PCDD/Fs, PCBs AND HCB IN LEACHATE AND COMPOST FROM DIFFERENT SPANISH LANDFILLS

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Introduction

Huge amounts of urban and industrial wastes are generated in the central region of Spain each year. Part of these wastes is disposed in landfill sites. Since, it is well known the presence of Persistent Organic Pollutants (POPs) in the different waste materials [1,2,3,4], a serious problem will arise if these compounds enter the environment from the landfill sites through leaching.

Due to the low aqueous solubility of POPs such as PCDD/Fs, PCBs, and HCB, their leaching behaviour has been rarely studied and therefore leachate was not considered as a source of POPs contamination.

Carsch et al[5], observed that only highly chlorinated PCDD/Fs leached in their leaching experiments both in landfills and column tests for fly ash and soil. In these experiments, most of the PCDD/Fs levels were under the detection limit. Recently, many studies [6,7,8] have suggested surfactants and surfactant-like substances such as linear alkylbenzene sulfonate(LAS) and humic acids, influence on the increase in the solubility of hydrophobic substances. In this way, PCDD/Fs and other dioxin-like compounds could leach from landfill sites both with dissolved and suspended solids.

This work constitutes a preliminary study of municipal solid waste landfills as a source of persistent organic pollutants in the central Region of Spain, being the main objective to determine the concentration and distribution of PCCD/Fs, dioxin-like and indicator PCBs, and HCB in leachate and compost from different landfill sites. These facilities only receive urban solid waste. Taking into account the major potential environmental impact related to landfill leachate is pollution of ground and surface waters, two samples taken from a stream next to a closed landfill has been included in the survey to evaluate the possible transfer of these compounds from landfills to the environment.

Materials and Methods

Sample collection:
Liquid samples (Leachate and Water) and solid samples (Compost and Soil) were sampled from five landfills situated in the Central Region of Spain. Features of samples analysed are described in Table 1. Facility A is a closed landfill; in this case, liquid samples were sampled in a stream next to the landfill, A.1 and A.2 corresponded to the stream influent and the effluent respectively, and the solid sample, A.3, was a soil sample of the closed landfill.

Sample analysis:
Upon receiving in the laboratory, Liquid Samples were stored into the fridge to preserve from light, humidity and other external factors which might changes its chemical composition. On the other hand, solid samples were dried at 40^{o}C until constant weight to avoid lack of volatile congeners and ground to a fine powder. Prior to extraction all samples were spiked with a known amount of 1613LCS-PCDD/Fs, and WP-PCBs and (Wellington Laboratories Inc., Canada).

Liquid samples, (1-2 L) were subjected three times to liquid-liquid extraction with 100 ml of dichloromethane, while solid samples (0.5 g d.w.) were extracted with a mixture of hexane:diclorometane (1:1) 100ºC, 1500 psi, 90% volume and three static cycles, using an ASE 100 system (Accelerated Solvent Extraction). Resulting extracts were transferred into a separation funnel and liquid-extracted with concentrated sulphuric acid to

remove organic matter. Clean-up stage was then performed in an automated purification Power Prep™ System (FMS, Inc., USA) including acidic silica gel, basic alumina and carbon columns. Different mixtures of hexane:dicloromethane and toluene were used to recover target analytes while retaining interfering compounds. Purified extracts were concentrated to incipient dryness and spiked with ^{13}C PCDDs (1,2,3,4-TeCDD and 1,2,3,7,8,9-HxCDD) and ^{13}C PCBs (70, 111 and 138) and analyzed by HRGC-HRMS at 10,000 resolving power using a 60 m chromatographic column (DB-5MS from J&W). Limits of detection, LODs, were defined as the smaller concentration giving a signal with S/N>3.

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

Results and Discussion

Concentration levels of the samples analyzed (liquid and solid samples, respectively) are summarized in Tables 2 and 3. Great differences can be found between levels related to leachates and composts. The case of PCDD/Fs is specially remarkable because nearly all the congeners in the leachate samples were under the detection limit. Only the OCDD presented levels over the detection limit in this matrix. Osako et al[9] observed similar behaviour with respect to the PCDD/Fs congeners, explaining that some entity accelerates the leachability of the highly chlorinated compounds, despite their low solubility. The detection limits ranged from 0.43 to 0.18 ppq I-TEQ and Total PCDD/Fs content ranged from 0.01 to 5.22 ppq I-TEQ. Recoveries for PCDD/Fs ranged from 30 to 82 %. These levels are similar to those found in leachates coming from other countries [4,10,11]. On the contrary, PCDD/Fs levels in solid samples (soil and compost) were much higher (Table 3), about three orders of magnitude, varying between 2.92 and 21.56 ppt I-TEQ. The detection limits ranged from 0.04 to 3.91 ppt I-TEQ. Recoveries ranged from60 to 89 %.

