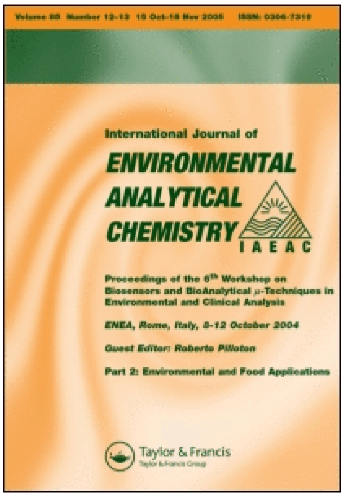

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Occurrence of organochlorine pesticides and polychlorinated biphenyls in soils and sediments from Eastern Romania

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Occurrence of organochlorine pesticides and polychlorinated biphenyls in soils and sediments from Eastern Romania

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Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), such as DDT and analogues, hexachlorocyclohexane (HCH) isomers and hexachlorobenzene (HCB), were measured in surface soils and sediments from Eastern Romania. Thirty-nine soil samples from the forested zone, eight soil samples from a municipal waste-disposal site, and 10 sediment samples from the Bahlui River along the Iassy city were analysed using accelerated solvent extraction (ASE) and gas chromatography coupled to electron capture detection or mass spectrometry. The low mean concentrations of OCPs (11–31 and 22–84 ng g^{-1} for HCHs and DDTs, respectively) and PCBs (8–43 ng g^{-1}) in soil samples from the forested zone suggest that contamination at most of these sites occurred predominantly through atmospheric transport from zones where these compounds were used and subsequently through atmospheric deposition. Contrarily, soil samples collected in the vicinity of a waste-disposal site near Iassy contained higher mean levels of PCBs (278 ng g^{-1}, range 34–1132 ng g^{-1}) than OCPs (6 and 101 ng g^{-1} of soil for HCHs and DDTs, respectively). The sediment samples collected along the Bahlui river throughout the Iassy city revealed higher mean levels of PCBs (59 ng g^{-1}, range 24–158 ng g^{-1}) compared with OCP levels (2 and 37 ng g^{-1} of soil for HCHs and DDTs, respectively). Furthermore, PCB profiles and concentrations in the sediment samples varied considerably along the river due to a wide variety of sources, such as different industries and waste sites. Although their sources are difficult to evaluate, the presence of POPs at most sites (especially at the waste-disposal site) may constitute a potential health hazard.

Keywords: Organochlorine pesticides; Polychlorinated biphenyls; Soil; Sediment; Romania

1. Introduction

Persistent organic pollutants (POPs), such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), have been released into the environment through agricultural and/or industrial activities, as well as accidental spills [1]. Soils are natural sinks where hydrophobic POPs may accumulate and be retained for many years [1–3].

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Various processes occur in soil, namely, exchange with the atmosphere, biodegradation, formation of strongly bound residues, and burial to depth [4, 5]. Some soils receive inputs of POPs from dumping procedures, pesticide usage, sewage sludge disposal, waste disposal, and agricultural amendments. However, all soils, even in remote areas, receive inputs from atmospheric deposition. The principal loss pathways are volatilization, degradation and leaching, which are highly dependent on the type of soil, environmental variables (e.g. temperature), and the physico-chemical properties of the pollutant [6, 7]. Therefore, soils are very important in the fate and distribution of POPs in the environment because of their huge retention capacity and role as re-emission source for the atmosphere [8, 9]. Also, sediments are one of the major sinks for these contaminants in the aquatic environment. The study of sediments is an important step in mapping possible exposure pathways to various aquatic organisms.

Information regarding POP distribution from Western Europe is abundant, and inventories of sources and polluted sites are being developed [1]. However, much less information is available on Eastern Europe, including Romania, although large amounts of POPs have been used for industrial and agricultural purposes [10]. In Romania, OCPs, in particular dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexanes (HCHs), were used extensively for agricultural purposes until their ban in 1985. However, owing to their high persistence, residues of these substances continue to be found in Romanian environmental compartments [11–13].

