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LEVELS OF PERSISTENT ORGANOCHLORINE COMPOUNDS IN SEWAGE SLUDGE FROM WASTEWATER TREATMENT PLANTS

Mihaela PREDA, Veronica TĂNASE, Nicoleta Olimpia VRÎNCEANU

National Research and Development Institute for Soil Science, Agrochemistry and Environment, Marasti 61, 011464, District 1, Bucharest,
phone: +40-0213184458, fax: +40-0213184348,
Emails: office@icpa.ro, mihaela.preda@icpa.ro, veronica.tanase@icpa.ro, nicoleta.vrinceanu@icpa.ro

Corresponding author email: mihaela.preda@icpa.ro

Abstract

The use of sewage sludge as fertilizer in agricultural soils is considered an economical way to use the high amounts produced by wastewater treatment plants. Besides the benefit, meaning high content of organic matter and nutrients, sewage sludge can have a negative impact on environment because it can contain persistent organic pollutants or heavy metals. The aim of this study is to establish the level of polychlorinated biphenyls (PCBs) and organochlorine insecticides in sewage sludge collected from 10 wastewater treatment plants. The PCB IUPAC no. 28, 52, 101, 118, 138, 153, 180 and ten organochlorines were extracted with organic solvents, purified with copper and silicagel and analysed by gas chromatography/time of flight mass spectrometry. The concentration of total PCBs ranged from 3ng/g to 59.2ng/g dry weight, levels below the upper limit for land application according to Romanian legislation law for agricultural use. The predominant congeners found in sewage sludge were PCB 28, PCB 52 and PCB 138. PCB homologue profiles are dominated by Tri-CBs and Tetra-CBs. The contamination of sewage sludge samples with organochlorine insecticides refers only to the presence of DDE and dieldrin. The other insecticides (aldrin, HCH, ppDDT and ppDDD) are undetectable.

Key words: *organochlorine insecticides, PCBs, sewage sludge.*

INTRODUCTION

Sewage sludge is a by-product of the waste water treatment processes. It contains nutrients and organic matter that can improve soil productivity, so it is widely used as soil amendments.

Land application of treated sewage sludge has been adopted worldwide as a sustainable and economical option for sewage management.

Besides the benefit, sewage sludge can have a negative impact on environment because it can contain persistent organic pollutants or heavy metals. Thus, sewage sludge can be a source of polychlorinated biphenyls.

Polychlorinated biphenyls (PCBs) and organochlorine insecticides (OCLs) constitute two classes of compounds which are of prime concern due to their extreme persistence in the environment and potential for biomagnification. They also could be responsible for a series of negative effects on life and environment even at low concentrations (Jones et al., 1991).

PCBs have an unusual high chemical stability, high electrical resistance, low volatility and resistance to degradation in the presence of high temperatures, so they have numerous industrial applications. Thus, PCBs were used as dielectric fluids in capacitors and transformers, as hydraulic fluids in mining equipment, as heat transfer fluids or vacuum pumps; they were also used as plasticizers and additives, as lubricating and cutting oils (Jones et al., 1991).

Because of their lipophilic nature, PCBs and OCLspreferentially partition on sludge during wastewater treatment. It seems that these organic pollutants enter the wastewater stream by direct or indirect release from household or industry or by atmospheric deposition on surface and then runoff into the wastewater treatment system (Blanchard et al., 2001).

In 1973 it was thought that PCBs are 210 compounds that differ in number and position of chlorine atoms (Jones et al., 1991). Later, the scientists considered the theoretical existence of 209 isomers of PCBs, of which about 150 was found in the environment (Larsen and Bowardt, 1993).

PCB isomers have different toxicities. Non-ortho substituted PCBs (IUPAC no. 77, 81, 126 and 169) belong to the group with the highest toxicity, the mono-ortho substituted (60, 105, 110, 114, 118, 156, 157, 167) are moderately toxic, while the remaining 197 are relatively nontoxic (Soniassy et al., 1994). Among these congeners, 12 have similar toxicity to that of dioxins (PCDD/Fs) and to avoid the complexity involved in the determination, 7 indicator have been selected to monitor PCBs (PCB with IUPAC no. 28, 52, 101, 118, 138, 153, 180).

Of the large number of insecticidal compunds produced, the HCH isomer, lindane (γ-hexa-chlorocyclohexane), aldrin, dieldrin, and dichlorodipheniltrichloroethane (DDT isomers and metabolites) have been those most frequently detected in environmental samples (Babish et al., 1981) although these residues have declined in recent years as a result of legislative proscription of their use. Due to these properties PCBs and part of OCLs were included on the list of Priority Organic Pollutants (POPs), adopted at Stochkolm Convention in 2001.

