Estimation of PCBs content in agricultural soils associated with long-term fertilization with organic waste

Juan M. Antolín-Rodríguez[a], Mercedes Sánchez-Báscones[a], Pablo Martín Ramos[b*], Carmen T. Bravo-Sánchez[a] and Jesús Martín-Gil[c]

[a] Agriculture and Forestry Science Department, ETSIIAA, Universidad de Valladolid, Avenida de Madrid 57, 34004 Palencia, Spain

[b] Agriculture and Forestry Engineering Department, ETSIIAA, Universidad de Valladolid, Avenida de Madrid 44, 34004 Palencia, Spain

[c] Department of Agricultural and Environmental Sciences, Higher Polytechnic School of Huesca, University of Zaragoza, Carretera de Cuarte, s/n, 22071 Huesca, Spain. E-mail: pmr@unizar.es; Tel: +34 (974) 292668; Fax: +34 (974) 239302.

Abstract

Polychlorinated biphenyls (PCBs) pollution related to the use of organic waste as fertilizers in agricultural soils is a cause of major concern. In the study presented herein, PCBs concentration was studied through a field trial conducted in two agricultural soils in the province of Palencia (Spain) over a four-year period, assessing the impact of irrigation and of different types of organic waste materials. The amounts of organic waste added to the soil were calculated according to the nitrogen needs of the crop and the concentration of PCBs was determined before and after the application of the organic waste. The resulting persistence of the total PCBs content in the agricultural soils, compared with the PCBs concentration in the original soils, ranged from 27% to 90%, with the lowest value corresponding to irrigated soils treated with municipal solid waste compost (MSWC) and the highest value to not-irrigated soils treated with composted sewage sludge (CSS). An estimate of the PCBs content in agricultural soils after the application of organic waste materials until year 2050 was obtained, resulting in a value below 5 ng·g^{-1}, considered a background value for soils in sites far away from potential pollution sources.

Keywords: agricultural soils; compost; fertilization; PCBs; pollution; sludge.

1. Introduction

EU directives 91/271/EC and 98/15/EC concerning urban wastewater treatment have promoted an increase in the number of plants and in the amount of generated sewage sludge. This fact has raised issues about its disposal and management. On the other hand, the increase in the price of mineral fertilizers traditionally used in agriculture offers an ideal scenario for the application of these waste materials to agricultural soils, thus reducing the use of chemical fertilizers (Tideström 1997).

Organic waste –in terms of its application to agricultural soils– can be deemed as beneficial, since it improves the physical, chemical and biological properties of soils, leading to increased crop yields (Diacono and Montemurro 2011). Provided that these compounds are rich in organic matter and nutrients, their utilization as fertilizers on agricultural land has been proposed as the best approach in order to reduce their economic and environmental disposal costs. Nevertheless, these waste materials have the disadvantage of containing a wide range of pollutants (such as PCBs) that may adversely affect the environment, as well as plants, animals and human health (European Commission 2000).

PCBs are regarded as one of the main twentieth-century environmental pollutants, because of their persistence in the environment and their potentially negative impact on biota due to their carcinogenic and endocrine disrupting effects. In 2001 they were included in the list of persistent organic pollutants adopted by the Stockholm Convention to prevent environmental pollution (UNEP 2011). In spite of the fact that their manufacture was banned in most countries between 1970 and 1980, they can still be found worldwide, even in places as remote and distant from industrial pollution sources as the Antarctic and the Arctic (Vecchiato et al. 2015; Zhu et al. 2015). The production of PCBs has been estimated at over 1 million tons, and one-third of this amount is still dispersed in the environment (Birkett and Lester 2002).

The chemical formula of PCBs can be presented as $C_{12}H_{10-n}Cl_n$, where *n* is the number of chlorine atoms, which ranges from 1 to 10 (Figure 1). Theoretically, 209 congeners would be possible, but only about 130 congeners are likely to be found in commercial products. Ballschmiter and Zell (1980) established a classification to identify each of the different congeners according to the number of chlorine atoms and their positions, which was then adopted by the International Union of Pure and Applied Chemists (IUPAC). Out of the 209 PCB congeners, seven of them are regarded as environmental indicators (namely congeners 28 (2,4,4'-trichlorobiphenyl), 52 (2,2',5,5'-tetrachlorobiphenyl), 101 (2,2',4,5,5'-pentachlorobiphenyl), 118 (2,3',4,4',5-pentachlorobiphenyl), 153 (2,2',3,4,4',5'-hexachlorobiphenyl), 138 (2,2',3,4,4',5'-hexachlorobiphenyl) and 180 (2,2',3,4,4',5,5'-heptachlorobiphenyl)). The choice of these congeners (usually referred to as the 'ICES 7') as environmental indicators is due to the fact that they are present in appreciable amounts in the environment, that they are part of most commercial PCB mixtures and that they correlate with the total PCBs content (Creaser et al. 1989; Yeo et al. 2004). It is worth noting that the listing of these environmental indicators in the literature usually differs from the classification established by Ballschmiter and Zell (1980), since they tend to be listed according to the order of elution in chromatographic analysis as PCBs 28, 52, 101, 118, 153, 138 and 180 (Mamontova et al. 2007).

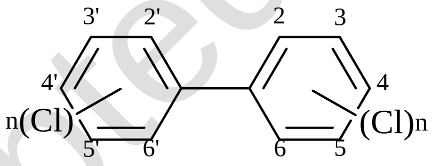

Figure 1. Chemical structure of PCBs. The possible positions of chlorine atoms on the benzene rings are denoted by numbers assigned to the carbon atoms.

Regarding the application of sewage sludge to agricultural land, Directive 86/278/EC sets limits on heavy metals concentration but there is no actual restriction for organic pollutants. The European Union is currently considering the enactment of legislation aimed at limiting the concentration of PCDDs (polychlorinated dibenzo-*p*-dioxins), PCDFs (polychlorinated dibenzofurans) and PCBs in organic waste materials for application to crop fields (European Commission 2010). Although Directive 86/278/EEC does not require a control of persistent organic pollutants, in countries like Germany the sewage sludge ordinance has set a limit of 200 $ng \cdot g^{-1}$ for six PCB congeners (28, 52, 101, 138, 153 and 180) in sludge (dry weight) since 1992.

Soil is a heterogeneous environmental compartment with a wide variety of properties that influence the organic pollutants persistence, such as that of PCBs. The mechanisms by which organic compounds bind to soil remain poorly understood. Soil properties (texture, organic matter content, moisture and porosity) influence aforementioned organic compounds persistence (Backe et al. 2004; Cousins et al. 1997). Furthermore, the persistence of PCBs after the application of organic waste materials to soil depends on volatilization, biodegradation, leaching and physical transport processes (Alcock et al. 1993; Backe et al. 2004; Bi et al. 2002; Umlauf et al. 2010; Wilson et al. 1997). The importance of each process depends on the physicochemical properties of the soil, organic waste and chemical, on environmental conditions (e.g., temperature and precipitation) and on anthropogenic factors such as cultivation and drainage (Beck et al. 1996).

