PBT levels in industrial waste samples

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Indroduction:

In the modern society, the increase in the quality of life has resulted in a rise and appearance of new wastes, as unwanted or discarded materials. These wastes, when improperly managed could pose a potential hazard to the human health or the environment.

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 (EC2001)) was established as a harmonized list of about 850 different waste types. This list 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 materials, 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 [1]. 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 [2].

Prior to establishing strategies for the control and treatment of a waste, its characterization is an essential requirement. In this sense, it is mandatory to know the presence of substances which are hazardous, such as Persistent, Bioaccumulable and Toxic Pollutants (PBTs) in the waste. The high chemical and physical heterogeneity of wastes complicate their characterization, making analytical methods designed to monitor PBTs, tedious, time consuming, and expensive.

The aim of this study, framed within the Spanish R&D Program (CAM Project: RESIDUOS S-0505/AMB-0352), is to evaluate the content of PBTs in wastes of different nature and origin, that could produce quality data, which allows incorporating new information helpful in the development of waste management strategies.

Materials and Methods:

Sample Collection:
As part of the work framed in the Spanish R&D project, nine waste samples of different nature were selected to analyse their levels of PCDD/Fs (17 toxic congeners), PCBs (dl-PCBs and i-PCBs), HCB and PBDEs. These samples were kindly provided by BEFESA, a Spanish Waste Management Company. Complete details of samples, including nature and origin are shown in Table 1.

Sample extraction and clean up:
Once received, the solid samples (excepting W3), were dried at 40 ºC until constant weight. Prior to extraction all the samples were spiked with a known amount of EPA-1613LCS, WP-LCS, and MBDE-MXE for PCDD/Fs, dl-PCBs and PBDE determination, respectively. Standard solutions were purchased from Wellington Laboratories Inc., Canada.

Solid samples, (except W3), were extracted using an ASE 200 system (Accelerated Solvent Extraction), using toluene as extracting agent, 100ºC as extraction temperature and three stationary cycles.

On the other hand, W3 sample, a varnish from can manufacture, due to its low melting point did not allow the use of ASE extraction. For this reason W3 was dissolved in methanol, and then added MilliQ water to increase the aqueous nature of the mixture and liquid-liquid extracted with dicloromethane. Sample W9 was also liquid-liquid extracted with dichloromethane. Samples W6 and W8, due to the presence of solid suspension should be pre-processed to separate them in two phases. This separation was performed by centrifugation for sample W6, and by filtration for sample W8. The liquid phase of W6 and W8 was liquid-liquid extracted with hexane and dichloromethane, respectively. The solid phase of both samples was extracted as solid samples were. The resulting extracts of both phases were mixed prior to further clean up. W7, as an organic solution, did not need the extraction step, and we proceeded directly with the clean up and purification steps.

Clean up stages were carried out, depending on the type of waste analysed, including: treatment with concentrated sulfuric acid, multilayer silica column and an automated purification method, carried out in a Power-Prep™ System (FMS, Inc., USA) with acidic silica gel, basic alumina and carbon columns. For some samples (W7 and W8), it was necessary to perform some additional purification steps after Power Prep purification.

Clean up resulting extracts were concentrated under N_2 flow, up to incipient dryness, and redisolved in nonane spiked with the recovery standards (EPA-1613ISS, WP-ISS and BDE-ISS, obtained from Wellington Lab, Canada).

Extraction, clean up, and purification steps for the samples assayed are summarized in Table 2.

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 [3].

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 [4]. Identification and quantification were 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 with every batch of samples as routine in the laboratory. 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:

Due to the chemical heterogeneity of samples, their different nature and origin, standard methods of analysis of PBTs could not be used. For this reason it has been necessary to modify and adapt the different steps of the methodology, mainly the clean up steps.

Sample W7, as a mixture of organochlorinated compounds, presented high levels of interferences, which share physicochemical properties with the analytes studied. This fact represents a challenge in the clean up step. In this way, purification step included: i) acidic and multilayer silica columns, ii) automated purification and fractionation with Power Prep System (FMS), and finally iii) carbon activated and acidic silica columns. Although the high complexity of the analytical method, recoveries obtained for this sample were 62% for PCBs, 87% for PCDD/Fs and 89% for PBDEs.

On the other hand, sample W9 presented less difficulty in the analysis. This sample proceeded from the synthesis of phosphomicyn, by the pharmaceutical industry. In this case recoveries obtained for PCDD/s, PCBs and PBDEs were above 70%.

Concentrations obtained for PCDD/Fs, PCBs, HCB, and PBDEs are listed in Table 3. In order to compare PBT levels obtained in the samples, contribution of each family to the total content were calculated, as shown in Figure 1.

PCDD/Fs were not detected in almost any sample except for sample W8, a sludge from the washing of the machines of a graphic arts industry. To explain that fact, we would need to know the solvents used in this activity, as well as the cleaning process of the machines, to determine the source of the PCDD/Fs. In this sample the contribution of PCDD/Fs to the total concentration raised up to 39 %, while in the other samples this contribution was lower that 0.4 %.

In sample W3 all the PCDD/Fs congeners were under the detection limit. However, in the rest of samples, OCDD was detected.

Dioxin-like PCBs was the family of compounds that showed a higher concentration to total levels, ranging from 59 to 93 %, with the exception of samples W5, W6 with contributions lower than 02 % and W8 where these compounds could not be analyzed due to the presence of interferences.