The occurence of PCBs in waste waters may arise from a number of sources, both industrial and domestic (Lester, 1983), including aqueous effluents from transformer and capacitormanu-facturing, investment cating plants, waste paper recyclingoperations (McIntyre and Lester, 1984).

One of the first reports of PCBs in sludge was of six USA sewage sludges (Bergh and Peoples, 1977). The concentration are very high compared with another studies, about 756000 ng/g, probably because at that time, PCBs were still commonly used (Clarke et al., 2010).

In 1990s, the concentrations of PCBs in sludges were declining and were often below 1000 ng/g. For example, italian sludges analysed had PCB concentration between 210 and 1010 ng/g (Ottaviani et al., 1993).

By the new millenium, the concentration of PCBs in sewage sludge had decreased to 500ng/g. For example, in a survey of Canadian sludges PCBs were not detected in any of the samples (Bright and Healey, 2003). A survey of Spanish sludges from twenty waste water plants reprted low PCB concentration ranging between 3 and 60 μg/kg (Abad et al., 2005). This is below the European recommended limit of 800 μg/kg. In fact, all European studies had concentrations lower than the European contaminant limit.

Regarding OCLs, theymay enter the waste water treatment plants process from industrial discharge or as a component of urban runoff or drainage into the system. However, little researh has been carried out to investigate the environmental pathways and source of these compounds in sludge. Clarke et al. in 2010 considered that the most iluminating work was a study by Nylund etal., in 1997 that measured the concentration of organic contaminants in sewage sludge during a dry and rainy period. They found that the concentrations of DDT increased from 39 μg/kg in a dry period to 68 μg/kg in a wet period and suggested that atmospheric deposition facilitates the move-ment of this pesticides to the wastewater treat-ment plants. This suggests that a significant portion of DDT are either washed out of the atmosphere with rain or rainfall washes out pesticide residues from the urban environment. The concentration of lindane was not signi-ficantly different between the two periods (8.7 and 7.8 μg/kg) which suggests that precipi-tations does not play an important role in the movement of lindane. Also, it was reported that 67±10% of lindane can be effectively removed by wastewater because it has a higher vapour pressure so it could be volatilised particularly in an aeration basin of an activated sludge (Kipopoulou et al., 2004).

Another study was developed by McIntyre and Lester in 1984 in UK.They reported the following concentration: lindan - 340 ng/g; aldrin - 30 ng/g; and dieldrin:- 500 ng/g.Also, in an analysis of digested sludge from fourteen UK waste water treatment plants, HCH, HCB, endosulfan, DDT, DDE, DDD and chlordan were often below the detectable limit (Stevans et al., 2003). The concentration of two of the compounds above the detection limit were HCB and DDE. This observation is related to declining use of OCLs in Europe. HCB, like other chlorobenzenes, has industrial applications, which may account for its continuing presence in all the samples (Clarke et al., 2010).

Another report of sewage sludge analysed for OCLs came from data collected from 31 waste water plants from China. Concentration of

HCH (all four isomers) were not regularly detected and the concentration was below limit of detection for all isomers (Wang et al., 2007). The presence of DDT was detected frequently and HCB was detected in all samples. The source of DDT may be diclofol which is still used in China, and HCB is associated with the production of pentachloronitrobenzene (Wang et al., 2007).

MATERIALS AND METHODS

Thesewage sludge samples were collected from 10 wastewater plants situated in urban and industrialized areas. From each plants were collected ten treated sewage sludge samples. Because both PCBs and OCLs are lipophilic compounds, their adsorption on solid particles depends on organic matter. Thus, an important propertie who has to be determined is organic carbon which has high values ranged between 19,2% and 30%. pH range between 5.4 and 7.2. Samples were packed in aluminium foil and directly delivered to the laboratory and stored in a refrigerator. The determination of the PCBs (IUPAC no. 28, 52, 101, 118, 138, 153 and 180) and OCLs (α, β, γ, δ-HCH, aldrin, dieldrin, pp DDE, ppDDT, ppDDD) were performed according with SR EN 15308 and EPA 8081, respectively.

10 g of air-dried sample was mixed with anhydrous sodium sulphate, placed in extraction thimble and Soxhlet extracted for a minimum of 100 extraction cycles with approximately 150 ml acetone/hexane mixture. Acetone is removed with water and organic extract is reduced to an appropriate volume.