Laboratory studies where PCBs are added as spikes do not provide a realistic assessment of environmental persistence, because spiked PCBs are more susceptible to losses than field-weathered residues (Alcock et al. 1996; Wilson et al. 1997). For this reason, it is necessary to quantify the content of PCBs in soils through field tests under real conditions. There are previous studies that have determined the possible accumulation of PCBs by the use of organic waste materials as fertilizers or amendments (Alcock et al. 1996; Eljarrat et al. 1997; Folch et al. 1996; McLachlan et al. 1994), but –to the best of the authors knowledge– these studies have not evaluated the influence of irrigation and of the type of organic waste.

Continuous application of organic waste as fertilizers to agricultural soil can lead to an increase of the concentration of organic pollutants such as PCBs, so that the soil would behave as a reservoir of these chemicals. As a consequence of the increase in global temperature due to greenhouse effect, these soils to which treated sewage sludge and municipal solid waste have been applied may in turn act as emitters of these pollutants, increasing their concentration in the atmosphere (Lamon et al. 2012; Wöhrnschimmel et al. 2012). Thus, it is essential to estimate the evolution of these pollutants in agricultural soils in longer periods.

The study presented herein has been conducted over a four-year period, assessing three types of organic waste materials, which were applied to two soils (irrigated and non-irrigated). While the different theoretical models on the behavior of PCBs in the environment available to date only determine the evolution of the PCBs over a brief period of time (Bi et al. 2002; Kobližková et al. 2009), this paper aims to estimate the resulting concentration after a long period after the application of the organic waste through the estimation of the concentration of the PCBs of the different waste materials till year 2050, taking into consideration the particularities of each type of organic waste and the impact of irrigation.

2. Materials and methods

2.1. *Experimental design*

The field test was performed following a random experimental design in two different agricultural plots (irrigated and non-irrigated soils) over a period of four years. Each plot was divided into 8 subplots of 12×8 m (96 m^2), corresponding to the three different organic waste materials under study (*viz.* composted sewage sludge (CSS), dehydrated sewage sludge (DSS) and municipal solid waste compost (MSWC)) plus a control sample (a subplot without fertilizer), with two replicates per treatment.

The experimental crop was barley (*Hordeum vulgare*), planted as an annual crop in the irrigated and non-irrigated soils (nitrogen needs: 24 $kg\cdot t^{-1}$; crop production: 3000 $kg\cdot ha^{-1}$ for the non-irrigated land and 5000 $kg\cdot ha^{-1}$ for the irrigated one).

The amounts of the three types of organic waste materials added to the soil were determined according to agricultural fertilization needs. Differences in the quantities used were due to the different nitrogen content in each type of organic waste (e.g., the DSS, which had the highest content of nitrogen, required the smallest rates of application). Doses were calculated on the basis that approximately 75% of the total nitrogen existing in the organic waste can be mineralized in one agricultural cycle. The doses commonly applied to agriculture in Spain range between 5 and 10 $t\cdot ha^{-1}\cdot year^{-1}$ (dw). The quantities of organic waste added to each subplot (in $t\cdot ha^{-1}\cdot year^{-1}$) were as follows:

6.3 (non-irrigated) and 10.3 (irrigated) for CSS; 2.1 (non-irrigated) and 3.5 (irrigated) for DSS; 6.8 (non-irrigated) and 11.4 (irrigated) for MSWC.

2.2. *Soil samples*

Two soils in an agricultural area located near Palencia (North of Spain), away from urban centers and big industries, were sampled. S1 soil corresponded to the non-irrigated land and S2 soil to the irrigated land. Soil samples for analysis were collected at the end of each growing season (after harvesting), in triplicate, at a depth of 0 to 5 cm. All samples were air dried, sieved through a 2 mm mesh size metal sieve and stored in glass containers. The physicochemical properties of the two soils are summarized in Table 1.

Table 1. Physicochemical soil properties before the application of organic waste.

Parameter (1)	Soil #1 (S1)	Soil #2 (S2)
Location	Villamediana (N 42° 2' W 4º 21')	Villamediana (N 41º 59' W 4° 22')
Area	Cerrato	Cerrato
Sand (%)	21.8	13.8
Silt (%)	53.9	28.9
Clay (%)	24.3	57.3
pH	8.43	8.58
EC (mmhos·cm $^{-1}$)	340	310
Organic matter (%)	1.77	1.35
Phosphorus (mg·kg^{-1})	18.8	17.5
$CaCO_3$ (%)	36.8	17.8
Total carbon (%)	7.15	4.13
Total nitrogen (%)	0.16	0.16
C/N ratio	17.1	12.3

(1) Variables expressed in air-dried soil.

2.3. *Organic waste samples*

The dehydrated sewage sludge (DSS) was obtained from an urban wastewater treatment plant located in Valladolid (Spain); the municipal solid waste compost (MSWC) was also from Valladolid and the composted sewage sludge (CSS) was supplied by a solid waste treatment plant located in Burgos (Spain). These plants treat wastewater and solid waste that are mainly from urban sources. All the materials complied with Spanish national legislation about the use of sludge in agricultural soils, derived from Directive 86/278/EEC.

The physical and chemical characteristics of the organic waste materials are presented in Table 2. Average organic matter content in these samples was 50%. The raw materials composition for the CSS compost process was: 50% pine bark, 3% straw and the rest was sewage sludge. The composition of the MSWC could not be reported by the supplier.

Table 2. Physicochemical properties of the organic waste materials under study (average values over 4 years).

Parameter (1)	Composted Sewage sludge (CSS)	Dehydrated sewage sludge (DSS)	MSW compost (MSWC)
Moisture (%)	36.8	26.5	36.9
pH	7.4	7.1	7.3
EC (dS·m^{-1})	1.71	1.64	2.06
Organic matter (%)	54.4	56.0	44.9
Total carbon (%)	17.5	19.6	19.5
Total nitrogen (%)	2.54	3.09	1.89

[(1)] Variables expressed on air-dried organic waste.

2.4. *Determination of PCBs in soil and in organic waste materials*

2.4.1. *Reagents and standards*

Hexane (CAS No. 110-54-3, gas chromatography grade) and acetone (CAS No. 67-64-1, gas chromatography grade) for residue analysis, *n*-heptane (CAS No. 142-82-5, HPLC grade), dichloromethane (CAS No. 75-09-2, HPLC grade), sulfuric acid (CAS No. 7664-93-9, 98%), pure copper (CAS No. 7440-50-8), silver nitrate (CAS No. 7761-88-8), silica gel (CAS No. 112926-00-8) 0.063-0.200 mm neutral, granular anhydrous sodium sulphate (CAS No. 7757-82-6) of 12-60 mesh and glass wool were supplied by Scharlau Chemie, SA (Spain).

PCB-Mix 3 containing the 28, 52, 101, 118, 138, 153 and 180 PCB congeners at a concentration of 10 ng·µL^{-1} and PCB-209 at a concentration of 10 ng·µL^{-1} were also obtained from Scharlau Chemie, SA (Spain).

Activated neutral silica was heated at 450 °C for 24 hours, cooled and stored in a desiccator. Silica modified with sulfuric acid (44%) was prepared with 18.3 mL of H_2SO_4 and 40 g of activated silica. Silica modified with silver nitrate was obtained by mixing a solution of 2.5 grams of $AgNO_3$ in 30 mL of deionized water with 22.5 g of activated neutral silica, followed by heating at 150 °C for 24 hours. Granular anhydrous Na_2SO_4 was heated at 450 °C for 24 hours, cooled and stored in a desiccator. The glass wool used in the extraction process was washed with CH_2Cl_2 for 24 hours in a Soxhlet extraction equipment. To avoid cross contamination of glassware, it was washed with the same solvent and subsequently with detergent and distilled water, and then dried for 24 hours at a temperature above 150 °C.