The main purpose of the present study was to investigate the levels and distribution of OCPs and PCBs in soil from several counties in Eastern Romania collected predominantly in forest zones. Additionally, soil samples from a waste-disposal site and sediment samples from Bahlui river (Iassy city) were also studied.

2. Experimental

2.1 *Sampling area and sample description*

Surface soil samples (depth 5 cm, $n = 39$) were collected in 2002 from eight counties (Botosani, Suceava, Neamt, Iasi, Bacau, Vrancea, Vaslui, and Galati) from the Moldavia region situated in Eastern Romania. Moldavia covers an area of 46,145 km^2, starting from the Eastern Carpathians and ending by the Prut River (figure 1). The sampling points were located at least 200–500 m from any principal road in forested zone. Additionally, soil samples ($n = 8$) were collected in March 2005 from a waste-disposal site near Iassy city, while sediment samples ($n = 10$) were collected downstream of Bahlui River (a tributary of Prut River) throughout Iassy city. Soil and sediment samples were dried at room temperature, stones and vegetation removed, homogenized, sieved through a steel mesh (500 µm grid size), and sealed in air-tight polyethylene containers for storage at room temperature until analysis.

2.2 *Materials*

The OCPs under investigation were α-, β-, γ-HCH, DDT, and analogues (o,p'-DDE; p,p'-DDE; o,p'-DDD; o,p'-DDT; p,p'-DDD; p,p'-DDT) and hexachlorobenzene (HCB). The following congeners (IUPAC numbers) were targeted: 28, 31, 52, 74, 95, 99, 101, 105, 110, 118, 128, 138, 149, 153, 156, 170, 180, 183, 187, 194, and 199. The internal

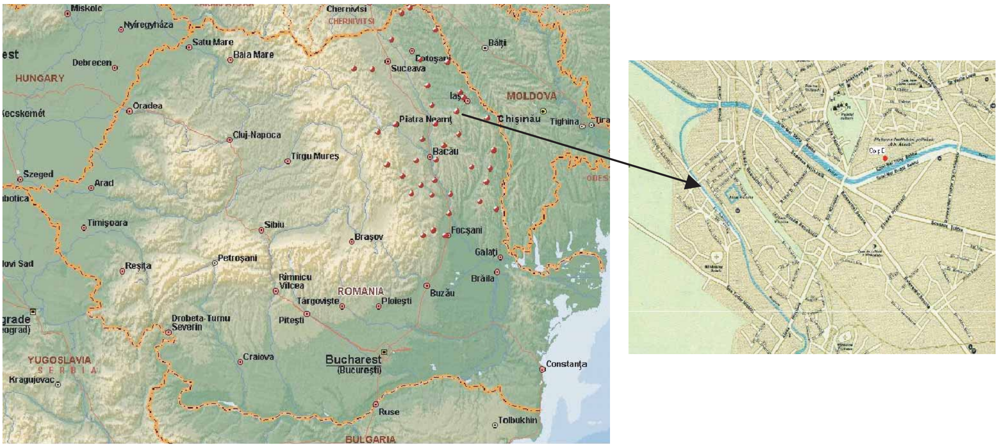

Figure 1. Map of Romania showing the sampling sites for the forested zone. The detailed map of the Bahlui River throughout Iassy City shows the sediment sampling sites.

standards were PCB 46, PCB 143, ε-HCH, while 1,2,3,4-tetrachloronaphthalene (TCN) was used as a recovery standard. All individual PCB and OCP standards were purchased from Dr. Ehrenstorfer Laboratories (Augsburg, Germany). Dilutions were made in iso-octane, in order to cover the entire of POPs expected in the samples, and stored at −20°C. Acetone, *n*-hexane, dichloromethane, and iso-octane were of pesticide grade (Merck, Germany). Analytical-grade concentrated sulphuric acid (95–97%) was purchased from Merck. Anhydrous sodium sulphate (Na_2SO_4), copper powder (63 µm), and silica gel (70–230 mesh) (Merck) were washed with hexane and used after heating overnight at 120°C. Acidified silica gel (44% H_2SO_4, w/w) was prepared as previously described [14]. Empty polyethylene cartridges (25 mL) were purchased from Alltech (Lokeren, Belgium).

