STUDY OF PCDD/Fs IN SPANISH SEWAGE SLUDGES. INFLUENCE OF SAMPLING METHOD AND TYPE OF CATCHMENT.

Begoña Fabrellas, Paloma Sanz and Esteban Abad[1]

POP's Study and Characterisation Project, Environmental and Technological Research Center. (CIEMAT). Ministry of Research and Technology. Avda. Complutense, 22. 28040-Madrid. Spain. Fax: 34-91-3466269, e-mail begona.fabrellas@ciemat.es
[1]Mass Spectrometry Lab. Dept.of Ecotechnologies. CID-CSIC. Jordi Girona 18-26, 08034 Barcelona, Spain

Introduction

The pollution of sewage sludges from waste water treatment plants by polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) has became a serious limitation for the application of them to agricultural land. According to next legislation based of an EU-Initiative, PCDD/Fs limit values for use of sewage sludges on land will be established in 100 ng TE/kg d.m (1). Only plants with more than 2,500 tonnes of dry matter will have to analyse once a year the content of these contaminants. This unique sample will have to be representative enough of the PCDD/F presence in the sludges and have to be taken with an adequate methodology. A preliminary survey, during the fulfilment of "*I Spanish Inventory for Industrial Sources of PCDD/Fs*" (2) was conducted to determine the concentrations, homologue profile and I-TEQs of several representative spanish plants to know the compliance of future legislation. They were located in different zones (North, South and Central of Spain) and with different origin of effluents (urban, urban with low and high industrial inputs, and urban with agricultural activity). The sampling period was April to May of 2.000 The influence of sampling method and the type of catchment was also evaluated.

Materials and Methods

Sampling of sewage sludges:

Simple sampling: These punctual samples belonged to the final product from the catchment (digested or stabilized sludge) obtained monthly.

Composed sampling: These sludges were made by the incorporation of subsamples of final products, weekly sampled and finally mixed to obtain the composed one. Each subsample were kept cooled at 2-5°C before mixing.

One simple sample and other composed one were collected in each installation during three consecutive months: March, April and May, and prepared for analysis by the operators of each plant, according to the same protocol: Following collection or mixing, sludge samples were immediately dried in open air, or very slowly at 40°C until constant weight for avoiding PCDD/PCDFs losses. After drying, they were powdered in clean mills and put in glass bottles for packing to the laboratory. The time between sample collection and sample preparation was as much short as possible, maintaining always the samples refrigerated. After the reception in the laboratory, they were dried again at 40 °C for avoiding re-hydration, and ground again if it was necessary.

Extraction and Clean-up

Dry samples were fortified with 10 µl of EPA 1613 LCS Standard Solution containing the sixteen $^{13}C_{12}$ –2,3,7,8- labelled compounds as described in EPA 1613. Ten grams of dried sludge were mixed with five grams of copper powder plus five grams of anhydrous sodium sulphate and then Soxhlet extracted for 48 hours in toluene. Next, sludge extracts were transferred to hexane followed by an acidic treatment with H_2SO_4 (c) and prepared for clean-up stage.

Clean-up was performed by means of an automated cleanup system including a multi-layered silica gel column, a basic alumina column and, a PX-21 active carbon column, all them packaged in Teflon and hermetically sealed. (3). Extracts were concentrated avoiding dryness and 5 µL of EPA 1613 ISS Solution and 5 µl of nonane were added immediately prior to injection to minimise the possibility of losses.

HRGC/HRMS conditions

HRGC/HRMS analysis were performed using a Fisons 8000 Series gas chromatograph coupled to an Autospec Ultima (Fisons Instruments) mass spectrometer, SIM mode at 10000 of resolving power. A DB-5 fused silica capillary columns (60 m, 025 mm ID, 0,25 um film thickness) was used for the HRGC. The GC conditions are detailed in reference (4).

Results and Discussion

Waste water treatment plants are classified in: Urban: High population and low industrialisation; Rural: Domestic households and Mixed: Urban and industrial activities. Treatment plants are identified in Table 1.

Table 1: Selected waste water treatment plants for this study.

