PERGAMON

Chemosphere 40 (2000) 1173–1178

CHEMOSPHERE

Study of evolution of PCDD/F in sewage sludge-amended soils for land restoration purposes

L. Molina [a,b], J. Díaz-Ferrero [a,b], M. Coll [a], R. Martí [a], F. Broto-Puig [b], L. Comellas [b], M.C. Rodríguez-Larena [a,*]

[a] Environmental Laboratory, Institut Químic de Sarrià, Ramon Llull University, Via Augusta 390, 08017, Barcelona, Spain
[b] Section of Chromatography, Institut Químic de Sarrià, Ramon Llull University, Via Augusta 390, 08017, Barcelona, Spain

Abstract

The evolution of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in sewage sludge-amended soils used in the restoration of degraded lands, like quarries, has been studied. Two experiments were performed: one in the lab, under controlled conditions, and another in a quarry. Two different doses of sewage sludge were applied in both experiments (with two types of application in the quarry experiment) and the evolution of the amended soils were compared with that of the respective control soils (without addition of sewage sludge). The samples were analyzed with a previously validated method by HRGC–HRMS after the extraction and the necessary clean-up steps. The results reveal that polluted sewage sludge increases PCDD/F concentration in soils and that these compounds are persistent in the matrix after long periods of time.

Keywords: Sewage sludge; Polychlorinated dibenzo-*p*-dioxins; Polychlorinated dibenzofurans; HRGC–HRMS; Land restoration

1. Introduction

The increasing amounts of sewage sludge produced by waste water treatment plants (WWTP) in Catalunya and the restrictions in the final fate of them (e.g., the banning of sewage sludge discharges into the sea since 1998) have increased the search of new possibilities to use these kind of material. On the other hand, the extractive activities, like quarries, which produce big extensions of land without vegetation, constitute an environmental problem that should be solved. The application of sewage sludge-amended soils in order to increase the fertility of these lands can be a solution for this problem and also an interesting application for sewage sludge (Alcaniz et al., 1996). However, sewage sludge could contain pollutants whose evolution in the amended soils should be monitored, mainly considering the high amounts of sludge used compared to those for agricultural purposes. Our research group has performed several studies about the fate of hydrocarbons, polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) in sewage sludge-amended soils (Mangas et al., 1998). This work faces on the evolution of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in the amended soils. These compounds are persistent organic pollutants of great concern due to their toxicological effects (endocrine disruption like thyroid dysfunction, developmental deficits, carcinogenicity, etc.) and their great stability, which allows bioaccumulation and biomagnification. Several authors have studied the presence and origin of PCDD/F in sewage sludge (Gihr et al., 1991; Hortsmann et al., 1993; McLachlan et al., 1996; Jones and Sewart, 1997; Tiernan et al., 1996; EPA, 1994). In this paper, we study the evolution of PCDD/F in sewage sludge-amended soils in two experiments, one in the laboratory, under controlled conditions, and one in a quarry near Girona (Spain).

* Corresponding author. Tel.: +349-3-203-8900; fax: +349-3-205-6266.
E-mail address: crlar@iqs.url.es (M.C. Rodríguez-Larena).

0045-6535/00/$ - see front matter
PII: S0045-6535(99)00366-5

2. Experimental

2.1. Experiment design

2.1.1. Laboratory experiment

Anaerobically established sewage sludge was obtained from DARGISA, an aerobic sewage treatment plant in Girona (Spain). The sludge was air-dried and ground to less than 0.4 mm before soil addition. The sludge was mixed with an alkaline soil (previously ground and sieved to less than 2 mm) and 12 kg of mixtures were placed in polyethylene containers (lysimeters). The experiment consisted of studying the evolution of PCDD/F in a control soil (0% of sludge) and two soils with different additions of sewage sludge (7.5% and 15%). Lysimeters were watered when necessary to maintain a 20% of moisture in order to assure 50% of the water holding capacity, appropriate to have best microbiological activity. Soils were sampled at the beginning of the experiment and after one year. Homogenous samples were guaranteed by sampling and mixing through all the container depths. The samples were stored in the freezer and in the dark.