2.3 *Sample extraction and clean-up*

Extractions were performed using an accelerated solvent extraction (ASE) system (Dionex, Sunnyvale, CA) using previously suggested instrumental settings [15, 16] with some modifications, such as the number of cycles, pressure, cell volume, purge time, and solvent mixture. The parameters used during the extraction procedure are described in table 1.

To eliminate interferences and avoid cross-contamination, extraction cells were pre-extracted with hexane–acetone (3 : 1, v/v) at 100°C and 2000 psi during 5 min. One gram of dried soil was introduced in the cell and spiked with 15 ng of each internal standard. Based on previous experiments, hexane–acetone (3 : 1, v/v) was selected as the most efficient mixture solvent for the extraction of OCPs and PCBs from soil samples [14].

The extract was concentrated to 2 mL under a nitrogen stream and further purified on 8 g of acidified silica as previously described [14] using 15 mL of hexane and 10 mL of dichloromethane for elution of analytes. The purified extract was concentrated under a nitrogen stream until dryness, resolubilized in 100 µL of iso-octane, and transferred

Table 1. Accelerated solvent extraction parameters.

Parameters	Values
Temperature	100°C
Pressure	2000 p.s.i.
Static time	5 min
Heat time	5 min
Solvent	*n*-hexane–acetone (3 : 1, v/v)
Cycle	3
Flush volume	60%
Purge time	100 s
Cell volume	5 mL

to a vial for GC analysis. For sediments, the procedure described by Covaci *et al.* [17] was used. The sediment sample (~1 g) was mixed with 3 g of copper powder (63 µm, Merck), extracted, and subjected to the clean-up described above for soil.

2.4 *Instrumentation*

Instrumental conditions have been described previously [14, 17] and are briefly presented below. An Agilent Technologies (Palo Alto, CA) 6890 GC-µECD was equipped with a 25 m × 0.25 mm × 0.25 µm HT-8 capillary column (SGE, Zulte, Belgium). One microlitre was injected in pulsed splitless mode (initial pressure = 17.9 psi, pulse pressure = 40 psi, pulse time = 1.5 min) with the split outlet opened after 1.5 min. The injector and detector temperatures were set at 300 and 330°C, respectively. Helium was used as the carrier gas at a constant flow (1.0 mL min^{-1}), while argon/methane (95/5, v/v) was used as the make-up gas (25 mL min^{-1}). The temperature programme of the oven was set to 90°C for 1.5 min, then 30°C min^{-1} to 180°C, and then 5°C min^{-1} to 300°C, kept for 15 min.

Samples with high concentrations of POPs were confirmed by GC/MS (Agilent Technologies) operated in electron impact ionization mode and equipped with a 30 m × 0.25 mm × 0.25 µm DB-1 capillary column (J&W Scientific, Folsom, CA). The ion source, quadrupole, and interface temperatures were 230, 150, and 300°C, respectively. Helium was used as carrier gas at a constant flow of 1.0 mL min^{-1}. The mass spectrometer was operated in the selected ion monitoring mode, and the electron multiplier voltage was set at 2200 V. One microlitre of the extract was injected in cold splitless mode (injector temperature at 100°C, (0.03 min), then heated at 700°C min^{-1} to 300°C, pulse time 1.5 min, splitless time 1.50 min, pulse pressure 25 psi). The temperature programme of the oven was set to 90°C for 1.5 min, then 15°C min^{-1} to 180°C, kept for 1 min, then 5°C min^{-1} to 280°C, and further by 40°C min^{-1} to 300°C, kept for 16 min. Dwell times were set to 25 ms. Specific ions for the investigated POPs were monitored for the entire run.

