

LEVELS IN THE ENVIRONMENT

PCDDs and PCDFs in Sewage Sludges from Spain. Examination of Sludge-amended Soils.

Ethel Eljarrat, Josep Caixach and Josep Rivera, Mass Spectrometry Lab., Ecotechnologies Dept., C.I.D., C.S.I.C., Jordi Girona 18-26, 08034 Barcelona, Spain

Abstract

Seven sewage sludges from rural and urban waste water treatment plants in Spain were analysed for PCDDs and PCDFs. Total I-TEQ values for these samples ranged from 14 to 90 pg/g. These results were compared with values obtained from archived sewage sludge samples collected in the eighties, ranged from 56 to 259 pg I-TEQ/g. A general decline in PCDDs and PCDFs inputs to the environment could explain the lowest values founded in contemporary samples.

The fate of PCDDs and PCDFs in sewage sludges after agricultural application was also analysed. The concentrations of PCDDs and PCDFs in soils were determined before and after the application of sewage sludges, and a general increase was observed with the applied rate, especially in the case of the PCDDs. The values of sludge treated areas were 1.2 to 11.6 times higher than the respective values of the non contaminated areas. Changes observed in the ratio between PCDD and PCDF levels and in the isomeric distribution also suggest the influence of the sewage sludge on the soil.

Introduction

The promulgation of the Directive COM 91/271 on wastewater treatment requires the installation of treatment systems in all populations exceeding 2000 inhabitants before the year 2005. Estimates for the year 2000 predict an increase in sewage sludge production of 185% in Spain, which means about 1 million tonnes per year. On the other hand, the effect of some new directives on treatment and elimination of toxic and dangerous wastes, the EU Directive on agricultural use of sludges (COM 86/278) and the banning of sewage sludge discharges into the sea from 1998 all combine to restrict the final fate of sewage sludges.

Land application has played an important role in sewage sludge disposal because its low cost and high efficiency. This operation accounts for about 50% of sewage sludge produced in UK and the Netherlands, 25% in France and Germany and 60% in Spain (*data of 1990*). But, there is a continuous discussion on the significance of sewage sludge fertilization of cultivated land in terms of soil contamination. In Germany, in 1992, the Ordinance on Sewage Sludge established a limit of 100 pg I-TEQ/g of sludge (d.w.) for PCDDs and PCDFs for agricultural purposes. Furthermore, this regulation set an application limit of 5 tonnes per hectare within a period of 3 years. This limit was also adopted by the regulation of Austria in 1994.

The purpose of this study was to determine the PCDD and PCDF levels in the spanish sewage

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sludges, and to assess the effects of these contaminants in sewage sludges applied to the soil.

Experimental Methods

The samples were manually ground before extraction. Ten g (d.w.) sludge samples and 30 g (d.w.) soil samples were spiked with a mixture of fifteen $^{13}\text{C}_{12}$ -labeled 2378-substituted isomers (Wellington, Guelph, Canada) and extracted in a Soxhlet apparatus for 48 hours with toluene. After extraction, crude extracts were transferred to hexane and treated with H_2SO_4 conc., followed by purification via a 3-stage open column chromatographic procedure¹⁾. Samples were finally concentrated to incipient dryness prior to the addition of a mixture of $^{13}\text{C}_{12}$ -1234-TCDD and $^{13}\text{C}_{12}$ -123789-HxCDD as the recovery standard.

Purified PCDD / PCDF extracts were analysed by HRGC-ERMS on a Thermo 8060 gas chromatograph fitted with a DB-5 (J&W Scientific, CA, USA) fused-silica capillary column (60 m x 0.25 mm ID, 0.25 μm film thickness) coupled to an AutoSpec-Ultima (Micromass, Manchester, UK) mass spectrometer operating in the electron impact ionization (electron energy 38 eV) at 10,000 resolving power. Quantitative determination was performed by the isotope dilution method using relative response factors (RRFs) previously obtained from five standard solutions (Wellington, Guelph, Canada).

Results and Discussion

The PCDD and PCDF I-TEQ values in the contemporary samples analysed are given in table 1, with levels lower than 100 pg I-TEQ/g (d.w.) for all the samples studied. The results for the archived samples are also showed, and the 65% of these samples exceeded the limit set for the German regulation. The variation in the I-TEQ concentration can be explained because the different sewage treatment works were exposed to varying loads during the sample collection period, and it seems to be that the total I-TEQ concentrations have declined from the eighties to nineties. This may reflect a general decline in PCDDs/PCDFs inputs to the environment due to tighter controls on organochlorine use and disposal.