2.1.2. Field experiment

This experiment was carried out in a quarry from RUBAU S.A. in Girona (Spain), near the WWTP of the city. Five plots were arranged on the quarry: one was used as control and, in the other four, the soil was mixed with different amounts of sewage sludge. The doses of sewage sludge added were the same as in the lab experiment: 7.5% and 15% (7 t/ha and 14 t/ha respectively), but on these experiment two different applications were studied for each amount: (a) direct application, where the sludge was directly applied on soil and then it was plowed to mix it and (b) previous mix, where the sludge and the soil were mixed previously to the application on the quarry. Each plot was 20 m long, 6 m wide and 40 cm deep. Soils were sampled at the beginning of the experiment (December 1992) and after four years (March 1997).

2.2. Reagents and materials

Hexane and dichloromethane (Pestipur) were obtained from SDS (Peypin, France) and toluene (glass distilled grade) was supplied by Rathburn (Walkerburn, Scotland). Sodium sulphate (GR) and silica were from Merck (Darmstadt, Germany), sulphuric acid (GR) from Scharlau (Barcelona, Spain), silver nitrate and sodium hydroxide from Panreac (Barcelona, Spain) and Florisil from Supelco (Bellefonte, PA, USA).

2.3. Analysis of sewage sludge and sewage sludge-amended soils

The samples were freeze-dried, ground and sieved (2 mm) before extraction. Six grams of dried sludge or soil, spiked with a mixture of $^{13}C_{12}$ labeled 2,3,7,8-PCDD/F (Wellington Laboratories, Ontario, Canada), were Soxhlet extracted with toluene for 24 h. Two grams of copper were added to the Soxhlet thimble to remove sulfur interferences. Afterwards, extracts were transferred to hexane and cleaned-up with concentrated sulphuric acid. This step was followed by a purification in a multilayer silica column (from bottom to top: glass wool, silver nitrate–silica, silica, sodium hydroxyde–silica, silica, sulphuric acid–silica, silica, sodium sulphate) eluted with hexane and a purification in a Florisil (activated at 450°C overnight) column eluted with hexane and hexane/dichloromethane (95.5) (PCB analysis) and dichloromethane (PCDD/F analysis). The dichloromethane fraction was concentrated in a Kuderna–Danish apparatus and under nitrogen stream up to 15 μl and the syringe standards ($^{13}C_{12}$-1234-TCDD and $^{13}C_{12}$-123789-HxCDD) were added. Finally, the samples were analysed by HRGC–HRMS in a CE 8000 gas chromatography coupled to an AutoSpec-Ultima (Micromass, Manchester, UK) mass spectrometer, operating in EI ionization (32 eV) at 10,000 resolving power. The samples were analysed on a DB-5 (60 m × 0.25 mm, 0.25 μm) capillary column and on a DB-DIOXIN (60 m × 0.25 mm, 0.25 μm) capillary column, both from J&W (Folsom, CA, USA). The latter was used to separate those 2,3,7,8-congeners that were not resolved on the DB-5 column. The temperature programme for the DB-5 column was from 150°C (held for 1 min) at 30°C/min to 200°C, at 3°C/min to 235°C (held for 10 min) and at 6°C/min to 300°C (held for 15 min). The temperature programme for the DB-DIOXIN column was from 150°C (held for 1 min) at 20°C/min to 180°C and at 2°C/min to 270°C (held for 65 min). Monitored masses were those proposed by EPA 1613 method (EPA, 1994).

2.4. QA/QC

The whole analytical procedure was validated before the analysis of samples. The accuracy (expressed as recovery), precision (repeatability and reproducibility) and limit of detection were studied using a sewage sludge sample from a WWTP (unpublished data).

3. Results and discussion

3.1. Laboratory experiment

The concentrations of PCDD/F in the sewage sludge used for the lab experiment and in the resulting sewage