2.5 *Quality assurance*

Multi-level curves were created for the quantification, and a good linearity ($r^2 > 0.999$) was achieved for the tested intervals that included the whole concentration range found in the samples. The identification of analytes was based on relative retention time and, for samples confirmed by GC-MS, on ion chromatograms for each analyte. A certified reference material CRM 481 (PCBs in industrial soil, BCR, Belgium) was analysed in triplicate throughout the study, and the values obtained for PCB congeners were all within 10–15% of the certified values. Recoveries of the internal standards (calculated based on TCN) in soil and sediment samples ranged between 63 and 90%. Procedural blanks were performed with each set of five samples, and the obtained values were subtracted from the values found in the samples. Method limits of quantification (LOQ) for individual PCBs and OCPs ranged between 0.1 and $1\,\mathrm{ng\,g^{-1}}$, except for CB 52 ($2.5\,\mathrm{ng\,g^{-1}}$). The LOQs were established at 3 × SD of the procedural blanks, resulting in a certainty of more than 95% for results given for the samples [17].

3. Results and discussion

3.1 *Soil samples from the forested zone*

The organochlorines analysed were detected in all soil samples from the forested zones and presented a wide range of variation between the eight counties (table 1). The concentrations of OCPs were in the following range: 0.2–1.4, 5–56, and $5–95\,\mathrm{ng\,g^{-1}}$ of soil for HCB, sum HCHs, and sum DDTs, respectively. Two samples containing higher concentrations of HCHs and DDTs collected from Bacau county (near industrial sites) were not included in the calculations of means.

The variation of HCH isomers in the analysed samples revealed a heterogeneous nature of distribution (figure 2). The γ-HCH isomer was predominant (54–74%), followed by β- and α-HCH isomers (8–22 and 18–28%, respectively). However, a higher contribution of β-HCH together with the highest HCH concentration ($180\,\mathrm{ng\,g^{-1}}$ of soil) measured in the samples was observed in one sample from Bacau. This sample exceeded the Romanian permitted value ($50\,\mathrm{ng\,g^{-1}}$ of soil) for β-HCH in agricultural soil [18]. In Romania, two HCH formulations were used in the past: technical lindane, containing 60–70% γ-HCH, 5–12% γ-HCH and 10–12% γ-HCH,

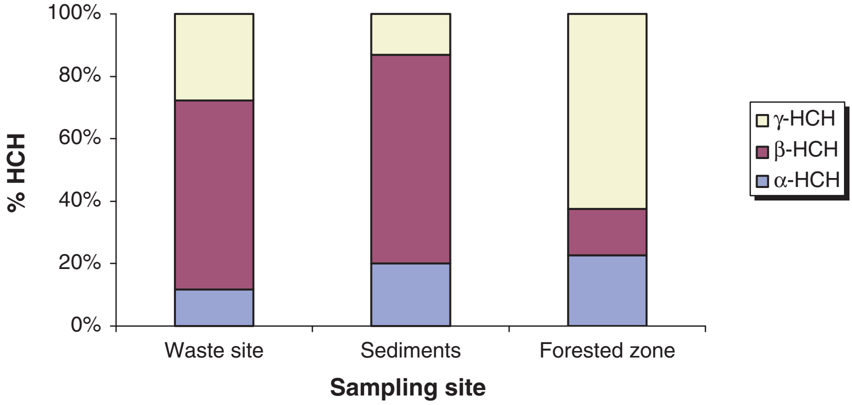

Figure 2. Percentage distribution of HCH isomers in soil and sediment samples from eastern Romania.

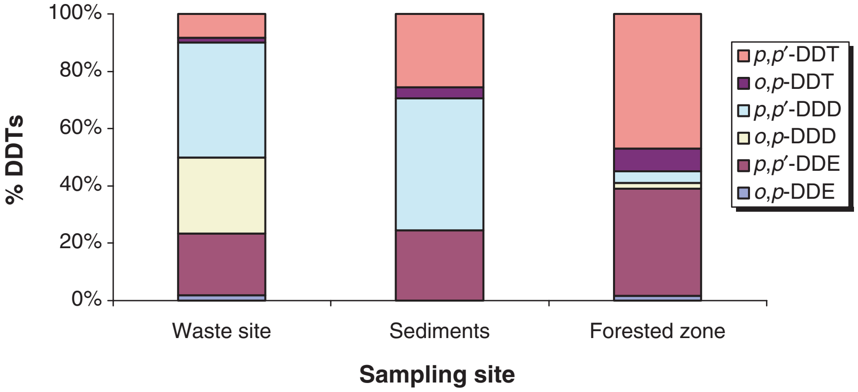

Figure 3. Percentage distribution of DDT analogues in soil and sediment samples from eastern Romania.