2.4.2. *Instrumentation*

A Retsch HM302 ball mill (BIOMETA, Spain) and a 2 mm pore size sieve were used in the homogenization process. The extraction process involved a 250 mL Soxhlet, a glass cartridge with porous plate 2 and an electric blanket (Selecta). For the purification process, glass columns for chromatography, a porous plate 0 of 15×300 mm, a 6 BarVap Zanntek analytical evaporator (CE-600, Glas-Col LLC, USA), a RE300B rotary evaporator (Stuart, UK) and an UN110 oven (Memmert, Germany) were used. The analytical apparatus consisted of a GC Autosystem XL (Perkin Elmer) equipped with an electron capture detector and a GC mass GP2100 (Shimadzu).

2.4.3. *Methodology*

All samples were air-dried and grinded to homogenize them before extraction. 2 g (dw) of organic waste sample and 25 g (dw) of soil were extracted in a conventional Soxhlet with pesticide-grade hexane-acetone (1:1) for 24 hours (US Environmental Protection Agency 1996). For soil samples, 1.5 g of copper -to remove sulphur interferences- and 1.5 g of Na_2SO_4 were added to the Soxhlet beaker; *vs*. 5 g of copper and 15 g of Na_2SO_4 for organic waste samples. The resulting solution was concentrated for purification with a column chromatographic procedure. In this procedure, two columns were used: a column for organic waste materials containing, from top to bottom, layers of Na_2SO_4 (2 g) and H_2SO_4-impregnated silica (20 g); and another column for soils containing, from top to bottom, layers of Na_2SO_4 (2 g), H_2SO_4-impreganted silica (5 g) and $AgNO_3$-impregnated silica (5 g). The columns were cleaned and eluted with hexane (150 mL for organic waste materials and 100 mL for soils). Samples were finally concentrated to dryness prior to the addition of a dissolution of PCB 209 (Scharlau Chemie, Spain) as the internal standard. The organic waste materials extracts were reconstituted with 1 mL of *n*-heptane and the soil extracts with 100 µL of *n*-heptane.

The identification and quantification was made by adding an internal standard and using gas chromatography with electron capture detector (ECD) equipment. Analysis by gas chromatography with mass detector was used so as to validate PCBs identification in samples, as required by EPA 8082 standard method (US Environmental Protection Agency 2007).

Chromatography equipment (Autosystem, Perkin Elmer) with ECD detector was used with a 50 m×0.25 mm×0.25 µm internal phase CP-SIL 8CB column. Operating parameters for chromatographic determination were as follows: carrier gas: nitrogen at 1 mL·min^{-1}; make-up gas at 40 mL·min^{-1}; injection temperature: 250ºC; ECD detector temperature: 300 ºC; injection volume: 2 µL; splitless time: 1.5 min. Chromatographic separation of components was conducted in the following sequence: temperature was raised from 50 ºC (for 3 min) to 180 ºC at 5 ºC·min^{-1} and then to 280 ºC at 2.5 ºC·min^{-1} (held isothermally for 10 min). Quantitative determination was performed by an internal patron using relative response factors (RRFs) previously obtained from five standard solutions. The compounds were assigned according to their retention times in comparison with the standard mixtures. Quantification was carried out by comparison with a mixture standard of PCB congeners 28, 52, 101, 118, 153, 138 and 180. Chromatography equipment (GP2010, Shimadzu) with mass detector was used with a 60 m×0.25 mm×0.25 µm internal phase Vf-5ms column. The operating parameters for the chromatographic determination were as follows: carrier gas: helium at 1 mL·min^{-1}; injection temperature: 280 ºC; detector temperature: 260 ºC; interface temperature: 280 ºC; injection volume: 2 µL; splitless time: 1.8 min. Chromatographic separation of components was achieved by heating from 50 ºC (for 1.8 min) to 200 ºC at 40 ºC·min^{-1} and then to 290 ºC at 2.5 ºC·min^{-1} (held isothermally for 10 min). The MS detector was operating in the selected ion monitoring (SIM) mode and the m/z values monitored were: 256, 258 and 260 (PCB 28); 290, 292 and 294 (PCB 52); 324, 326 and 328 (PCB 101 and 118); 360, 362 and 364 (PCB 153); 392, 394 and 396 (PCB 180); 496, 498 and 500 (PCB 209).

2.5. *Calculation of PCB persistence*

At the end of fourth-year crop, accumulation of PCBs in the soil was examined. Soils were sampled at the beginning of the experiment, and each field subplot was sampled after harvesting on a yearly basis over the four-year period. Soil samples inputs via organic wastes were analysed to determine PCBs content. Concentrations of PCBs in agricultural soils were calculated using the concentrations of PCBs in the organic waste, the rate of application for each type of waste, the surface of each subplot and the soil density over the 4-year experiment (Alcock et al. 1996):

$$C_{soil\ (t)} = C_{soil\ (t0)} + \frac{C_{waste(t)} \cdot R}{S_z \cdot D \cdot CF} \qquad \text{Eq. [1]}$$

where $C_{soil\ (t)}$ is the theoretical PCBs concentration in the soil (ng·g^{-1} dw), $C_{soil\ (t0)}$ is the initial PBCs concentration in the soil (ng·g^{-1} dw), C_{waste} is the PCBs concentration in the organic waste (ng·g^{-1} dw), R is the application rate (kg·ha^{-1}), S_z is the soil depth (5 cm), D is the soil density (kg·cm^{-3}) and CF is a conversion factor (1×10^8 cm^2·ha^{-1}).

2.6. *Statistical analysis*

Data statistical analysis was conducted with a general linear model for analysis of variance. For *post-hoc* comparison of means, Tukey's multiple range test with a significance level of 5% was used. All tests were carried out using STATISTICA software 8.0 (StatSoft).

3. Results and discussion

3.1. *Concentration of PCBs in the organic waste materials*

The PCBs concentration in the organic waste materials ranged from 34.08±4.08 ng·g^{-1} for municipal solid waste compost (MSWC) in 2006 to 118.93±14.02 ng·g^{-1} for MSWC in 2004, with an average value of 63.16 ng·g^{-1}. In the “Working Document on Sludge and Biowaste" (European Commission 2010), a concentration limit of 800 ng·g^{-1} for Σ7PCBs in sludge was proposed, so the concentrations in the organic waste materials studied herein would be well below this limit. The profile of PCBs in CSS and DSS sewage sludge showed a high content of hexachlorinated (PCBs 153 and 138) and heptachlorinated (PCB 180) congeners, while MSWC had a significant percentage of low-chlorinated congeners, namely tri- and tetrachlorinated ones (PCBs 28 and 52) (Antolín-Rodríguez 2011).

3.2. *Quantities of PCBs applied to agricultural soils*

The amounts of the PCBs congeners added to each subplot were calculated using the average concentration of PCBs and the amount of each organic waste applied to each soil (non-irrigated and irrigated) over the four years period (see Table 3).

Table 3. Total amount of PCBs (in mg) applied over the 4 years period, broken down considering irrigation and type of organic waste (*viz*. composted sewage sludge, CSS; dehydrated sewage sludge, DSS; or municipal solid waste compost, MSWC). Standard deviations are indicated below each value in italics.