Table 1
Results from the laboratory experiment

PCDD/F	Concentration of PCDD/F (pg/g d.w.)						
	Control soil		7.5% Amended soil		15% Amended soil		Sewage sludge
	0 yr	1 yr	0 yr	1 yr	0 yr	1 yr	
2,3,7,8-TCDF	0.22	0.38	0.67	0.87	0.83	1.47	4.17
1,2,3,7,8-PeCDF	0.29	0.32	0.68	0.54	0.81	0.92	3.72
2,3,4,7,8-PeCDF	0.21	0.31	0.82	0.68	1.08	1.41	4.94
1,2,3,4,7,8-HxCDF	0.26	0.29	1.05	0.84	1.40	1.41	6.29
1,2,3,6,7,8-HxCDF	0.25	0.26	0.95	0.80	1.25	1.63	5.75
2,3,4,6,7,8-HxCDF	<0.22	0.19	1.25	1.09	1.79	2.14	8.34
1,2,3,7,8,9-HxCDF	<0.08	<0.07	<0.20	<0.16	<0.19	<0.20	<0.50
1,2,3,4,6,7,8-HpCDF	2.22	2.80	9.42	8.33	12.7	16.3	53.5
1,2,3,4,7,8,9-HpCDF	0.17	<0.11	0.72	0.66	1.06	1.38	5.65
OCDF	3.01	2.03	16.7	13.8	28.7	31.2	165
2,3,7,8-TCDD	<0.11	<0.04	<0.11	0.1	0.16	0.17	0.8
1,2,3,7,8-PeCDD	0.13	<0.08	0.65	0.53	1.07	1.06	5.62
1,2,3,4,7,8-HxCDD	<0.08	<0.11	0.65	0.50	0.88	1.02	6.38
1,2,3,6,7,8-HxCDD	0.17	0.21	1.89	1.51	3.71	3.75	119
1,2,3,7,8,9-HxCDD	<0.29	0.21	1.05	0.94	1.78	1.65	32.6
1,2,3,4,6,7,8-HpCDD	2.54	2.67	37.0	38.7	120	78.1	2813
OCDD	13.4	13.2	422	493	1470	1000	14700
Total TCDF	3.18	2.53	13.7	9.44	16.9	23.0	74.0
Total PeCDF	1.93	1.84	8.89	8.17	12.2	19.4	72.0
Total HxCDF	2.15	2.58	12.2	11.3	17.1	21.2	81.3
Total HpCDF	3.25	3.24	18.2	17.4	27.3	34.0	141
Total TCDD	1.11	1.29	8.18	5.88	11.1	12.7	164
Total PeCDD	1.29	1.79	15.3	19.2	59.4	32.7	5640
Total HxCDD	1.56	2.89	18.9	11.2	31.4	32.9	630
Total HpCDD	4.91	5.29	71.0	77.2	236	148	4490
I-TEQ	0.34	0.39	2.43	2.37	5.28	4.61	68.1
	(0.52)[a]	(0.49)[a]	(2.56)[a]	(2.39)[a]	(5.30)[a]	(4.63)[a]	(68.2)[a]
$R_{(PCDD/PCDF)}$	1.6	2.0	7.7	10	18	9.5	48

[a] Values in parentheses include detection limits.

sludge-amended soils (sampled at the beginning of the experience and after one year) are shown in Table 1. The PCDD/F concentration in the sewage sludge used in this experiment was 68.1 pg I-TEQ/g d.w., a value in the range usually reported in the literature for this kind of samples (Jones and Sewart, 1997). Concentrations of PCDD (specially hepta- and octa-congeners) were higher than PCDF, which is the trend reported by other authors for most urban sewage sludges (Sewart et al., 1995; Eljarrat et al., 1996; Tiernan et al., 1996), with a ratio $R_{(PCDD/PCDF)}$ [1] $= 48$. This ratio shows the influence of sewage sludge in the concentration of PCDD/F in the amended soils: for control soils $R_{(PCDD/PCDF)}$ was 2 whereas it ranged from 7.7 to 17.7 for amended soils. In addition, the profile of sewage sludge-amended soils was more similar to that of the sludge than to that of the control soil (Fig. 1). These results are similar to those obtained by Eljarrat et al. (1996) in a study with addition of sewage sludge in agricultural soils.

[1] $R_{(PCDD/PCDF)}$ has been calculated as the ratio between total PCDD (in pg/g) and total PCDF (in pg/g).

Moreover, the PCDD/F concentration in amended soils is directly related to the sewage sludge dose applied and after one year, no evolution is observed in any sample. The levels remain constant in all of them (Fig. 2). These results confirm those obtained by Schwartz and McLachlan, 1993 in a experiment with amended soils for agricultural purposes over a 6-week period.

3.2. Quarry experiment

The high content of organic matter in the sewage sludge, the presence of nitrogen, phosphorus, etc. increased the fertility of those plots that have been arranged with sewage sludge-amended soils. Therefore, those plots showed an important revegetation already in the first year, having been accomplished the land restoration purposes.