A similar behaviour could be observed for dl-PCBs, i-PCBs and HCB, although in this case the majority of congeners were over the detection limit. Regarding to leachates, LODs ranged between 0.3 and 12.4 ppq for dl-PCBs, 0.46 and 3.4 ppq for i-PCBs and 0.41 and 1.70 ppq for HCB. Recoveries for dl-PCBs were 54 -112 %. Related to compost matrix, LODs ranged between 0.97 and 11.7 ppt for dl-PCBs, 0.6 and 6.2 ppt for i-PCBs and 0.6 and 2.9 ppt for HCB. The corresponding recoveries were 83-130 %. Total dl-PCBs, expressed as WHO-TEQs, varied from 0.18 to 12.69 ppq in leachate and from 1.15 to 3.91 ppt in solid samples.

It is noticeable that while in leachate samples the highest contribution to total toxic level (WHO-TEQ) is due to the dl-PCBs, the tendency is the opposite in solid samples: the highest contribution to total TEQ levels is due the PCDD/Fs.

Besides, the highest levels of these compounds found in leachate samples corresponded to compost leachates, B.1 > B.2, D.3 > D.1 and D.2 (except for dl-PCBs in the facility D) suggesting that these POPs leaches more easily from the compost matrix to the liquid phase.

In Facility E, a leachate sampled from an Osmosis Plant was analysed. Thus, it could be observed that POPs content decreased in comparison to that for the leachate sampled before the osmosis process took place , E.3<E.1. This fact suggests that Osmosis treatment could decrease the organochlorinated pollutant content.

Regarding maturation (B.3) and fermentation (B.4) composts, although in other work presented to this meeting[12], it could be observed that the fermentation compost B.4 presents a lower level of PBDEs than the maturation compost, B.3, no significant differences were found in the levels of PCDD/Fs, PCBs and HCB between these two composting stages.

On the other hand, analyses carried out in the closed landfill A, revealed that no significant pollution of PCDD/Fs and dl-PCBs is observed in the stream, while the HCB and i-PCBs levels are similar to those found in the working landfills.

Data obtained evidence that although the POPs content is low, leachates could be a potential source of organochlorinated pollution, demonstrating the importance of landfill leachate collection systems for minimizing release of these pollutants into environment.

These data are preliminary results of an on-going research. As the leachate composition varies significantly among landfills depending on waste composition, waste age and landfill technology, future campaigns are performing in the same facilities to determine time trends, besides including other different landfills.

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Table 1: **Outline of facilities and samples studied**

Facility	Liquid Samples		Solid Samples	
A	A.1	**Stream Influent**	A.3	**Soil sample**
Closed landfill	A.2	**Stream Effluent**		
B	B.1	**Compost leachate**	B.3	**Maturation compost**
	B.2	**Landfill leachate**	B.4	**Fermentation compost**
C	C.1	**Landfill leachate**		
	C.2	**Landfill leachate**		
D	D.1	**Landfill leachate**	D.4	**Maturation compost**
	D.2	**Landfill leachate**	D.5	**Maturation compost**
	D.3	**Compost leachate**		
E	E.1	**Landfill leachate**	E.4	**Maturation compost**
	E.2	**Compost leachate**		
	E.3	**Osmosis Plant**		

Table 2:PCDD/Fs, PCBs, & HCB concentration (pg/l or ppq) of the liquid samples analyzed: S.I. Stream influent; S.E. Stream effluent; C.L Compost leachate; L.L Landfill leachate; O.P. Osmosis plant