Irrigation	Type of organic waste	PCB congeners							Total
		PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180	
Non-Irrigated soils	CSS	0.66	0.53	1.09	0.25	3.05	1.85	3.32	10.75
		0.09	*0.09*	*0.25*	*0.14*	*0.22*	*0.17*	*0.26*	*0.80*
	DSS	0.14	0.15	0.27	0.10	0.90	0.55	0.85	2.96
		0.03	*0.02*	*0.02*	*0.01*	*0.08*	*0.06*	*0.10*	*0.24*
	MSWC	3.54	1.53	1.22	0.80	1.74	1.36	2.69	12.88
		0.49	*0.32*	*0.17*	*0.12*	*0.17*	*0.13*	*0.55*	*1.58*
Irrigated soils	CSS	1.09	0.87	1.81	0.41	5.03	3.06	5.48	17.75
		0.15	*0.15*	*0.41*	*0.23*	*0.36*	*0.28*	*0.43*	*1.32*
	DSS	0.23	0.25	0.46	0.15	1.54	0.93	1.44	5.00
		0.05	*0.04*	*0.04*	*0.02*	*0.14*	*0.10*	*0.17*	*0.41*
	MSWC	5.93	2.57	2.05	1.35	2.92	2.27	4.51	21.60
		0.82	*0.54*	*0.29*	*0.20*	*0.28*	*0.22*	*0.93*	*2.66*

The total amount of PCBs added in agricultural soils ranged from 2.96±0.24 mg in the non-irrigated subplots treated with DSS to 21.60±2.66 mg in the irrigated subplots treated with MSWC.

The amounts of PCBs applied were different depending on irrigation (non-irrigated *vs*. irrigated soil) and on the amount of each organic waste fertilizer needed in order to meet the nitrogen requirements of the crop. Since a barley production of 5000 kg·ha^{-1} was estimated for the irrigated land, higher than that of the non-irrigated land (3000 kg·ha^{-1}), the contributions to total PCBs were higher in the irrigated soil (ranging from 5.00±0.41 mg to 21.60±2.66 mg) than in the non-irrigated one (in the 2.96±0.24 mg to 12.88±1.58 mg range).

With regard to the total PCBs amounts contributed by each organic waste, the highest corresponded to the application of MSWC to the soils, followed by CSS and finally by DSS. The composition of the PCBs supplied by each organic waste was also different: the greatest contribution of PCBs with low-degree of chlorination was performed in subplots where MSWC was applied, in particular for PCB 28 (from 3.54±0.49 mg to 5.93±0.82 mg) and PCB 52 (from 1.53±0.32 mg to 2.57±0.54 mg), while CSS and DSS added significantly lower amounts for PCB 28 (from 0.14±0.03 mg to 1.09±0.15 mg) and for PCB 52 (from 0.15±0.02 mg to 0.87±0.15 mg). The major contribution of PCBs with a high-degree of chlorination was associated to CSS, followed by MSWC and finally by DSS.

The physico-chemical properties of PCBs vary with the number of chlorine atoms, so that PCB congeners with a higher degree of chlorination (i.e., PCB congeners 138, 153 and 180) have higher adsorption coefficients and vapor pressure values and lower solubility in water than PCB congeners with a lower degree of chlorination (i.e., PCB congeners 28 and 52). With regard to the persistence of the PCBs content in soils, the hexa- and heptachlorinated congeners would be more easily retained, while the tri- and tetraclorinated congeners would be more prone to undergo leaching and volatilization processes. As reported in other studies concerning the application of sewage sludge to pastures (Smith 2009), most soil PCB concentrations were little affected by sludge applications and the ones with higher influence were those congeners with a high-degree of chlorination (Rhind et al. 2013).

3.3. *Concentration of PCBs in soils*

PCBs were found in all soil samples, that is, both in the control sample (non-treated subplot) and in soil samples from the subplots treated with the various organic waste materials. The concentrations of PCBs in soils are shown in Table 4. As expected, the concentration values in the control soils were lower than those obtained in soils treated with organic waste. It is also worth noting that while PCBs concentrations significantly differed depending on the organic waste added to each subplot, the effect of irrigation on soil (S1 *vs*. S2) did not lead to significant differences.

Table 4. Concentration of PCBs in the agricultural soils under study after four years of organic waste materials application. All concentrations are expressed in ng·g^{-1} of dry matter ± standard deviation (*in italics*) of three replicates for two samples. For readability reasons, P values are not shown, but those mean values which are significantly different from those of control soil according to Tukey's HSD test (p<0.05) are marked with an asterisk.

Irrigation	Type of organic waste	PCB congeners							Total
		PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180	
Non-irrigated Soil	Control	0.023	0.026	0.031	0.020	0.042	0.045	0.025	0.231
		0.006	*0.007*	*0.004*	*0.002*	*0.004*	*0.004*	*0.003*	*0.054*
	CSS	0.051	0.082 *	0.140 *	0.091 *	0.459 *	0.411 *	0.437 *	1.670 *
		0.013	*0.029*	*0.047*	*0.025*	*0.162*	*0.139*	*0.156*	*0.538*
	DSS	0.031	0.044	0.054	0.031	0.129	0.130	0.103	0.521
		0.007	*0.015*	*0.013*	*0.005*	*0.032*	*0.034*	*0.037*	*0.136*
	MSWC	0.110 *	0.138 *	0.180 *	0.145 *	0.317 *	0.366 *	0.251 *	1.507 *
		0.021	*0.018*	*0.076*	*0.065*	*0.141*	*0.197*	*0.050*	*0.550*
Irrigated soil	Control	0.015	0.015	0.018	0.012	0.026	0.026	0.014	0.130
		0.005	*0.004*	*0.003*	*0.002*	*0.005*	*0.006*	*0.004*	*0.020*
	CSS	0.072 *	0.101 *	0.165 *	0.125 *	0.523 *	0.492 *	0.518 *	1.994 *
		0.037	*0.071*	*0.080*	*0.021*	*0.157*	*0.129*	*0.078*	*0.554*
	DSS	0.049	0.043	0.053	0.041	0.132	0.135	0.125	0.577
		0.020	*0.011*	*0.020*	*0.012*	*0.054*	*0.053*	*0.065*	*0.214*
	MSWC	0.098 *	0.088 *	0.116 *	0.094 *	0.204	0.220	0.177 *	0.997 *
		0.048	*0.043*	*0.061*	*0.049*	*0.097*	*0.112*	*0.094*	*0.499*

As regards the PCBs content in the control soils, values of 0.231±0.054 ng·g^{-1} were obtained for control soil S1 and of 0.130±0.020 ng·g^{-1} for control soil S2, with a very low Σ7PCBs content, even below the average value of 5.41 ng·g^{-1} proposed by Meijer et al. (2003) for the background concentration of PCBs in soils. This value is indicative of the fact that the geographic area in which these soils are located is far from any source of contamination (e.g., proximity to large urban and industrial areas).