The concentrations of PCDD/F obtained in the samples from this experience, both at the beginning of the experiment and after four years, are shown in Table 2. The most important congeners in the homologue profiles

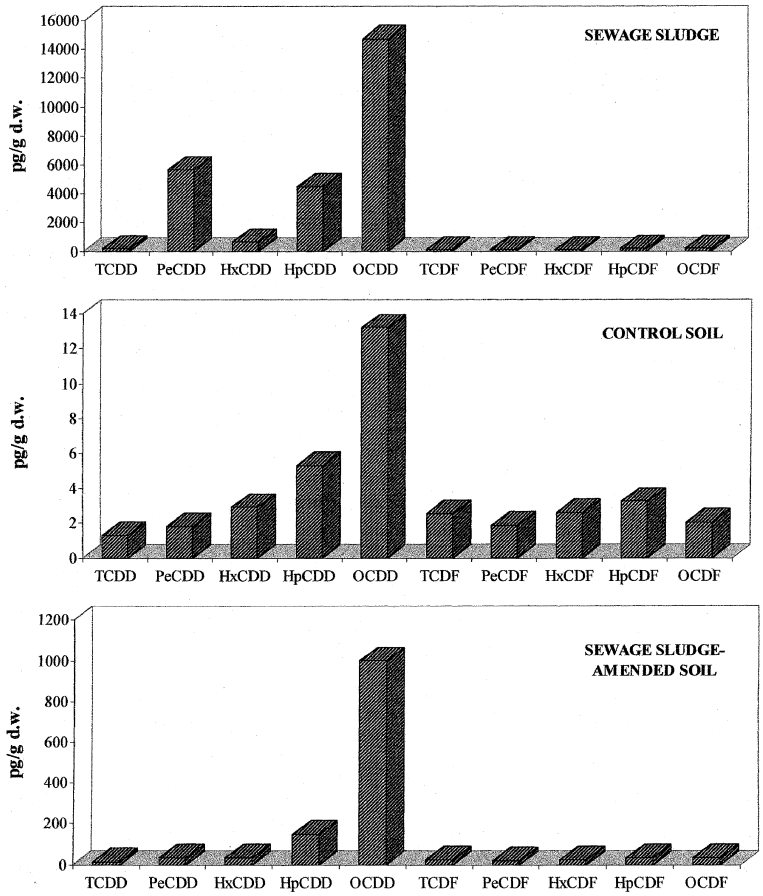

Fig. 1. Homologue profiles of sewage sludge, control soil and sewage sludge-ammended soil.

of the samples of the amended soils were hepta- and octachlorinated dioxins, in a similar way to lysimeters results. The ratio $R_{(\mathrm{PCDD/PCDF})}$ ranged between 2.9 and 4.9 although in this experiment the difference in this parameter between control soils and amended ones was not so high. In any case, the concentration of PCDD/F was higher in the amended soils than in those without addition of sewage sludge (Fig. 3).

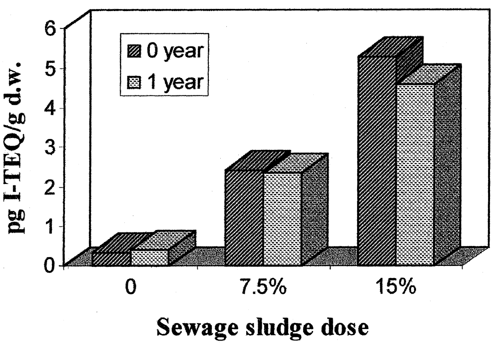

Fig. 2. Evolution of PCDD/F concentration (pg I-TEQ/g d.w.) in soils from laboratory experiment.

Results of PCDD/F from amended soils in this experiment showed high dispersion, which did not allow to establish a trend about the different kinds of application or about the PCDD/F evolution in the plots. The variability in PCDD/F concentrations is not due to the analytical method because it is clearly higher than the reproducibility variability. This dispersion, obtained in spite of sampling carefully, is attributed to the lack of homogeneity in the plots when high amounts of soils and sewage sludge are used, big machines are needed to mix them and the conditions (temperature, humidity, etc.) during the evolution time can not be as controlled as in a lab experiment. This theory is confirmed by the dispersion also found in other parameters (e.g. organic matter, Fig. 4). In addition, other authors have reported similar problems in variability of results due to a lack of homogeneity in plots amended with sewage sludge (Wilson et al., 1977).