FACILITY	CATCHMENT TYPE	Location
A	RURAL	Central Spain
B	URBAN WITH AGRICULTURAL ACTIVITY	Southern of Spain
C	URBAN	Central Spain
D	MIXED WITH INDUSTRIAL CONTENT	Central Spain (Low population)
E	MIXED WITH INDUSTRIAL CONTENT	Northern of Spain (Congested industrial zone)

Wastewater processing are physicochemical plus biological treatment of conventional active sludges. Only urban C has biological treatment with long aeration. The sludges processing are aerobic stabilisation and filter band dehydration. Only Mixed E has filter press dehydration and, actually, final incineration. PCDD/Fs results of the 29 sewage sludge samples are given in Table 2. In the light of these results we observe:

PCDD/Fs concentrations:

- None of the sludges analysed in this survey exceed the limit value for land application of 100 I-TEQ pg/g
- Facility E presented the highest mean PCDD/Fs content with 60.89 I-TEQ pg/g in a punctual sample on March. It is situated in a very congested industrial zone in the North of Spain and

receives mainly industrial waste water. Otherwise, facility A had the lowest PCDD/Fs levels. It treats only household waste water.

- The results seem *that it wouldn't be necessary to make composed sampling* for realise studies in sludges from these high waste water plants. The PCDD/Fs results were very similar in all facilities for simple or composed samples of different sampling days. Meanwhile there are same results were lower (facility C March-Simple; facility D May-mixed) or higher (facility B May-mixed; facility E March-Simple) than the others for the same plant, these disappointing values will have into account in next surveys.

Table 2: I-TEQ (pg/g) of PCDD/Fs and D/F ratio for 29 sludge samples.

Date of Sampling		A: Rural		B: Urban/Agricult		C: Urban		D: Mixed		E: Mixed	
		Simple I-TEQ (pg/g)	Mixed I-TEQ (pg/g)	Simple I-TEQ (pg/g)	Mixed I-TEQ (pg/g)	Simple I-TEQ (pg/g)	Mixed I-TEQ (pg/g)	Simple I-TEQ (pg/g)	Mixed I-TEQ (pg/g)	Simple I-TEQ (pg/g)	Mixed I-TEQ (pg/g)
March	Total	8,27	8.46	10.73	10.12	**6.34**	19.12	9.14	9.14	**60.98**	20.52
	ΣPCDs	5.18	5.68	6.21	6.71	3.3	14.82	6.83	6.57	18.08	6.89
	ΣPCDFs	3.09	2.78	4.52	3.41	3.04	4.3	2.31	2.57	42.9	13.63
	D/F	1.68	2	1.37	1.96	1.1	3.44	3	2.5	0.42	0.5
April	Total	14.98	8.47	9.63	9.57	15.85	15.06	14.49	13.64	26.76	24.38
	ΣPCDs	9.48	5.21	6.37	5.65	7.83	7.37	12.29	11.53	8.6	8.5
	ΣPCDFs	5.49	3.26	3.27	3.92	8.03	7.71	2.21	2.12	18.18	15.9
	D/F	1.7	1.6	1.9	1.4	0.97	0.95	5.5	5.4	0.47	0.5
May	Total	6.63	----	10.41	**54.24**	14.63	17.14	11.70	**5.40**	26.94	35.58
	ΣPCDs	3.73	----	6.37	22.66	7.71	8.99	9.49	4.43	10.8	11.64
	ΣPCDFs	2.92	----	4.06	31.59	6.92	8.15	2.21	0.97	16.14	23.94
	D/F	1.3	----	1.57	0.71	1.1	1.1	4.3	4.5	0.7	0.48

Homologue Groups: The homologue profile of sewage sludges is dominated by hepta and octa-PCDDs and to a lesser extent by hepta and octafurans, in accordance with a typical distribution (5, 6). Four of the five facilities studied in this work, have a representation of total PCDD/Fs isomers similar to graph a) of Figure 1. Only facility D (mixed industrial in Madrid) shows a very high content in total PeCDDs in all the samples, that could implicate an important contribution of a local industry. (Figure 1b)