The entry of PCBs in agricultural soils has two main pollution sources: atmospheric deposition processes or the application of organic waste, mainly sewage sludge and municipal solid waste. To determine the effect of atmospheric deposition, the Σ7PCBs content was determined in the control soils at the beginning of the experiment. The Σ7PCBs in the non-irrigated (S1) and irrigated (S2) control soils was 0.331±0.088 $ng\cdot g^{-1}$ and 0.211±0.062 $ng\cdot g^{-1}$, respectively (Antolín-Rodríguez 2011). In relation to the values obtained in the last year of the experiment, it was observed that the content of PCBs in control soils slightly decreased over time, so an increase of the PCBs content due to atmospheric deposition processes could be excluded. The PCBs transfer processes between air and ground tend towards equilibrium as a result of the restrictions that exist on this type of compounds (Cousins et al. 1997).

The total concentration of PCBs in soils treated with organic waste materials ranged from 0.521±0.136 $ng\cdot g^{-1}$ to 1.994±0.554 $ng\cdot g^{-1}$. The total concentration of PCBs was higher in soils treated with CSS, followed by MSWC and finally by DSS. This result is consistent with the amount of PCBs with a high degree of chlorination supplied by each organic waste, in particular CSS and MSWC, which –as noted above– have characteristics that make them more persistent in soils.

In addition, the total concentration of PCBs was higher in irrigated soils than in non-irrigated ones for the same type of organic waste material, except for soils treated with MSWC.

This apparent incongruity may be explained by a higher PCBs elimination in this particular type of organic waste material as a consequence of irrigation which would not only depend on leaching (which has a more pronounced effect on those PCB congeners with a lower degree of chlorination than on their highly chlorinated counterparts), but also on other phenomena that would affect all PCB congeners and which would depend on the actual material that contains the PCBs.

According to Alcock et al. (1996), the rate of compound release may be limited by intra-organic matter diffusion in the organic waste, in such a way that differences in the type of organic waste would influence compound loss rates. Similarly, Beck et al. (1996) observed different PCBs losses for different sludges applied to the same type of soil. This variation in PCBs losses was due to the different desorption rates observed in the different sludge matrices under study, concluding that the elimination rate was limited by low-chlorination grade congeners intra-organic matter diffusion in the sludge solids.

Since the state of aggregation of the three types of organic residues studied herein was different (MSWC had the lowest state of aggregation, followed by CSS and DSS), it is reasonable to expect that when these materials were applied to the soil, the effects of surface exchange (such as intra-organic matter diffusion) would have been more pronounced on materials like MSWC, which has a larger surface area and a lower state of aggregation, than on DSS, which features a granular and very compact appearance.

3.4. *Calculation of PCB persistence in soils*

Concentrations of PCBs in the agricultural soils (Figure 2) were calculated using the concentrations of PCBs in the organic waste, the application rate for each type of organic waste, the soil surface of each subplot and the soil density over the 4-year experiment, according to Eq. [1] (Alcock et al. 1996).

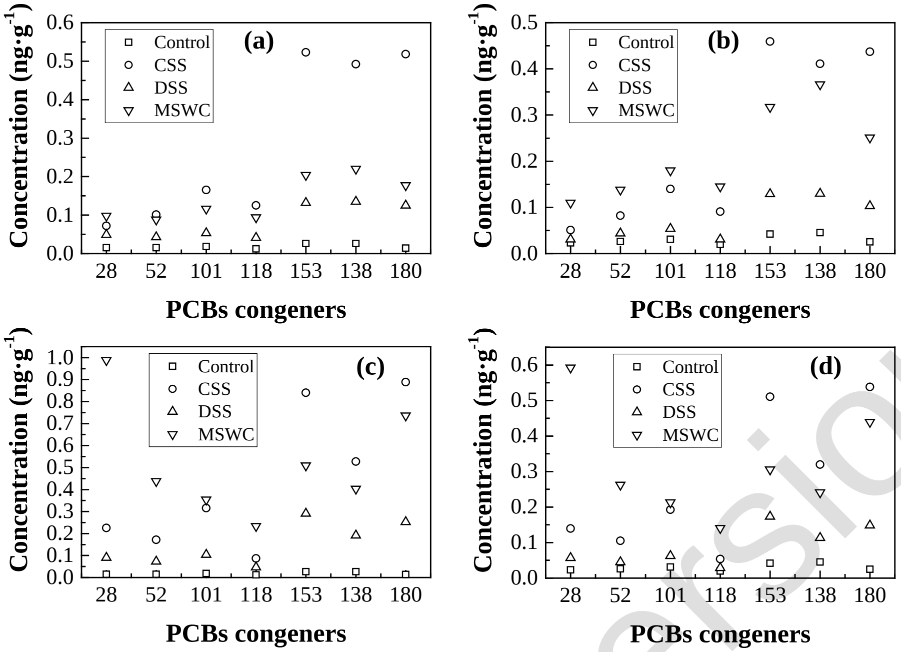

Figure 2. Mean values of PCBs in soils treated with organic waste and control soil (ng·g $^{-1}$): (*a*) experimental concentrations in the irrigated soil (S2); (*b*) experimental concentrations in the non-irrigated soil (S1); (*c*) theoretical concentrations in the irrigated soil (S2); (*d*) theoretical concentrations in the non-irrigated soil (S1).

A good agreement was observed between experimental (Figure 2*a*, Figure 2.*b*) and theoretical concentrations (Figure 2*c*, Figure 2*d*). Therefore, the theoretically obtained concentration of PCBs could be used as an estimate for determining the PCBs concentration when organic wastes are used as fertilizers in agricultural soil.

Measured concentrations and theoretical concentrations in soil were compared to estimate the proportion of remaining individual PCBs over the four-year period. The persistence –depending on the type of organic waste and on the influence of irrigation (see Table 5)– was estimated by the ratio between the experimentally determined concentration and the theoretical concentration of each PCB. The concentration values used in the calculation of the persistence are average values. The presence of values higher than 100% can be ascribed to the conditions in which the field tests were conducted, affected by the lack of homogeneity of the plots and of the organic waste materials, the dispersion in the application of the organic waste to the soil and to the influence of weather conditions. Such variability in data from field tests has also been reported by other authors (Molina et al. 2000; Wilson et al. 1997).

Table 5. Persistence (%) of the various PCB congeners depending on irrigation and on the type of organic waste used as fertilizer after 4 years of application of the organic waste materials.

Irrigation	Type of organic waste	PCB congener							Total
		PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180	
Non-irrigated soil	CSS	36	77	73	169	90	129	81	90
	DSS	55	97	85	108	74	114	70	83
	MSWC	19	53	84	103	104	152	57	69
Irrigated soil	CSS	32	59	52	143	62	93	58	65
	DSS	54	58	51	88	45	70	50	55
	MSWC	10	20	33	40	40	55	24	27

The percentage of total PCBs which remained in the soil after 4 years ranged from 27% to 90%. Persistence values were higher in non-irrigated soils (69-90%) than in irrigated ones (27-65%). The similar (and low) organic matter content of the two agricultural soils under study (below 2%, see Table 1) should not have a marked effect on the PCBs persistence in the soil, so other factors may influence this result.

Amongst the different types of organic waste, the highest values of persistence were obtained in soils treated with CSS, followed by DSS and finally by MSWC. This may indicate greater sorption of organic compounds in these organic wastes, thereby limiting the availability for loss (Alcock et al. 1996; Beck et al. 1996). Among the different PCB congeners, the persistence was higher for those PCBs with a higher-grade of chlorination, due to their lower solubility and volatility (Liu et al. 2007). The lowest persistence, achieved for PCBs 28 and 52 had already been well-established in the literature (Alcock et al. 1993; Backe et al. 2004; Bi et al. 2002; Umlauf et al. 2010; Wilson et al. 1997).