Table 2
Results from the quarry experiments

PCDD/F	Concentration of PCDD/F (pg/g d.w.)									
	Control soil		7.5% Amended soil				15% Amended soil			
			Direct application		Previous mix		Direct application		Previous mix	
	0 yr	4 yr	0 yr	4 yr	0 yr	4 yr	0 yr	4 yr	0 yr	4 yr
2,3,7,8-TCDF	0.26	0.42	0.22	1.78	0.42	<3.53	0.56	1.56	0.32	0.94
1,2,3,7,8-PeCDF	0.29	0.36	0.33	2.49	0.58	1.35	1.04	1.83	0.57	1.00
2,3,4,7,8-PeCDF	0.37	0.49	0.39	4.42	1.06	1.80	1.88	3.18	0.87	1.57
1,2,3,4,7,8-HxCDF	0.40	0.58	0.69	6.11	1.69	6.73	2.57	4.09	1.29	2.15
1,2,3,6,7,8-HxCDF	0.49	0.44	0.79	6.83	1.64	1.94	3.08	4.71	1.30	2.24
2,3,4,6,7,8-HxCDF	1.00	0.59	1.54	9.75	2.85	11.6	4.88	6.48	2.20	2.87
1,2,3,7,8,9-HxCDF	0.26	<0.11	0.30	<0.82	0.31	<0.87	0.47	0.59	0.28	<0.42
1,2,3,4,6,7,8-HpCDF	2.78	2.66	5.14	39.9	15.4	14.5	20.7	28.9	10.2	17.7
1,2,3,4,7,8,9-HpCDF	<0.11	0.34	0.55	6.20	1.25	<0.07	2.57	4.20	0.97	1.96
OCDF	2.65	5.85	5.70	51.6	17.4	39.7	21.1	41.5	11.5	24.2
2,3,7,8-TCDD	<0.12	<0.06	<0.12	0.42	0.25	<2.98	0.35	0.35	0.23	0.23
1,2,3,7,8-PeCDD	0.55	0.13	0.72	3.67	1.12	<0.48	1.75	2.50	0.97	1.14
1,2,3,4,7,8-HxCDD	0.61	0.20	0.87	6.53	1.46	1.78	3.16	4.24	1.31	1.69
1,2,3,6,7,8-HxCDD	0.46	0.38	0.85	9.90	1.81	3.06	3.58	6.66	1.52	3.08
1,2,3,7,8,9-HxCDD	<0.29	0.39	0.60	8.02	1.26	<7.20	3.02	5.08	1.22	2.33
1,2,3,4,6,7,8-HpCDD	4.43	5.63	10.2	128	25.1	36.1	43.6	90.6	18.8	44.1
OCDD	26.0	36.9	76.1	804	182	211	222	602	125	406
Total TCDF	4.62	7.12	4.58	34.7	12.3	12.8	14.6	26.7	8.56	17.1
Total PeCDF	2.84	3.89	5.32	43.5	15.9	7.74	20.8	32.4	10.6	15.6
Total HxCDF	4.90	5.25	7.51	71.6	21.2	20.4	28.2	49.3	13.8	25.3
Total HpCDF	4.60	4.58	8.66	73.3	26.7	26.5	36.8	54.2	16.9	31.3
Total TCDD	2.62	1.99	3.03	22.7	8.77	8.86	14.3	16.8	7.25	9.77
Total PeCDD	2.30	0.75	5.01	55.6	10.6	19.4	20.2	37.1	9.19	17.7
Total HxCDD	3.38	3.25	9.37	113	21.1	35.1	45.0	76.1	18.5	35.0
Total HpCDD	8.07	11.0	19.2	237	46.0	69.6	78.4	168	33.4	82.6
I-TEQ	0.92	0.76	1.4	12.1	3.14	4.24	5.26	8.50	2.56	4.24
	(1.07)[a]	(0.83)[a]	(1.52)[a]	(12.2)[a]		(8.62)[a]				(4.27)[a]
$R_{(PCDD/PDDF)}$	2.2	2.0	3.5	4.5	2.9	3.2	3.1	4.4	3.2	4.9

[a] Values in parentheses include detection limits.

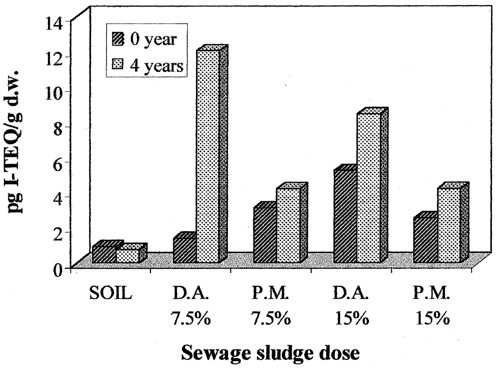

Fig. 3. Evolution of PCDD/F concentration (pg-I-TEQ/g d.w.) in soils from quarry experiment (D.A. = direct application; P.M. = previous mix).

