PCDD/F ASSESSMENT IN WASTE WATER TREATMENT PLANT SLUDGES AND RELATED MATRICES

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Introduction

The generation of sewage sludge as a result of the waste water treatment processes has increased significantly in from the last decade of the 20th century until present times. In Europe the total amount of sludge generated in urban waste water treatment plants has increased from 5.5 million tones dry matter in 1992 to 7.0 million tones in 2000(EC). This amount is expected to increase until at least 9.4 million tones in 2005 as owing to many new treatment plants are coming into operation in 2005 according to the COUNCIL DIRECTIVE 91/271/EEC concerning urban waste water treatment (EC).
The article 14 of this directive states that sludge arising from waste water treatment shall be re-used whenever appropriate. It is well known that this substrate is rich in organic materials as well as in nitrogen and phosphorous becoming it in a very appropriate substrate to be used in agriculture as fertilizer or soil conditioner. Nevertheless, metals and organic contaminants which are not removed during the water treatment process are also present in sludge. That is why it is necessary to perform comprehensive controls to assure that these pollutants will not contaminate the agricultural soils and as a consequence enter in the food chain.
Among the organic pollutants listed in this document, polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) stand out owing to their high toxicity at very low concentrations. The aim of this work is to assess the levels of PCDD/PCDF, in sewage sludges (S), thermal dried slduges (TD) and composted sludges (CM) from Catalonian WWTPs according to the recommendations stated in the Working document on sludge and therefore with the current European waste management strategies (EC).

Materials and Methods

71 samples were collected from 15 Catalan WWTPs from December 2003 to January 2006. About 10g of the sludge sample were spiked with a known amount of $^{13}C_{12}$- PCDD/PCDFs (EPA-1613LCS, Wellington Laboratories, Canada) and two hours later the sample was Soxhlet extracted with 400 mL toluene for 24 h. Purification was based on solid-liquid adsorption chromatography. The clean-up step was performed by means of an automated system (Power Prep TM, FMS, Inc, MA, USA). The clean-up procedure consists of a sequential array of the three different Teflon prepacked columns: multilayer silica, alumina and PX-21 carbon adsorbents, respectively (FMS Inc, Boston, USA) Instrumental analysis was based on the used of high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC-HRMS) using the isotopic dilution as the quantification method. All analyses were performed on a Agilent gas chromtograph fitted with a 40m x 0.18 mm i.d. x 0.18µm film thickness DB-5ms fused silica column (J&W Scientific, CA, USA) connected through a heated transfer line kept at 280ºC to a Micromass Ultima NT high resolution mass spectrometer.

Results and Discussion

PCDD/F I-TEQ levels in sewage sludge samples from Catalan WWTP as well as thermal dried and composted sludge analyzed in this survey are lower than the 100 ng/kg I-TEQ limit suggested by the Working Document on Sludge (table 1). The higher I-TEQ concentrations were found in the thermal dried sludges with values closed to the reference limit established in the above-mentioned document. In this sense, OCDD and HpCDD formation even at low temperatures (20^{O}C) during the water treatment process and in particular during the stabilization and storage of sludges has been demonstrated by Klimm et. al. (1998).

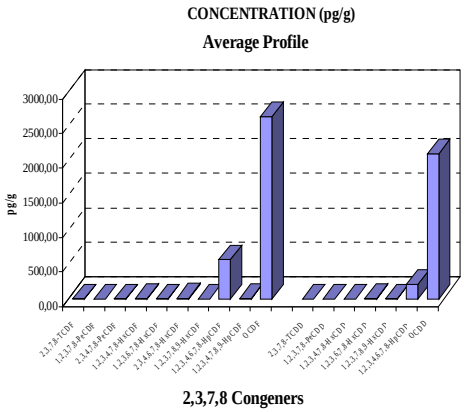
ble 1.- Overall results of PCDD/Fs in composted, thermal dried and raw sludges found in this study.