The most common loss processes for PCBs in agricultural soil are volatilization, leaching and biodegradation. Volatilization is the fundamental process leading to the disappearance of PCBs (Alcock et al. 1996; Wilson et al. 1997). Volatilization speeds vary between congeners and depend on temperature, moisture and the strength of interactions with organic matter (Ryan et al. 1988). Lower chlorinated PCB congeners, with higher solubility and vapor pressure, are more susceptible to volatilization and leaching processes. The similarity in the persistence values of PCB 28 for the same type of organic waste and different irrigation conditions suggests that the elimination of this congener would be primarily influence by volatilization processes (Alcock et al. 1996; Bi et al. 2002), with lower values for the remaining congeners in the irrigated soil than in the non-irrigated one.

In addition, it should be noted that the lower the concentration of PCBs in the environment is, the higher volatilization-dependent environmental PCBs concentration will be: PCBs behavior is governed by a kinetic partitioning between the air and ground concentrations due to a reduction of PCBs in the environment (Alcock et al. 1996). The final concentration in the soil tends to be reduced with time, as a consequence of the continuous reduction of the PCBs concentration in the environment. Agricultural tillage conditions leave organic waste in the upper soil layers, allowing greater volatilization, especially in hot and dry periods (Wilson et al. 1997), and PCBs migration processes to lower layers have not been deemed as very important (McLachlan et al. 1996; Wilson et al. 1997), finding that PCBs are located mainly in the topsoil, which corresponds to the plowing depth applied (Umlauf et al. 2010). On the other hand, watering crops with a high concentration of PCB congeners with a low-degree of chlorination can lead to their migration to deeper soil layers through pore water, whereas higher chlorinated PCB congeners are retained by adsorption mechanisms in the soil particles (Bi et al. 2002).

3.5. *Trends in PCBs concentration due to organic waste use in agricultural soils*

The trend in the PCBs concentration due to the application of the various types of organic waste materials as fertilizers till 2050 was estimated taking into account the contribution and persistence of PCBs for each type of organic waste and soil, using the mathematical equation that fitted best to the experimental data considering the assumption of exponential reduction of PCBs content in organic waste (Alcock et al. 1996; Beck et al. 1996; Zennegg et al. 2013). The origin of PCBs in the sludges would mainly be the atmospheric deposition of particulate matter, both by dry and wet deposition, whereas in the case of MSWC it would be due to the accumulation of PCBs in the structural plant material (Umlauf et al. 2010). Thus, the decrease in the atmospheric concentration of PCBs should lead to a reduction in the PCB content both in the sludges and in the municipal solid waste materials (Clarke et al. 2010).

A first-order exponential model was chosen to estimate the extrapolation of the Σ7PCBs content till 2050 (46 years after the completion of the experiment). The resulting equations (parameters are summarized in Table 6) are of the type $C_{t\,waste} = C_{o\,waste} \cdot \exp(-kt)$, where $C_{o\,waste}$ ($ng \cdot g^{-1}$) is the initial concentration of residue at *t*=0 (Alcock et al. 1996; Dalla Valle et al. 2005). The decay trends in the PCBs concentration are related to the regulatory status of the compounds. PCBs have been banned since the 70s, observing a decline of the median concentration ranging from 69% to 87% over the past 20 years (Zennegg et al. 2013).

Table 6. Parameters of the equation used to estimate PCBs content till 2050.

Type of organic waste	$C_{o\,waste}$ ($ng \cdot g^{-1}$)	*k*	R^2
Composted Sewage Sludge (CSS)	77.046	-0.145	0.987
Dehydrated sewage sludge (DSS)	58.839	-0.139	0.998
MSW compost (MSWC)	80.411	-0.146	0.982

The average lifetime for Σ7PCBs was 2.1 years for MSWC, followed by 4.0 years for CSS and 5.1 years for DSS. These values are within the ranges reported by other authors for sludges. In agreement with the data published by Alcock et al. (1996) and Clarke et al. (2010), the highest values were obtained for those sludges which featured a higher adsorption capacity for organic compounds, thus limiting their PCBs release capacity.

The calculated evolution of the concentration of PCBs until 2050 in the agricultural soils as a function of the type of organic waste used as fertilizer and irrigation is depicted in Figure 3. As noted above, this should be regarded as a rough estimation due to the limited amount of experimental data. The total PCBs concentration would depend on irrigation (S1 non-irrigated *vs.* S2 irrigated) and on the organic waste used as fertilizer in each subplot, obtaining the highest concentration values in soils treated with CSS, followed by soils treated with MSWC and finally by soils treated with DSS.

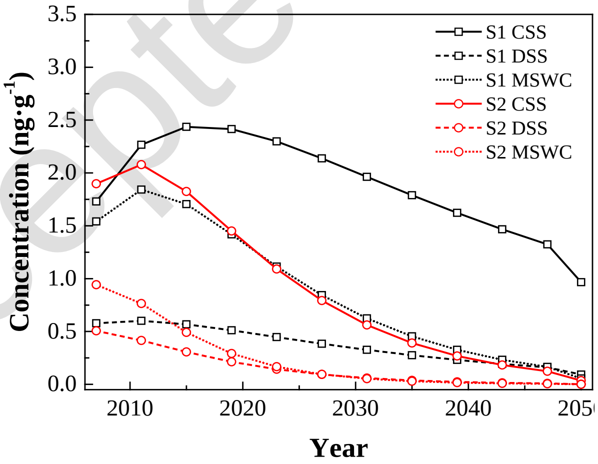

Figure 3. Estimation of total PCBs content till year 2050 due to the use of organic residues as fertilizers in non-irrigated (S1, black) and in irrigated agricultural land (S2, red).

The trends in the calculated PCBs concentration in the agricultural soils (Figure 3) are influenced by factors such as the amount of PCBs applied, the composition of each type of organic waste material, the persistence of the different PCB congeners (volatilization and lixiviation processes) and the type of soil.

The concentration of PCBs in the non-irrigated soils would be higher in those treated with CSS, followed by MSWC and DSS, attaining similar concentrations in the soils treated with MSWC and DSS after 2045. In the irrigated soils, the order of the treatments in terms of PCBs concentration would be analogous to that of their non-irrigated counterparts, reaching similar concentrations for the MSWC- and DSS-treated soils after 2025, and for all treatments after 2050.

As it may observed in Table 3, the amounts of PCB congeners with a high degree of chlorination (hexa- (PCB 153 and 138) and heptachlorinated (PCB 180)) added to each type of soil for each organic waste material were higher for CSS, followed by MSWC and DSS. Considering that –as noted above- PCBs with a low degree of chlorination show higher adsorption capacity and lower solubility, and thus higher persistence, they should have a more prevalent influence in the final PCBs content in the soils, as it is actually the case. Hence, the trend in the PCBs concentration in the soil will depend on the amounts of PCBs with a high degree of chlorination supplied by each type of organic waste material, i.e., on the PCBs concentration and on the amount of organic waste required to cover the nitrogen needs of the plant. This implies that crops with higher nitrogen needs would involve an increase in the PCBs in the agricultural soil if the organic waste material used as a fertilizer has a higher content of PCB 153, 138 and 180 congeners.