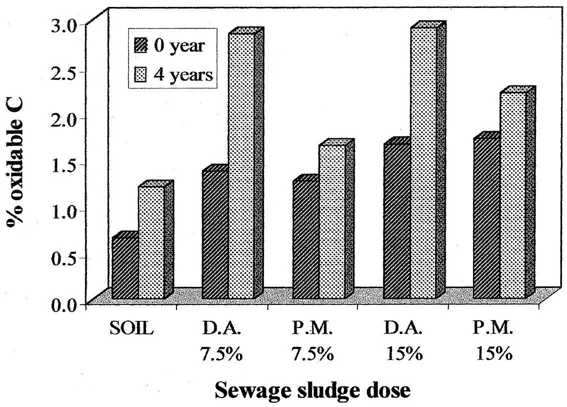

Fig. 4. Organic matter (% oxidable C) in soils from quarry experiment (D.A. = direct application; P.M. = previous mix).

4. Conclusions

The revegetation of degradated lands, like quarries, with sewage sludge-amended soils is successful. However, and in spite of the variability of results in the field experiment, we can conclude that the amendment with polluted sewage sludge increases PCDD/F concentration in soils. In addition, these compounds are persistent in soils after long periods of time (one year) as can be concluded according to the controlled experiment in lysimeters.

Acknowledgements

The authors are indebted to CREAF (Universitat Autónoma de Barcelona, Bellaterra), specially to Dr. J.M. Alcañiz, for the determinations of organic matter. The authors thank Junta de Sanejament (Generalitat de Catalunya) and the CICYT (Spain) for financial support (AMB-95-0728). J.D.F. gratefully acknowledges the support of the CIRIT, Generalitat de Catalunya.

References

Alcañiz, J.M., Comellas, L., Pujolá, M., 1996. Manual de Restauració d' Activitats Extractives amb Fangs de Depuradora. Recuperació de Terrenys Marginals 1st Edn. Generalitat de Catalunya-Dept. Medi Ambient, Barcelona.

Mangas, E., Vaquero, M.T., Comellas, L., Broto-Puig, F., 1998. Analysis and fate of aliphatic hydrocarbons linear alkylbenzenes polychlorinated biphenyls and polycyclic aromatic hydrocarbons in sewage sludge-ammended soils. Chemosphere 36, 61–72.

Gihr, R., Klöpffer, W., Rippen, G., Partscht, H., 1991. Investigations on potential sources of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sewage sludges. Chemosphere 23, 1653–1659.

Hortsmann, M., McLachlan, M.S., Reissinger, M., 1993. Investigations of the origin of PCDD/F in municipal sewage sludge. Chemosphere 27, 113–120.

McLachlan, M.S., Horstmann, M., Hinkel, M., 1996. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sewage sludge: sources and fate following sludge application to land. Sci. Tot. Environ. 185, 109–123.

Jones, K.C., Sewart, A.P., 1997. Dioxins and furans in sewage sludges: a review of their occurrence and sources in sludge and of their environmental fate behavior and significance in sludge-amended agricultural systems. Crit. Rev. Environ. Sci. Technol. 27, 1–85.

Tiernan, T.O., Garrett, J.H., Solch, J.G., VanNess, G.F., Wagel, D.J., Rukunda, F., 1996. Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDF)s in sewage sludges from rural and urban/industrial wastewater treatment plants (WWTPs). Organohalogen Compound 32, 98–102.

EPA, 1994. 1613 Method: Tetra-Through Octa Chlorinated Dioxins and Furans by Isotope Dilution HRGC-HRMS, Revision B.

Sewart, A., Harrad, S.J., McLachlan, M.S., McGrath, S.P., Jones, K.C., 1995. PCDD/Fs and non-*o*-PCBs in digested UK sewage sludges. Chemosphere 30, 51–67.

Eljarrat, E., Caixach, J., Rivera, J., 1996. Effects of sewage sludges contaminated with polychlorinated dibenzo-*p*-dioxins dibenzofurans and biphenyls on agricultural soils. Environ. Sci. Technol. 31, 2765–2771.

Schwartz, K., McLachlan, M.S., 1993. The fate of PCDD/F in sewage sludge applied to an agricultural soil. Organohalogen Compound 12, 155–158.

Wilson, S.C., Alcock, R.E., Sewart, A.P., Jones, K.C., 1977. Persistence of organic contaminants in sewage sludge-amended soil a field experiment. J. Environ. Qual. 26, 1467–1477.