The extract clean-up is a very important step and involved purification with copper (to remove sulfur), sulfuric acid (to remove lipids). The resulting extract is separated on silicagel column and it is divided in two fractions. The first fraction contain PCBs, aldrin and DDT, and the second fraction contains HCH and dieldrin. The final extract is injected in a gas chromatograf coupled with time of flight mass spectrometer.

Separation and identification of the target compounds were performed with an Agilent 7890A gas chromatograph coupled with a time-of-flight mass spectrometer TruTOF™HT.

This system operate with a non-polar stationary phase cappillary column (DB-5MS with 60 m x 0.25 mm x 0.25 μm) with programmed temperature (from 100°C to 330°C with 20°C/minute).

The injector and transfer line temperatures were 250°C and 270°C, respectively. The carrier gas was helium 6.0 at 1ml/min. Injection volume was 1μl in splitless mode. HRMS was operated in selected ion monitoring (SIM) mode. The calibration curve is made from at least five standard solutions with equidistant concentrations.

All solvents are high purity grade for chromatographycompliyng with SR EN 15308 and EPA 8081.

Quality control is assured through the use of a certified reference material (LG6184). All samples are analyzed in three replicates and to avoid the contamination, a blank is running parallel with the samples. The blank shall be less than 50% of the lowest reporting limit. Also, before extraction, Soxhlet equipment were washed for 6 hours with 250 ml hexane.

RESULTS AND DISCUSSIONS

The analytical results of PCBs concentration in sewage sludge samples collected from wastewater plants (W) are presented below (Table 1). The total concentration of PCBs ranged from 3 ng/g to 59.2 ng/g.

The highest levels were detected at W5, were all isomers are presents, suggesting a possible industrial effluent discharge source. According to Romanian Regulation (Order no. 344/2004) PCBs levels should be less than 0.8mg/kg dry weight for agricultural use. We have to mention that, from all PCB compounds, in this study were quantified only seven.

Regarding the isomers concentration, it can be observed that trichloro- and tetrachloro-biphenyls (PCB 28 and PCB 52) are the most dominant (21.8% - 46.8% for PCB 28 and 20.7% - 53.3% for PCB 52). Contribution of pentachlorobiphenyls (PCB 101 and PCB 118) at total concentration is less than 17% and hexachlorobiphenyls (PCB 138 and PCB 153) represents less than 25% from total concentration of PCBs.

The higher concentration of PCB 180 (isomer with seven chlorine atoms) is 5.2 ng/g and it was detected in W5 (Figure 1).

Table 1. Mean concentration (ng/g) of PCBs in sludge from waste water plants (W)

PCB congener	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10
PCB 28	5.8	2.8	3.8	8.9	15.4	2.3	1.4	1.4	3.4	2.8
PCB 52	6.5	2.7	4.3	5.8	21.6	2.1	2.6	1.6	3.4	2.4
PCB 101	1.5	1.7	1.6	1.2	5.8	0.3	0.8	-	1.9	0.8
PCB 118	-	0.4	-	0.1	0.4	-	-	-	0.3	-
PCB 138	0.6	1.9	-	1.5	2.6	0.8	0.7	-	1.6	0.3
PCB 153	0.8	1.1	-	0.6	8.2	0.6	0.4	-	1.4	0.6
PCB 180	1.3	2.4	-	0.9	5.2	0.2	0.5	-	1.3	0.2
Total PCB	**16.5**	**13**	**9.7**	**19**	**59.2**	**6.3**	**6.4**	**3**	**13.3**	**7.1**

Similar concentration were reported in sludge in Beijing were the isomers concentration ranged between 7.5-19.4 ng/g (Guo Li et al., 2009).
Another studies gave contents between 0.19 ng/g and 72.5ng/g (Souze Pereira and Kuch, 2005).
The concentrations founded in this study are lower than those founded in Germany were the PCBs concentration range between 60 ng/g and 212 ng/g (Lindholm-Lehto et al., 2016). Regarding the profiles of PCB isomers, this study indicate similar results with those obtained by the researchers from Valencia who also observed that PCBs in sludge samples were dominated by low chlorinated compounds (Gomez-Rico et al., 2007).