Regarding PBDEs, it is noticeable the high contribution of this family in samples W5 and W8, which represents 98% and 52% of the total concentration for each sample.W5 sample levels could be explained by the fact that cutting oils are used as refrigerant and lubricant in machining processes. Due to the working temperatures in theses processes, it is reasonable the presence of flame retardants in this sample. As previously commented, in sample W8, would be necessary to know the solvents used in this activity, as well as the cleaning process of the machines, to determine the source of the pollutants.

Hexachlorobenzene levels, as shown in Table 3, were lower than 0.03 ng/g in solid samples and 0.04 ng/L in liquid samples. The highest i-PCBs content is related to W5, the Sludge from the washing of cardboard industry machinery, showing a concentration of 44.55 ng/g.

Data obtained in this study, demonstrate that the waste characterization should include PBTs analyses in order to elucidate their hazardous potential and to take into account the presence of these compounds in the design of disposal or recycling strategies, but also the need of information about the nature and the origin of the samples in order to plan the analytical strategy.

Acknowledgments:

The authors would like to thank BEFESA 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).

References:

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Table 1: Nature and origin of the samples assayed.

Code	Sample	Sample Type
W1	Mixture of expired cosmetics	Solid
W2	Silica gel used in chemical processes	
W3	Varnishes from can manufactures	
W4	Sludge of cutting oil mixture from machining processes	
W5	Sludge from the washing of cardboard industry machinery	
W6	Mixture of polyethileneglycol and silicon carbide from the cutting of silicon carbide	Liquid
W7	Organohalogenated solvent mixture	
W8	Waste from washing of graphic arts machinery	
W9	Wastes from the synthesis of fosfomycin	

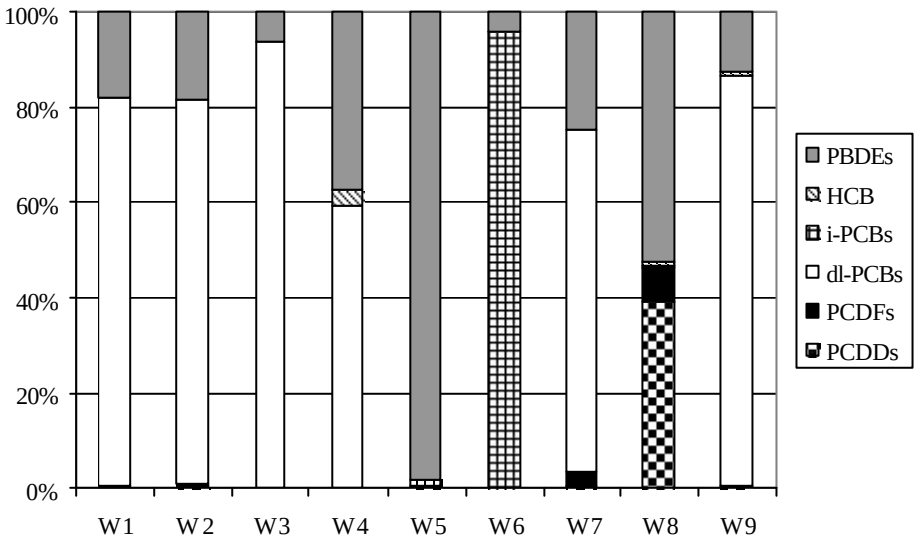

Figure 1. Contribution percentage to the total PBT levels of each pollutant family.

Table 2. Extraction, clean up and purification steps.

	Quantity	Extraction		Cleanup		Purification		
W1	4 g	ASE (Tol. 100ºC)		Sulfuric acid	acidic silica (x2)	FMS		
W2	4 g	ASE (Tol. 100ºC)		Sulfuric acid	acidic silica (x2)	FMS		
W3	20 g	Disolve (MeOH)	LLE (DCM:H2O)	Sulfuric acid (x2)	Multilayer	FMS		
W4	6 g	ASE (Tol. 100ºC)		Sulfuric acid (x2)	Multilayer	FMS		
W5	10 g	ASE (Tol. 100ºC)		Sulfuric acid (x2)	Multilayer	FMS		
W6	24 g	Centrifugation	LLE (Hex) Soxhlet (Tol)	Sulfuric acid	Multilayer	FMS		
W7	0.5 L	--		Sulfuric acid	Acidic silica (x2)	Multilayer	Acidic silica	FMS	Carbon	Acidic silica
W8	0.926 L	Filtration	LLE (DCM) soxhlet (Tol)	Sulfuric acid (x4)	Multilayer	FMS	Florisil	Alumina
W9	2 L	LLE (DCM)		Sulfuric acid	Multilayer	FMS		

Table 3. Total levels (ng/g) or (ng/L) of PCDDs, PCDFs, dl-PCBs, i-PCBs, HCB and PBDEs (N.D.: not detected; N/A.: Not analysed).

	ng/g						ng/L		
	W1	**W2**	**W3**	**W4**	**W5**	**W6**	**W7**	**W8**	**W9**
PCDDs	N.D	0.0090	N.D.	0.0595	0.0066	0.0018	0.0786	1.0041	0.0154
PCDFs	0.0058	0.0087	N.D.	0.0033	0.0002	0.0003	0.6355	0.1940	0.0039
dl-PCBs	3.2434	2.4039	0.5728	0.0335	0.0247	2.7728	14.6620	N/A	7.0619
i-PCBs	N/A	N/A	0.0006	0.2461	44.5551	0.0014	N/A	0.0111	0.0147
HCB	N/A	N/A	0.0293	0.0280	0.0136	0.0002	N/A	0.0143	0.0451
PBDEs	0.7091	0.5412	0.3617	18.9317	2.0294	0.1862	5.0580	1.3455	1.0288