and pure γ-HCH (lindane). Only γ-HCH is insecticidal, while β-HCH is more bioaccumulative [19]. Additionally, α-HCH has higher values for the Henry's law constant and vapour pressure than β- and γ-HCH [19], indicating a greater affinity for atmospheric transport than other isomers. These factors may account for the presence of α-HCH in all soil samples. Moreover, low values of the α-HCH/γ-HCH ratio (<1) obtained for 38 out of 39 samples suggested the usage of pure lindane rather than technical lindane and thereby a predominant contamination through atmospheric deposition of isomers volatilized from treated agricultural soils [20].

The DDTs were detected in all samples, but the contribution of individual analogues showed a great variation (figure 3). In general, *p,p′*-DDT and *p,p′*-DDE had a higher relative contribution than the other isomers (50% and 40% for *p,p′*-DDT and *p,p′*-DDE, respectively). The occurrence of DDT analogues varied in the following order: *p,p′*-DDT > *p,p′*-DDE ≫ *p,p′*-DDD > *o,p′*-DDD > *o,p′*-DDE > *o,p′*-DDT. A *p,p′*-DDT/*p,p′*-DDE ratio higher than 1 for most samples can be attributed to the more recent use of DDT in Romanian agriculture compared with Western Europe (DDT was banned in 1985 in Romania) and to a very slow degradability with a half-life in soil of 672 days [21]. The dominance of *p,p′*-DDT in soil samples in Romania has been previously reported [12, 22]. Furthermore, the concentrations of DDTs were higher than those of HCHs, probably due to the use of DDT in agriculture in larger amounts than the HCH formulations and to a lesser extent due to differences in physico-chemical and biological properties. HCHs have a higher water solubility, higher vapour pressure, higher biodegradability, lower lipophilicity, and lower affinity for particles compared with DDTs [23].

Concentrations of HCB were very low (up to $1.4\,\mathrm{ng\,g^{-1}}$ of soil) in accordance with previously reported concentrations of HCB in Romanian agricultural soils [12]. Although HCB was used as fungicide and can be generated as a by-product during the production of chlorinated chemicals or during waste incineration [24], the low levels of HCB in soil from the forested zone are consistent with its limited sources and its volatile nature. Atmospheric deposition is seen as the main source of HCB.

The PCB levels were lower than the levels of DDTs and HCHs. In all samples, tetra-CB congeners were predominant, followed by tri- and penta-CBs (figure 4). Congeners PCB 52 and PCB 74 were found to be the major contributors to the total

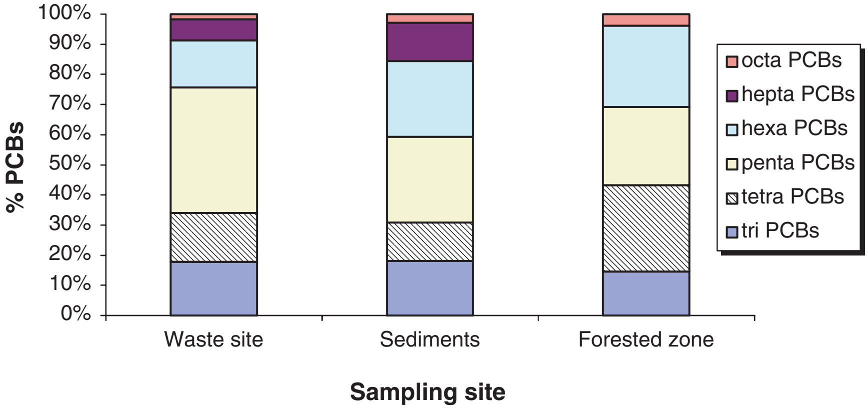

Figure 4. Percentage distribution of PCB congeners in soil and sediment samples from Eastern Romania.

PCB levels, and their contribution ranged between 6 and 18% and between 3 and 20%, respectively. The presence of PCBs in low concentrations in soil samples from the forested zones, together with a predominance of low chlorinated congeners (more volatile), points to atmospheric transport and deposition as principal mechanisms of PCB pollution.

