DETERMINATION OF PCDD/F LEVELS IN SPANISH SEWAGE SLUDGE FOR BEING APPLIED AS RAW IN COMPOSTING AND AGRICULTURE

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Introduction

According with the European Directive 91/271/CEE, since 2000 all the cities in the European Union over 15000 inhabitants and since 2005 those cities exceeding 2000 inhabitants, have to treat their wastewater before disposing it. Therefore, in the last years, increasing amounts of sewage sludge have been generated by wastewater treatment plants (WWTPs), with the subsequent problem of their management.

These sewage sludges originated from the treatment of wastewater are rich in organic material and other compounds such as nitrogen and phosphorous. The enrichment in these compounds makes the sewage sludge a very appropriate substrate to be used in agriculture as fertilizer. Nevertheless, during the wastewater treatment most of the pollutants are also concentrated in the sludge, and consequently, heavy metals and organic compounds should be monitored.

At present, the application of sewage sludges to soils is limited by guideline concentrations of heavy metals in the soil through the EU Directive on the use of sewage sludge in agriculture (86/278/CEE). Since 1999, several Drafts of a new European Directive have been published and the levels of other organic pollutants are considered (AOX, LAS, DEHP, NPE, PAHs, PCBs and PCDD/Fs). These Drafts are based in the German Ordinance on Sewage Sludge[1] that established a limit of 100 pg I-TEQ/g dry weight (d.w.) of sludge for PCDD/Fs and 200 ng/g of sludge (d.w.) for seven PCB congeners (28, 58, 101, 118, 138, 153, 180) for agricultural purposes[2].

The contamination of PCDDs and PCDFs in sewage sludge is well documented. Analytical results have been reported from different countries as the United States[3], Germany[4], Sweden[5] and the United Kingdom[6]. In the last years, the PCDD/F levels of Spanish sewage sludge have been also reported [7,8,9,10], principally of WWTPs placed in Catalonia (NE Spain). The present study want to complete the first preliminary survey realized in 2001, during the fulfillment of "I Spanish Inventory for Industrial Sources of PCDD/Fs"[11], to determine the compliance of the future legislation for the Spanish sewage sludge. In the first study, only five representative Spanish plants located in different zones from Spain and with different effluent origin (urban, industrial and mixture) were analyzed.

Material and Methods

Sample collection:

Seventeen Sewage sludges were sampled in WWTP, at different locations spread in the Spanish geography. Samples were taken by plant staff, air-dried (or at 40^{o}C) until constant weight and poured into sealed amber-glass flasks. Upon receiving in the laboratory, they were ground to a fine powder, reducing as much as possible time between collection and analysis.

According to type of influent stream and number of inhabitants, the different facilities were divided into the categories shown in Table 1. "Urban" refers to wastewater from highly-populated/low-industrialized sites; "Industrial", to zones with high industrial activity cores and "Mixed", to mixed urban and industrial activities.

Table 1: Type of influent and number of inhabitants related to each facility evaluated.

Category	Type of Influent	Number of inhabitants
U1-	Urban	Lowly populated (< 500.000)
U2-	Urban	Medium populated (500.000 – 1.000.000)
U3-	Urban	Highly populated (> 1.000.000
M1-	Mixed	Low populated (< 500.000)
M2-	Mixed	Medium populated (500.000 – 1.000.000)
I1-	Industrial	Low populated (< 500.000)

Sample Extraction and Clean-up:

Approximately 0.5 g of dried sewage sludge was spiked with ^{13}C-labeled solution of 2,3,7,8-PCDD/Fs and extracted in an ASE 100 system (Accelerated Solvent Extraction), as published elsewhere[12]. A mixture of hexane:dicloromethane (1:1) as extraction solvent was used. Resulting extracts were transferred into a separation funnel and liquid-extracted with concentrated sulphuric acid to remove organic matter. Clean-up stage was performed in an automated purification Power PrepTM System (FMS, Inc., USA) including acidic silica gel and basic alumina columns. Purified extracts were analyzed by HRGC-HRMS at 10,000 resolving power using a 30 m chromatographic column (TRB-5MS from Teknochroma). Monitored masses were those proposed by EPA 1613 method[13].