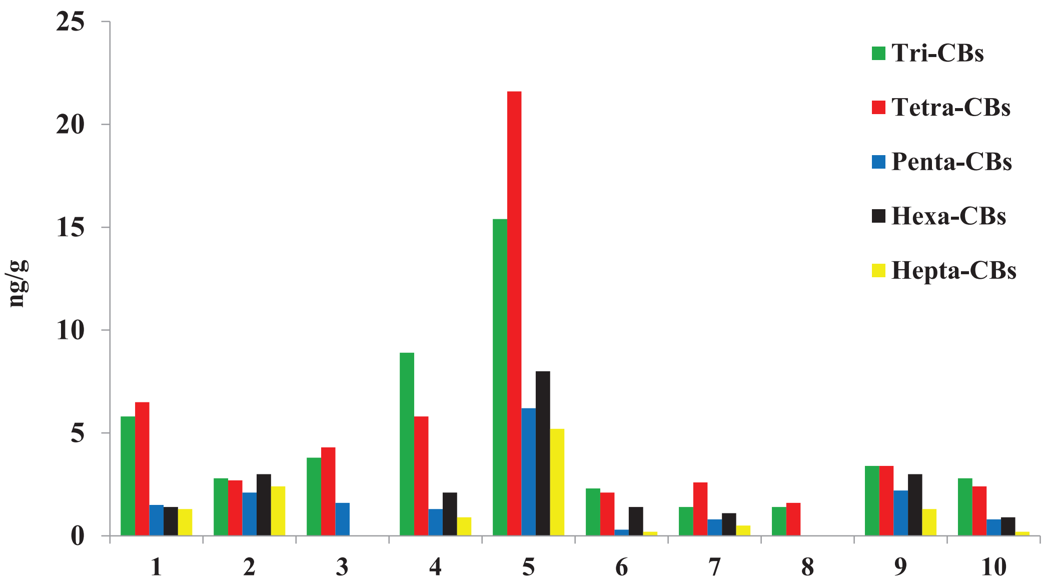

Figure 1. PCB homologue profiles of the sewage sludge samples

Regarding the contamination of sewage sludge with organochlorine insecticides it can be observed that HCH isomers, aldrin, ppDDD and ppDDTare not detectable in all samples. Dieldrin was found sporadically only in two samples with concentrations 26 ng/g, respectively 28 ng/g. ppDDE contaminate 4 samples with concentrations ranged between 18 ng/g and 56 ng/g.

Total DDT is a sum of ppDDE, ppDDD and ppDDT, so it is reasonable to assume that the contribution of total DDT is comprised of ppDDE.
The presence of DDE in sewage sludge samples may be connected to breakdown of DDT to DDE in environment (Figure 2).

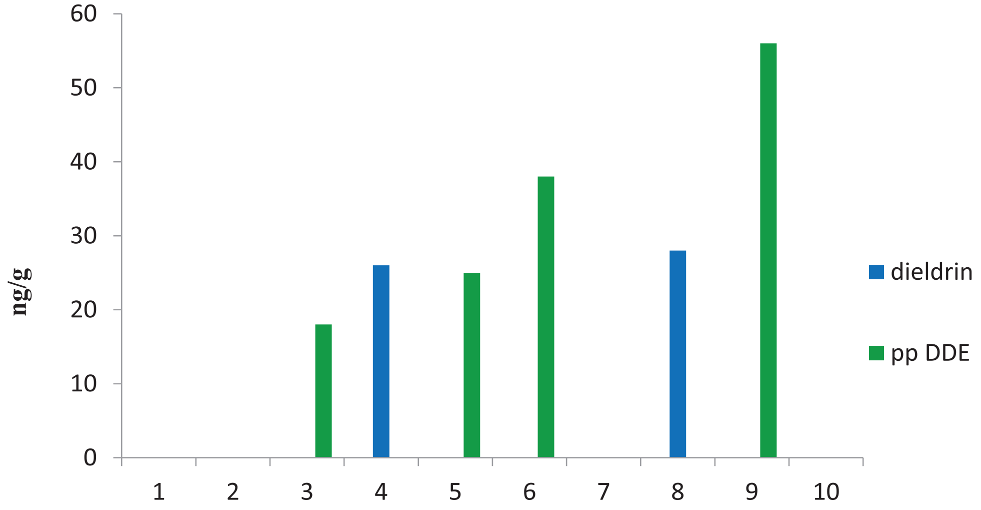

Figure 2. Distribution of organochlorine insecticides in sewage sludge samples

CONCLUSIONS

The present sudy indicate a low contamination of sewage sludge with PCBs and organochlorine insecticide.

PCB homologue profiles are dominated by trichloro biphenyls (PCB 28) and tetrachloro biphenyls (PCB 52).

HCH isomers, aldrin, pp DDT and pp DDD were not detected in any sewage sludge samples, instead DDE contaminate 4 samples.

The presence of pp DDE is connected with breakdown of pp DDT. Dieldrin was only sporadically detected.

The presence of these organic pollutants in sewage sludge samples, even at low levels, draws attention to the necessity of monitoring its content in sludge in order to avoid contamination of land and to assure human and environmental safety.

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