.

i-PCBs, HCB and PBDEs
PCB 101, 138 and 153, were the predominant congeners in the samples analyzed, whereas, PCBs 28, 52, and HCB were in the range of the procedural blank.

The ash from a municipal incineration plant, presented the highest concentration of PBDEs, 10 and 20 times higher than those obtained for SOI and WOO samples. This is due to the presence of DecaBDE in INC sample, with a 90 % contribution to the total PBDEs concentration, while for the other samples, SOI and WOO DecaBDE were below LOD.

Data obtained in this study, reveal that the characterization of wastes, should include analyses of PBTs in order to elucidate their potential hazardous and to take into account the presence of these compounds in the designing of disposal or recycling strategies.

Acknowledgments

The authors would like to thank Dr. Carbonell and Dr. Tarazona for providing the samples. This work has been supported in the framework of the Spanish R&D Program (CAM Project: RESIDUOS S-0505/AMB-0352).

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Table 1.- Analytical conditions of Extraction and Clean up

		ASE Extraction			**Purification**		
Sample	**Compounds**	g	Solvent	Temperature (ºC)	Acid treatment	Silica Column	FMS
INC	PCDD/Fs, dl-PCBs, HCB	1	Toluene	185	No	No	Yes
	PBDEs	0.5	Toluene	150	No	No	Yes
SOI	PCDD/Fs, dlPCBs, HCB	1	Toluene	185	Yes	Yes	Yes
	PBDEs	0.5	Hx:DCM 50%	100	Yes	Yes	Yes
WOO	PCDD/Fs, dlPCBs, HCB	8	Toluene	185	Yes	Yes	Yes
	PBDEs	0.5	Hx:DCM 50%	100	Yes	Yes	Yes

Table 2.- PBTs concentration in pg g^{-1} d.w. of the wastes analysed

		Ash	Soil	Wood	Blank
PCDDs	2,3,7,8- TCDD	2.27	0.47	0.12	<1.51
	1,2,3,7,8- PeCDD	9.66	2.27	2.36	<7.59
	1,2,3,4,7,8- HxCDD	9.89	2.40	9.75	<2.46
	1,2,3,6,7,8- HxCDD	9.99	3.95	21.47	<3.14
	1,2,3,7,8,9- HxCDD	10.88	3.08	21.16	<3.13
	1,2,3,4,6,7,8- HpCDD	56.91	45.29	483.36	<2.19
	OCDD	296.57	250.08	2154.48	<3.52
PCDFs	2,3,7,8- TCDF	11.25	6.45	1.05	<1.03
	1,2,3,7,8- PeCDF	15.21	5.72	0.29	<1.12
	2,3,4,7,8- PeCDF	19.83	5.68	0.51	<1.97
	1,2,3,4,7,8- HxCDF	24.20	4,93	0.80	<1.29
	1,2,3,6,7,8- HxCDF	17.55	3.88	0.62	<1.43
	2,3,4,6,7,8- HxCDF	19.14	3.58	0.67	<1.18
	1,2,3,7,8,9- HxCDF	12.95	2.79	0.56	<4.12
	1,2,3,4,6,7,8- HpCDF	61.83	13.22	12.41	<1.39
	1,2,3,4,7,8,9- HpCDF	12.88	2.83	1.42	<2.73
	OCDF	96.87	15.73	16.71	<3.13
	Total	687.88	372.35	2727.74	<42.94
	PCDD/Fs I-TEQ	31.07	8.71	14.32	<8.20
	PCDD/Fs WHO-TEQ	35.55	9.61	13.56	<11.98
dl PCBs	TeCB 81	-	2.39	0.88	<0.9
	TeCB 77	229.67	29.38	7.89	30.33
	PeCB 123	-	141.62	29.66	396.32
	PeCB 118	2010.8	535.98	227.30	5085.63
	PeCB 114	123.85	22.64	6.30	120.27
	PeCB 105	1340.35	272.84	67.47	1494.31
	PeCB 126	24.53	7.60	0.95	4.67
	HxCB 167	83.35	129.53	11.87	99.83
	HxCB 156	316.67	192.20	25.65	213.03
	HxCB 157	51.73	47.35	3.65	47.75
	HxCB 169	2.43	3.13	0.20	<1.26
	HpCB 189	9.71	36.75	1.73	3.42
	Total	4192.87	1421.41	383.55	7495.57
	dl-PCBs WHO-TEQ	3.08	1.03	0.15	3.46
	Total WHO-TEQ	38.63	10.64	13.71	3.46
i- PCBs	PCB-28	309.7	37.25	212.86	402.89
	PCB-52	-	63.65	99.37	3930.43
	PCB-101	6697.15	1566.26	807.76	4268.21
	PCB-153	3748.36	2989.43	804.27	1592.77
	PCB-138	5493.05	3992.97	1030.36	2737.25
	PCB-180	927.09	2455.85	287.41	316.73
	TOTAL (pg/g)	17175.36	11125.96	3269.20	13248.28
HCB		-	20.54	27.18	161.10
PBDEs	Tri-BDE 28	51.21	-	22.42	24.04
	Tetra-BDE 47	468.14	1558.49	283.97	214.38
	Tetra-BDE 66	131.94	950.46	742.36	234.00
	Tetra-BDE 77	-	-	-	-
	Penta-BDE 85	-	-	-	-
	Penta-BDE 99	108.76	41.84	243.35	93.36
	Penta-BDE 100	-	-	-	-
	Penta-BDE 119	-	-	-	-
	Penta-BDE 126	-	-	-	-
	Hexa-BDE 138	-	-	-	-
	Hexa-BDE 153	266.68	-	-	-
	Hexa-BDE 154	139.06	-	-	-
	Hexa-BDE 156	-	-	-	-
	Hepta-BDE 183	259.32	-	-	-
	Hepta-BDE 184	-	-	-	-
	Hepta-BDE 191	-	-	-	-
	Octa-BDE 196	-	-	-	-
	Octa-BDE 197	-	-	-	-
	Nona-BDE-206	-	-	-	-
	Nona-BDE-207	-	-	-	-
	Deca-BDE 209	17663.54	-	-	-
	Total	19088.22	2550.39	1291.68	565.78

- = Non detected