Results and Discussion:

In Table 2 the PCDD/F levels of the seventeen sewage sludges sampled are shown. Concentrations found in all samples are lower than the value of 100 pg (I-TEQ)/g proposed in the German Ordinance on Sewage Sludge, and probably in the next European Directive on Sewage Sludge.

Table 2. PCDD/F Levels of sewage sludges analyzed.

Sample	S PCDDs (pg/g)	S PCDFs (pg/g)	Total (pg/g)	I-TEQ (pg/g)	WHO-TEQ (pg/g)	R(I-TEQ PCDDs / I-TEQ PCDFs)
U1-1	464,3	195,3	659,7	5,7	6,4	0,8
U1-2	511,6	218,4	730,0	6,6	6,8	0,6
U1-3	777,7	216,7	994,4	7,6	7,6	0,5
U2-4	540,5	252,8	793,3	10,8	11,3	0,5
U2-5	583,9	188,1	772,0	8,9	9,3	0,4
U3-6	478,3	150,1	628,4	5,6	5,7	0,5
U3-7	1.913,9	340,6	2.254,4	22,6	21,9	0,3
M1-8	322,3	141,1	463,5	5,1	5,1	0,3
M1-9	682,9	262,0	944,9	7,4	8,0	0,8
M2-10	708,5	375,5	1.083,9	10,5	10,1	0,3
M2-11	781,4	206,5	987,9	7,7	7,8	0,5
M2-12	954,8	320,8	1.287,7	6,8	6,3	0,8
I1-13	363,7	406,0	769,6	7,7	8,0	0,3
I1-14	503,2	316,3	819,5	6,8	6,8	0,4
I1-15	1.599,7	3.900,4	5.500,1	16,9	13,1	0,3
I1-16	1.299,2	976,5	2.275,7	10,2	9,4	0,7
I1-17	362,1	85,6	447,7	5,3	5,4	0,4

The ratio $R_{(I\text{-}TEQ\,PCDDs/I\text{-}TEQ\,PCDFs)}$ was calculated, and the values ranged between 0,3 and 0,8, with a mean value of 0,6. Generally, sewage sludge samples are characterized by a $R_{(I\text{-}TEQ\,PCDDs/I\text{-}TEQ\,PCDFs)} > 1$[7,8,14]. However, all samples analyzed in our study presented a $R_{(I\text{-}TEQ\ PCDDs/I\text{-}TEQ\ PCDFs)} < 1$, although the sum of PCDDs concentrations is in all cases higher than the related to PCDFs, except for two industrial samples (I1-13 and I1-15).

Average PCDD/F levels regarding the population are plotted in Figure 1. As can be seen , PCDD/Fs content increases as population raises.

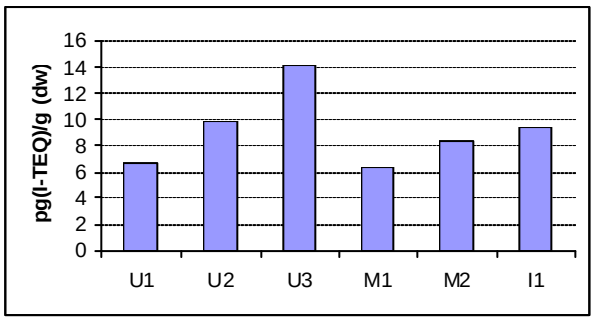

Figure 1. Average levels of PCDD/Fs.

The congener profile was very similar in all samples. Generally it was dominated by OCDD and OCDF, and contained relatively high concentrations of HpCDDs and HpCDFs, except for two industrial samples (I1-13 and I1-15). In case of I1-13 sample, the congener distribution was OCDD > 1,2,3,4,6,7,8-HpCDF > OCDF > 1,2,3,4,6,7,8-HpCDD and it was OCDF > OCDD > 1,2,3,4,6,7,8-HpCDF > 1,2,3,4,6,7,8-HpCDD for I1-15 sample. These differences in the congener distribution should be related to the distinct features of the industrial wastewater discharges. In Figure 2 PCDD/F concentration profiles of different samples (one urban and two industrial ones) are represented.