Facility	A		B		C		D			E			Laboratory
SAMPLE	A.1	A.2	B.1	B.2	C.1	C.2	D.1	D.2	D.3	E.1	E.2	E.3	Blank
	S.I.	S.E.	C.L.	L.L.	L.L.	L.L.	L.L.	L.L.	C.L.	L.L.	C.L.	O.P.	
PCDD/Fs I-TEQ (pg/l or ppq)	0,01	0,46	1,28	0,57	1,04	2,54	0,01	0,27	5,22	0,42	0,00*	0,13	0,00*
PCDD/Fs WHO-TEQ (pg/l or ppq)	0,01	0,44	0,85	0,47	0,87	2,25	0,01	0,27	4,90	0,24	0,00*	0,12	0,00*
dl-PCBs WHO-TEQ (pg/lor ppq)	0,69	0,45	0,79	0,64	0,18	3,79	1,84	12,69	2,94	2,17	0,94	1,00	0,00*
Total WHO-TEQ (pg/lor ppq)	**0,70**	**0,89**	**1,64**	**1,11**	**1,05**	**6,04**	**1,85**	**12,96**	**7,84**	**2,41**	**0,94**	**1,12**	
HCB	64,31	55,01	92,82	114,33	221,49	290,78	0,00	0,00	670,42	406,63	6,89	95,26	50,81
PCB-28	234,04	171,51	671,81	165,59	2186,60	8876,31	1455,60	92,67	5710,31	5548,23	303,38	3235,10	45,28
PCB-52	3949,71	2014,90	2589,36	2097,64	2959,30	8585,00	357,55	899,25	11147,11	7012,55	2199,88	3990,89	594,19
PCB-101	5018,58	3349,81	4007,02	2789,34	3974,46	11807,63	3885,18	3390,91	13441,82	7374,03	2714,28	4160,34	1117,19
PCB-153	1652,37	1309,10	1787,44	912,09	1643,33	4274,40	1549,35	1804,00	5878,26	3636,81	919,32	1873,61	388,44
PCB-138	2022,40	1443,97	2009,82	989,93	2275,51	6867,39	1830,15	2292,22	6094,35	3396,63	1179,07	2168,83	793,58
PCB-180	273,63	260,59	490,70	136,63	595,04	1346,67	336,79	420,72	2907,60	2020,37	160,58	906,68	77,98
TOTAL i-PCBs (pg/l or ppq)	**13150,74**	**8549,89**	**11556,15**	**7091,23**	**13634,24**	**41757,39**	**9414,61**	**8899,76**	**45179,44**	**28988,63**	**7476,52**	**16335,45**	**3016,66**

***All the congeners were under LOD, and therefore I-TEQ or WHO-TEQ considered was zero.**

Table 3: PCDD/Fs, PCBs, HCB concentration in solid samples (pg/g or ppt): S Soil; M Maturation compost; F Fermentation compost

Facility	A	B		D		E	Laboratory
Sample	A.3	B.3	B.4	D.4	D.5	E.4	Blank
	S	M	F	M	M	M	
PCDD/Fs I-TEQ (pg/g or ppt)	21,56	9,22	7,40	2,92	4,06	4,04	0,00*
PCDD/Fs WHO-TEQ (pg/g or ppt)	20,70	5,26	4,23	1,53	2,39	2,74	0,00*
dl-PCBs WHO-TEQ (pg/g or ppt)	3,91	1,46	1,15	2,62	3,62	1,99	0,00*
Total WHO-TEQ (pg/g or ppt)	**24,61**	**6,72**	**5,38**	**4,15**	**6,01**	**4,73**	
HCB	852,60	592,07	456,20	732,04	869,91	586,10	40,22
PCB-28	1659,63	2632,09	534,80	9679,76	8520,17	4282,93	30,52
PCB-52	4810,56	3563,91	3950,63	6590,59	10283,79	4152,51	41,69
PCB-101	6299,79	4588,64	4624,10	6920,10	11514,99	4938,29	109,45
PCB-153	2770,45	2041,46	1542,94	3976,97	5190,24	2654,83	35,19
PCB-138	3284,18	2453,22	1871,30	5023,10	5708,53	2792,46	214,64
PCB-180	1431,01	1207,76	738,27	3841,58	2542,45	6774,22	29,38
TOTAL i-PCBs (pg/g or ppt)	**20255,62**	**16487,08**	**13262,03**	**36032,10**	**43760,17**	**25595,25**	**460,86**

***All the congeners were under LOD, and therefore I-TEQ or WHO-TEQ considered was zero.**