Another of the most relevant factors to be considered would be the trend towards the accumulation of PCBs in the soil. During a 10-year period after the beginning of the experiment, an increase in the PCBs concentration is observed in the non-irrigated soils for all the treatments, and for the irrigated soils treated with CSS too. Assuming that the persistence values of the various congeners and the composition of the PCBs in the organic waste materials would not change, the factor that influences the absence of PCBs accumulation in the soils is their concentration in the organic waste material. So that this accumulation would occur, the PCBs input should be larger than the losses (primarily by factors such as lixiviation and volatilization). The progressive reduction in the atmospheric concentration of PCBs implies that the organic waste materials will have lower PCBs concentration values, and the amount of PCBs added to the agricultural soil –directly dependent on the PCBs concentration in each of the organic waste materials- should then be lower than that removed. The absence of accumulation of PCBs for DSS in irrigated soils should be ascribed to the low amount of PCBs added and to the fact that phenomena associated to PCBs removal have more influence in irrigated soils than in non-irrigated ones (as it can be readily observed from the persistence values in Table 5). On the other hand, for the MSWC treatment in irrigated soils, in spite of the fact that the amount of PCBs was very similar to that of the CSS treatment, the low values of persistence influenced by the loss mechanisms in irrigated soils and an additional factor dependent on the aggregation state, such as the elimination by intra-organic matter diffusion processes, explain the much larger PCBs losses than for the other types of organic waste materials.

In 2050, the majority of the treatments, applied either to irrigated or to non-irrigated soils, show PCBs concentration values very close to zero, except for the CSS treatment applied to non-irrigated soils, which should be referred to the high amounts of PCBs added, the high content in congeners with a high degree of chlorination, the absence of loss mechanisms associated to irrigation and a state of aggregation that hinders surface exchange processes.

In relation to the PCBs concentration reduction as a function of time for the different treatments, the slowest would correspond to DSS in S1, followed by CSS in S1, MSWC in S1 –with rates similar to those of CSS in S2-, DSS in S2 and finally MSWC in S2. The rate of removal in the soils will depend on the PCBs composition (the higher the concentration in PCBs with a high degree of chlorination, the lower the removal rate), on the state of aggregation (the higher the state of aggregation of the organic waste material, the slower the removal) and on the influence of factors associated to irrigated soils, in which the effect of leaching and movement of particles may favor the disappearance of PCBs (Alcock et al. 1996; Thao et al. 1993). Consequently, the PCBs removal rate should be higher in irrigated soils than in non-irrigated ones, and the highest removal rate would correspond to MSWC (higher content in PCBs with a low degree of chlorination and lowest state of aggregation), followed by CSS and DSS (as the later features the highest state of aggregation).

In short, it may be concluded that –as regards the PCBs content in the soils– there are a number of different factors that influence their concentration and the trend towards their removal: the highest concentration values are observed for those organic waste materials that supply the highest amounts of PCBs with a high degree of chlorination (depending on concentration and amount of organic waste material added) and with longer persistence values (as a function of the type of irrigation, the type of organic waste material and the different PCBs congeners content).

The mean PCBs concentration, established as a background for soils, was expected to be about 5 ng·g^{-1} (Meijer et al. 2003), but the actual values were lower, as a result of the low initial concentration of PCBs in the soils object of this study and their gradual loss to the environment. Therefore, the use of organic waste materials as fertilizers should pose no risk to human health in terms of PCBs content (Rhind et al. 2013). Furthermore, the ban on PCBs manufacture dating from the 70s is leading to a slow disappearance of these chemicals in the environment, thus reducing the risk of exposure with time.

4. Conclusions

PCBs persistence in the agricultural soil was confirmed to depend on the effect of irrigation, organic waste choice and PCBs composition. Irrigation was found to have a major impact: non-irrigated soils showed a greater persistence of PCBs, reaching values up to 90% after four years of application of the organic waste, in comparison to a value of 65% in irrigated soils. The effect of the type of organic waste could be associated with the state of aggregation and the adsorption of PCBs, while PCBs composition in terms of congeners would influence leaching and volatilization processes (provided that congeners with a low-degree of chlorination exhibit higher vapor pressures, lower organic matter adsorption capacity and higher solubility in water). Consequently, the lowest PCB residue would be associated with irrigated soils treated with organic wastes with low aggregation states and an increased content of low-degree of chlorination PCBs. Finally, in view of the results obtained, a rational use of organic waste from urban origin (sewage sludge and municipal solid waste) as fertilizers (< 15 t·ha^{-1}) in agricultural soils with low organic matter content should not lead to an accumulation of PCBs in the soil, neither in the short nor in the long term.

5. References

Alcock RE, Bacon J, Bardget RD, Beck AJ, Haygarth PM, Lee RGM, Parker CA, Jones KC (1996) Persistence and fate of polychlorinated biphenyls (PCBs) in sewage sludge-amended agricultural soils. Environ Pollut 93:83-92. doi:10.1016/0269-7491(96)00002-4

Alcock RE, Johnston AE, McGrath SP, Berrow ML, Jones KC (1993) Long-term changes in the polychlorinated biphenyl content of United Kingdom soils. Environ Sci Technol 27:1918-1923. doi:10.1021/es00046a022

Antolín-Rodríguez JM (2011) Influencia en la acumulación de PCBs por fertilización con bio-residuos en suelos agrícolas. Universidad de Valladolid

Backe C, Cousins IT, Larsson P (2004) PCB in soils and estimated soil–air exchange fluxes of selected PCB congeners in the south of Sweden. Environ Pollut 128:59-72. doi:10.1016/j.envpol.2003.08.038

Ballschmiter K, Zell M (1980) Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. Fresenius' Zeitschrift für Analytische Chemie 302:20-31. doi:10.1007/bf00469758

Beck AJ, Johnson DL, Jones KC (1996) The form and bioavailability of non-ionic organic chemicals in sewage sludge-amended agricultural soils. Sci Total Environ 185:125-149. doi:10.1016/0048-9697(96)05047-4

Bi X, Chu S, Meng Q, Xu X (2002) Movement and Retention of Polychlorinated Biphenyls in a Paddy Field of WenTai Area in China. Agric, Ecosyst Environ 89:241-252. doi:10.1016/s0167-8809(01)00210-9

Birkett JW, Lester JN (2002) Endocrine disrupters in wastewater and sludge treatment processes. CRC Press. doi:10.1201/9781420032185

Clarke BO, Porter NA, Marriott PJ, Blackbeard JR (2010) Investigating the levels and trends of organochlorine pesticides and polychlorinated biphenyl in sewage sludge. Environ Int 36:323-329. doi:10.1016/j.envint.2010.01.004

Cousins IT, Hartlieb N, Teichmann C, Jones KC (1997) Measured and predicted volatilisation fluxes of PCBs from contaminated sludge-amended soils. Environ Pollut 97:229-238. doi:10.1016/s0269-7491(97)00096-1

Creaser CS, Fernandes AR, Harrad SJ, Hurst T, Cox EA (1989) Background levels of polychlorinated biphenyls in British soils - II. Chemosphere 19:1457-1466. doi:10.1016/0045-6535(89)90094-5

Dalla Valle M, Marcomini A, Jones KC, Sweetman AJ (2005) Reconstruction of historical trends of PCDD/Fs and PCBs in the Venice Lagoon, Italy. Environ Int 31:1047-1052. doi:10.1016/j.envint.2005.05.015