The concentrations of the sum of PCDD were higher than those of the sum of PCDF, with the ratio $R_{(I\text{-TEQ}_{\text{PCDDs}}/I\text{-TEQ}_{\text{PCDFs}})} > 1$ (except for the WWTP 9, 1994 and for the WWTP 10), with values ranged between 2 and 17, which matched reasonably well those observed by Rappe *et al.*²⁾. Lower chlorinated PCDD are found in much lower concentrations than higher chlorinated PCDD. The PCDD and PCDF distribution observed is in contrast to the congener distribution found in stack gas emissions of waste incineration plants.

The study of the effects of PCDDs and PCDFs in sewage sludges applied to the soil was based on an experiment devised during the eighties. Two doses of sewage sludges were applied to two different soils for four consecutive years. The characterization of these soils before the experiment and after the application gives the PCDD and PCDF I-TEQ values showed in table 2. A general increase was observed with the applied rate. The I-TEQ values of sludge treated areas were 1.2 to 2.8 times higher than the respective values of the non contaminated areas for the basic experiment, and from 7.4 to 11.6 for the acid experiment. The latter values were consistent with the data obtained by Albrecht *et al.*³⁾ who found a factor increase of 10.

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Table 1 I-TEQ Values (expressed in pg/g d.w.) in sewage sludge samples.

	Total PCDDs	Total PCDFs	TOTAL I-TEQ
<i>Archived Samples</i>			
WWTP 1, 1982	98.28	8.53	106.81
WWTP 1, 1983	45.77	10.33	56.10
WWTP 2, 1983	64.38	9.47	73.85
WWTP 3, 1984	218.99	39.53	258.52
WWTP 3, 1985	125.71	25.06	150.77
WWTP 3, 1986	238.11	14.46	252.57
<i>Contemporary Samples</i>			
WWTP 4, 1994	11.76	2.72	14.48
WWTP 5, 1994	21.93	2.56	24.49
WWTP 6, 1995	19.93	2.97	22.90
WWTP 7, 1996	22.20	5.79	27.99
WWTP 8, 1996	11.03	8.59	19.62
WWTP 9, 1994	18.82	23.60	42.42
WWTP 9, 1996	74.30	15.20	89.50
WWTP 10, 1996	11.74	39.04	50.78

The measured TEQ values from the investigation of sludge treated areas were compared with the limits proposed by the Federal Health Office (FHO) of Germany in a report published in 1991. This report contains reference values and recommends action for agricultural and horticultural land uses and soil reclamation. Five pg TEQ/g (d.w.) was the established limit restricting the cultivation of certain vegetables. Our results of the soil investigation showed that in the case of an initial soil with low contamination (0.3 pg I-TEQ/g), the final soil did not exceed the limit and presented concentrations below the 5 pg I-TEQ/g (2.4 and 3.7 pg I-TEQ/g). But, in the case of an initial soil with considerable contamination (3.1 pg I-TEQ/g), after an application with a high dosis of sewage sludge, the final soil (8.6 pg I-TEQ/g) exceeded the limit set at 5 pg I-TEQ/g which restricts the cultivation of certain vegetables.

It is interesting to notice the difference observed in the ratio $R_{(I-TEQ\ PCDDs/I-TEQ\ PCDFs)}$. Whereas the $R < 1$ showed higher levels of PCDFs in the initial soil samples, the inverse occurred when the sewage

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sludge is applied, with values of R ranging from 1.3 to 1.8. This variation shows the effect of the sewage sludge on the soil. Whereas there was a prevalence of furans in the initial soil, dioxins, especially, hexa-, hepta- and octa isomers, prevailed in the final soils. This is the distribution observed in the applied sewage sludges.

Table 2 I-TEQ Values (expressed in pg/g d.w.) in soil samples, before and after sewage sludge application

	Total PCDDs	Total PCDFs	TOTAL I-TEQ
<i>Experiment on Basic Soil</i>			
<i>Initial Soil</i>	0.93	2.13	3.06
<i>Final Soil (low dosis)</i>	2.13	1.68	3.81
<i>Final Soil (high dosis)</i>	5.51	3.12	8.64
<i>Experiment on Acid Soil</i>			
<i>Initial Soil</i>	0.12	0.20	0.32
<i>Final Soil (low dosis)</i>	1.48	0.88	2.36
<i>Final Soil (high dosis)</i>	2.17	1.56	3.73

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