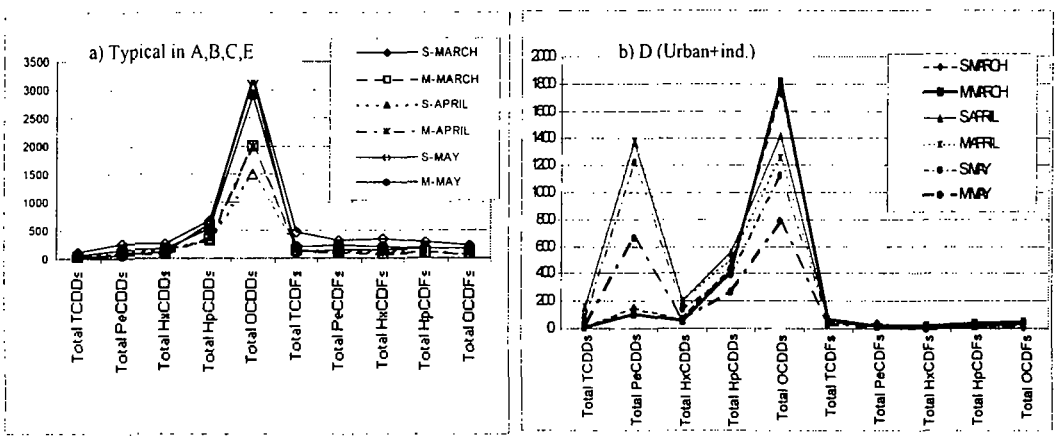
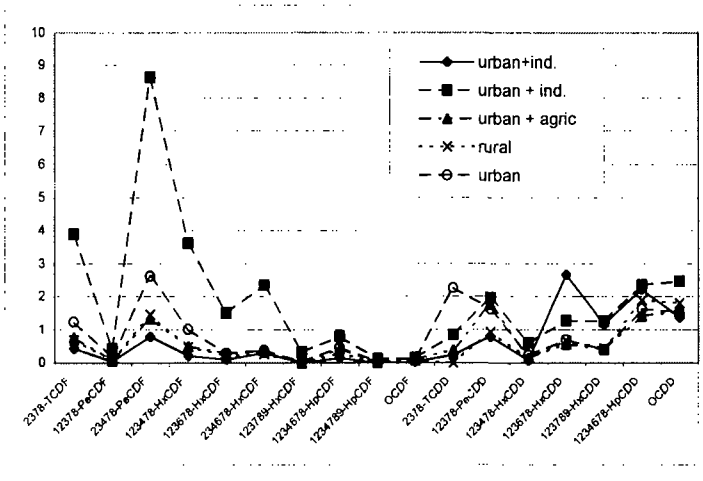


Figure1: Homologue profile of the tetra to octachorinated PCDD/Fs. (pg/g)

Also, it is observed that in facility E, (situated in a congested industrial zone in the North of Spain) the tetra to octafurans make up a light increased proportion, that is corroborated in the distribution of isomer congeners.

I-TEQs: Figure 2 shows the normalised mean 2,3,7,8 isomers distribution for all simple sewage sludges analysed. We observed that some facilities had their own profile:

- In the rural facility HpCDD and OCDD are the predominant isomers, following in concentration by 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD.
- In the urban with agricultural influence (B), OCDD, HpCDD, 1,2,3,7,8-PeCDD are the predominant ones, and 2,3,4,7,8-PeCDF has, also, a very important contribution.
- In facility C, urban, 2,3,4,7,8-PeCDF presents the highest concentration, following by 2,3,7,8, TCDD and 1,2,3,7,8-PeCDD, HpCDD and OCDD.
- Facility D and E received waste water industrial but their 2,3,7,8-isomers distribution are very different one with regard to other: 1,2,3,6,7,8-HxCDD, HpCDD and OCDD are the isomers predominant in Facility D; 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF and 2,3,4,6,7,8 HxCDF have the highest concentration in Facility E. D/F mean value is 4 in D and 0,4 in E, the other facilities have a D/F mean of 1.5.



Although levels of PCDD/Fs are very low respect limit values and previous data (4), the patterns show different distribution depending on the origin of the effluents, mainly in industrial ones. In a future, a new programme of punctual samples will be made to increase the number of facilities analysed and to point at the origin of this different distribution.

Figure 2: Normalised mean 2,3,7,8 isomers distribution for all simple sewage sludges.

Acknowledgements

The authors wish to thank the operators and facilities staff for collecting the samples and co-operating in the sampling programm.

References

1. Working Document on Sludge. 3RD DRAFT. Brussels, 27 April 2000. ENV.E.3/LM
2. Fabrellas, B., Sanz, P., Abad, E., Rivera, J. (1.999Organohalogen Compounds, 41, 491-494
3. Fabrellas, B, Sanz, P, Larrazabal, D. (2.000) PE.CF-OP-04. Ed CIEMAT
4. Eljarrat, E, Caixach, J, Rivera, J. (1.998) Organohalogen Compounds, 39, 211-214.
5. Stevens, J., Green, N., Jones, K.(1.999) Organohalogen Compounds, 43, 425-428.
6. Rappe, C., Andersson, R., Bonner, M.S., Cooper, K.R., Fiedler, H., Howell, F.G., Lau, C. (1.996) Organohalogen Compounds, 28, 105-110.