Diacono M, Montemurro F (2011) Long-Term Effects of Organic Amendments on Soil Fertility. In: Lichtfouse E, Hamelin M, Navarrete M, Debaeke P (eds) Sustainable Agriculture Volume 2. Springer, Netherlands, pp 761-786. doi:10.1007/978-94-007-0394-0_34

Eljarrat E, Caixach J, Rivera J (1997) Effects of Sewage Sludges Contaminated with Polychlorinated Dibenzo-p-dioxins, Dibenzofurans, and Biphenyls on Agricultural Soils. Environ Sci Technol 31:2765-2771. doi:10.1021/es9610601

European Commission EUR 19657 EN. In: Langenkamp H, Marmo L (eds) Workshop on Problems Around Sewage Sludge, Stresa, Italy, 2000. European Commission, Joint Research Centre,

European Commission (2010) Working Document on Sludge and Biowaste. Brussels, Belgium

Folch I, Vaquero MT, Comellas L, Broto-Puig F (1996) Extraction and clean-up methods for improvement of the chromatographic determination of polychlorinated biphenyls in sewage sludge-amended soils: elimination of lipids and sulphur. J Chromatogr A 719:121-130. doi:10.1016/0021-9673(95)00326-6

Kobližková M, Růžičková P, Čupr P, Komprda Ji, Holoubek I, Klánová J (2009) Soil Burdens of Persistent Organic Pollutants: Their Levels, Fate, and Risks. Part IV. Quantification of Volatilization Fluxes of Organochlorine Pesticides and Polychlorinated Biphenyls from Contaminated Soil Surfaces. Environ Sci Technol 43:3588-3595. doi:10.1021/es9003944

Lamon L, MacLeod M, Marcomini A, Hungerbühler K (2012) Modeling the influence of climate change on the mass balance of polychlorinated biphenyls in the Adriatic Sea. Chemosphere 87:1045-1051. doi:10.1016/j.chemosphere.2012.02.010

Liu L, Tindall JA, Friedel MJ (2007) Biodegradation of PAHs and PCBs in Soils and Sludges. Water, Air, Soil Pollut 181:281-296. doi:10.1007/s11270-006-9299-3

Mamontova EA, Tarasova EN, Mamontov AA, Kuzmin MI, McLachlan MS, Khomutova MI (2007) The influence of soil contamination on the concentrations of PCBs in milk in Siberia. Chemosphere 67:S71-S78. doi:10.1016/j.chemosphere.2006.05.092

McLachlan MD, Horstmann M, Hinkel M (1996) Polychlorinated dibenzo-p-dioxins and dibenzofurans in sewage sludge: sources and fate following sludge application to land. Sci Total Environ 185:109-123. doi:10.1016/0048-9697(96)05046-2

McLachlan MS, Hinkel M, Reissinger M, Hippelein M, Kaupp H (1994) A study of the influence of sewage sludge fertilization on the concentrations of PCDD/F and PCB in soil and milk. Environ Pollut 85:337-343. doi:10.1016/0269-7491(94)90056-6

Meijer SN, Ockenden WA, Sweetman A, Breivik K, Grimalt JO, Jones KC (2003) Global Distribution and Budget of PCBs and HCB in Background Surface Soils: Implications for Sources and Environmental Processes. Environ Sci Technol 37:667-672. doi:10.1021/es025809l

Molina L, Díaz-Ferrero J, Coll M, Martí R, Broto-Puig F, Comellas L, Rodríguez-Larena MC (2000) Study of evolution of PCDD/F in sewage sludge-amended soils for land restoration purposes. Chemosphere 40:1173-1178. doi:10.1016/s0045-6535(99)00366-5

Rhind SM, Kyle CE, Ruffie H, Calmettes E, Osprey M, Zhang ZL, Hamilton D, McKenzie C (2013) Short- and long-term temporal changes in soil concentrations of selected endocrine disrupting compounds (EDCs) following single or multiple applications of sewage sludge to pastures. Environ Pollut 181:262-270. doi:10.1016/j.envpol.2013.06.011

Ryan JA, Bell RM, Davidson JM, O'Connor GA (1988) Plant uptake of non-ionic organic chemicals from soils. Chemosphere 17:2299-2323. doi:10.1016/0045-6535(88)90142-7

Smith SR (2009) Organic contaminants in sewage sludge (biosolids) and their significance for agricultural recycling. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 367:4005-4041. doi:10.1098/rsta.2009.0154

Thao VD, Kawano M, Tatsukawa R (1993) Persistent organochlorine residues in soils from tropical and sub-tropical asian countries. Environ Pollut 81:61-71. doi:10.1016/0269-7491(93)90029-n

Tideström H Swedish Regulation on the Use of Sewage Sludge in Agriculture. In: Specialty conference on management and fate of toxic organics in sludge applied to land. Copenhagen, 1997.

Umlauf G, Christoph EH, Lanzini L, Savolainen R, Skejo H, Bidoglio G, Clemens J, Goldbach H, Scherer H (2010) PCDD/F and dioxin-like PCB profiles in soils amended with sewage sludge, compost, farmyard manure, and mineral fertilizer since 1962. Environmental Science and Pollution Research 18:461-470. doi:10.1007/s11356-010-0389-9

UNEP (2011) Report of the Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants on the work of its fifth meeting, 5th edn., Geneva, Switzerland

US Environmental Protection Agency (1996) Method 3540C: Soxhlet Extraction, Revision 3. U.S. EPA, Washington DC, United States

US Environmental Protection Agency (2007) Method 8082A (SW-846): Polychlorinated Biphenyls (PCBs) by Gas Chromatography, Revision 1. U.S. EPA, Washington DC, United States

Vecchiato M, Zambon S, Argiriadis E, Barbante C, Gambaro A, Piazza R (2015) Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in Antarctic ice-free areas: Influence of local sources on lakes and soils. Microchem J 120:26-33. doi:10.1016/j.microc.2014.12.008

Wilson SC, Alcock RE, Sewart AP, Jones KC (1997) Persistence of Organic Contaminants in Sewage Sludge-Amended Soil: A Field Experiment. J Environ Qual 26:1467. doi:10.2134/jeq1997.00472425002600060004x

Wöhrnschimmel H, MacLeod M, Hungerbuhler K (2012) Global multimedia source-receptor relationships for persistent organic pollutants during use and after phase-out. Atmospheric Pollution Research 3:392-398. doi:10.5094/apr.2012.045

Yeo H, Choi M, Chun M, Kim T, Cho K, Sunwoo Y (2004) Concentration characteristics of atmospheric PCBs for urban and rural area, Korea. Sci Total Environ 324:261-270. doi:10.1016/j.scitotenv.2003.10.031

Zennegg M, Munoz M, Schmid P, Gerecke AC (2013) Temporal trends of persistent organic pollutants in digested sewage sludge (1993–2012). Environ Int 60:202-208. doi:10.1016/j.envint.2013.08.020

Zhu C, Li Y, Wang P, Chen Z, Ren D, Ssebugere P, Zhang Q, Jiang G (2015) Polychlorinated biphenyls (PCBs) and polybrominated biphenyl ethers (PBDEs) in environmental samples from Ny-Ålesund and London Island, Svalbard, the Arctic. Chemosphere 126:40-46. doi:10.1016/j.chemosphere.2015.01.043