		Sampling date										
Sampling points	**Sample code**	**15/12/2003**	**29/03/2004**	**19/05/2004**	**12/07/2005**	**12/11/2004**	**18/02/2005**	**06/04/2005**	**25/04/2005**	**20/07/2005**	**08/11/2005**	**18/01/200**
Plant 2	CM	12.03	12.24		7.89	9.29	11.17	10.58		12.45	18.88	10.40
Plant 1	CM	12.40	11.53		13.49	10.54	15.20	17.53		14.69	13.04	14.19
Plant 3	CM	35.95	10.61		14.20	25.26	41.25	35.45		44.42	25.14	23.94
Plant 13	CM							4.26		11.26	17.43	15.62
Plant 24	S		32.78									
Plant 7	S		4.86									
Plant 6	S				9.15					11.03		
Plant 26	S										11.74	
Plant 9	TD	26.00		50.11	91.70	26.17	15.77		18.05	26.10	20.32	18.04
Plant 10	TD	10.45	10.82		64.43	27.32	51.64	86.86		46.03	32.57	36.60
Plant 6	TD		7.40					5.18				3.35
Plant 25	TD								7.39		18.35	10.44
Plant 23	TD						14.43	11.43		11.76	24.33	11.21
Plant 8	TD										10.84	17.63
Plant 4	TD										24.43	8.34
Plant 5	TD											4.83
Plant 7	TD											17.74

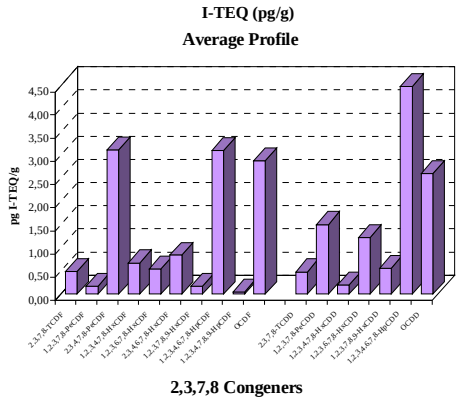
Another importantfact that can be observed in table 1 is the decrease of the I-TEQ values observed from mid 2004 until 2006. For instance, Plant 9 and 10 with concentrations of 91.70 and 86.86 pg I-TEQ/g respectively, have not surpassed the 40 pg I-TEQ/g. in the 2006 January sampling campaing.

Figure 1.- Mean 2,3,7,8 PCDD/F congener distribution in the samples analyzed.

A



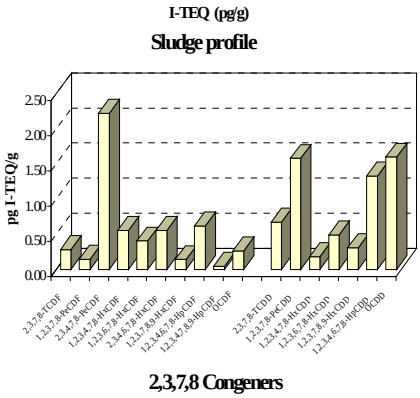
B

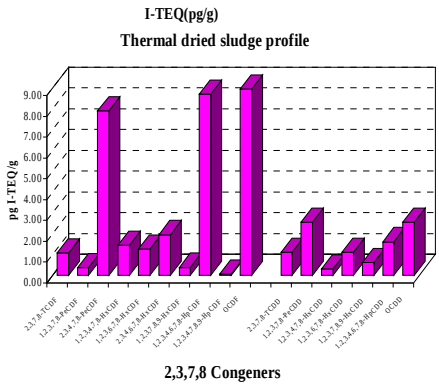


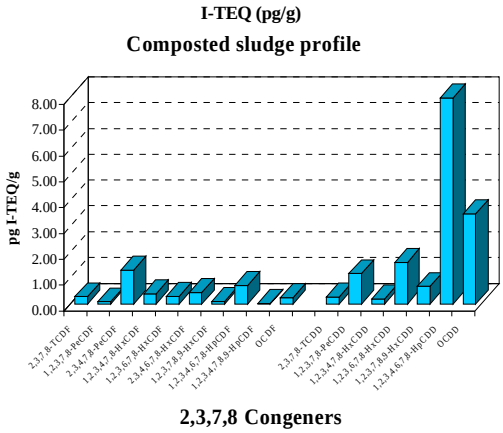
The PCDD/F profile found in the different samples analyzed in this survey is characterized by OCDD/Fs and HpCDD/Fs as the dominant congeners (figure 1A). This profile is similar to the ones reported by other authors in sludge samples and match with a PCDD/Fs deposition one indicating that deposition is one of the sources of these compounds in sewage sludges.

Average I-TEQ profile of the samples analyzed in this survey present and irregular profile dominated by the 2,3,4,7,8 PeCDF and the hepta and octa chlorinated congeners (figure 1B). Nevertheless, if different samples type profiles are analyzed separately, it is easy to observe that the influence of the congeners varies significantly among each sample type (figure 2). Composted sludges sample profile is very different from the other matrixes analyzed in this work, probably due to the introduction of other solid material during the composting (pine bark) and the as a consequence of the fermentation that take place during this process.

Figure 2.- 2,3,7,8 PCDD/F congener I-TEQ profiles







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