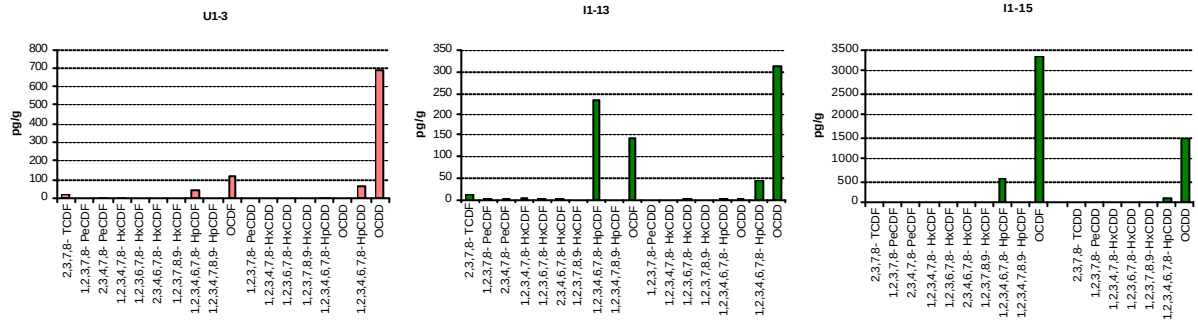

Figure 2. PCDD/Fs concentration profiles (pg/g) of one urban and two industrial sludges.

In Figure 3 the PCDD/F profiles of sludges sampled in urban, mixed and industrial environments are shown. It can be observed that related to sludge from the urban and mixed treatment plants are very similar. In both cases congeners with higher toxic contribution are 2,3,4,7,8-PeCDF and 2,3,7,8-TCDF. Regarding the dioxin congeners, those with higher contribution to total I-TEQ level are 1,2,3,7,8-PeCDD, 1,2,3,4,6,7,8-HpCDD and OCDD, being the 1,2,3,7,8-PeCDD level the main difference between both profiles.

A higher difference can be observed in the profile of the industrial sewage sludge. An increase in the most chlorinated congeners contribution is noticed. That is the case of 1,2,3,4,6,7,8-HpCDF and OCDF regarding furans and 1,2,3,4,6,7,8-HpCDD and OCDD regarding dioxins. But the predominance of 2,3,4,7,8-PeCDF and 2,3,7,8-TCDF is maintained as in the other profiles.

The 1,2,3,4,6,7,8-HpCDF and the OCDF have passed from having a low contribution to the total PCDF levels (9 and 2 %), to have a contribution of 21 % and 14 % respectively. On the other hand, the contributions to the total PCDD/F levels corresponding with the Hepta- and OctaCDD have raised from approximately 8 % in urban and mixed sludge to 14 % and 11 % respectively in the industrial sludge.

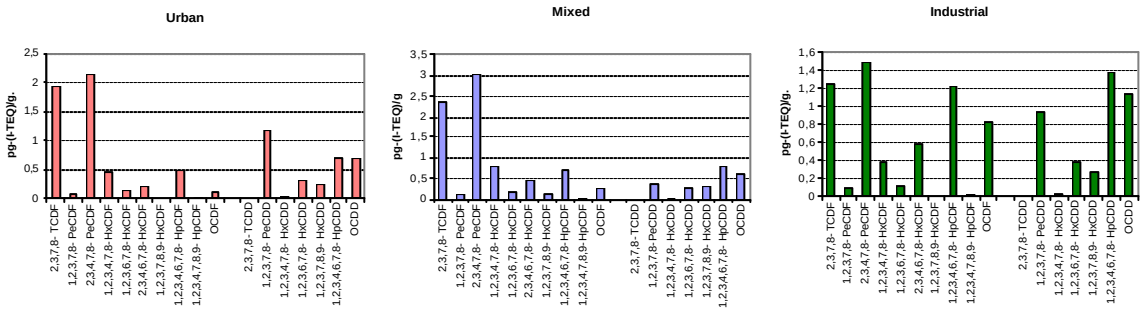

Figure 3. PCDD/F profiles (pg I-TEQ/g) of urban, mixed and industrial sludges.

From these findings, we can conclude that PCDD/F levels found in the Spanish sewage sludges evaluated are lower than the value proposed in the German Ordinance on Sewage Sludge. Subsequently, and according with it, there would be no problem in using them as raw in composting and agriculture, although it should be monitored the temporary evolution of PCDD/F levels in soil treated with these sludges.

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