3.2 *Soil samples from the waste-disposal site*

Means, standard deviations, and ranges of concentrations of PCBs and OCPs in soil samples from the waste-disposal site are shown in table 2. Concentrations of PCB congeners range from 34–1132 ng g^{-1} of soil, with a mean value of 278 ng g^{-1} of soil, and these are higher than the levels measured in soil samples from the forested zone. These values also exceeded previously reported levels in soils from urban, industrial, and waste sites in Romania (58, 722, and 63 ng g^{-1} of soil, respectively) [12]. In all samples, the relative contribution of penta-CB congeners was predominant (37%), followed by tri- and tetra-CBs (figure 4). This particular PCB profile, together with the high PCB levels, suggests the presence of two Aroclor mixtures (1242 and 1248) in this area. Two samples containing 371 and 1131 ng g^{-1} of soil for the sum PCBs exceeded the Romanian reference value (250 ng g^{-1} of soil) for PCBs [18].

The major OCPs in the soil samples from the waste-disposal site were DDTs (8–210 ng g^{-1} of soil for sum DDTs, mean 101 ng g^{-1} of soil). The ratio between p,p'-DDT and p,p'-DDE was between 1.3 and 2.5, indicating that extensive DDT contamination had occurred in the past. Concentrations of sum HCHs ranged from 1.5 to 12 ng g^{-1} of soil, with a mean of 6.2 ng g^{-1} of soil. In comparison with samples from the forested zone, β-HCH was predominant (60%), followed by γ-HCH (28%) and α-HCH (12%) (figure 2). This profile could be explained by the high accumulative properties of β-HCH in biological samples and by the presence of large quantities of organic residues at the waste site. The wastes are dumped from a plateau at a distance of 300 m from Iassy city. The wastes were simply burned without any control for many years, while the burning is self-supported due to the high levels of organic matter. The uncontrolled burning of the solid wastes in an open landfill may result in the formation

Table 2. Mean, standard deviation, and range of OCP and PCB concentrations (ng g^{-1} dry weight) in soil and sediment samples from Eastern Romania.

		Sum HCHs		Sum DDTs		Sum PCBs	
Sampling site	*n*	Mean (SD)	Range	Mean (SD)	Range	Mean (SD)	Range
Vaslui	5	13 (6)	8–21	24 (11)	9–34	37 (18)	18–58
Galati	2	19 (15)	9–29	84 (15)	73–95	43 (32)	21–65
Vrancea	5	14 (16)	7–22	39 (35)	8–82	22 (8)	14–31
Neamt	4	31 (18)	13–56	35 (31)	9–78	27 (25)	6–62
Suceava	2	28 (1)	28–29	24 (11)	16–32	9 (1)	8–10
Botosani	6	11 (6)	5–20	22 (22)	5–66	8 (3)	6–14
Bacau	7	21 (10)	8–39	33 (27)	6–75	27 (14)	14–52
	2	143 (109)	66–220	148 (47)	115–182	53 (5)	50–57
Iasi							
Forested zone	6	11 (3)	8–15	55 (50)	9–130	19 (6)	13–28
Waste site							
Sediments	8	6 (4)	2–12	101 (84)	8–210	278 (373)	34–1132
	10	2 (2)	0.5–6	37 (19)	16–78	59 (44)	24–158

of environmentally hazardous pollutants (such as the much-feared polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans), which can be further transferred to the atmosphere, land, and Bahlui River.

3.3 *Sediment samples from the Bahlui River*

The mean concentrations of HCB, sum HCHs, sum DDTs, and sum PCBs in 10 surface sediment samples from the Bahlui River were 1.4, 1.7, 37, and 59 ng g^{-1}, respectively. The sum PCB concentrations from sediment samples ranged from 24 to 158 ng g^{-1} (table 2). The PCB concentrations presented a strong variation along the river with the higher concentrations measured in samples (B1 and B10) located at the extremities of the city (near waste-disposal sites) and in sample B7 (located near an industrial area). In all samples, penta- and hexa-CB congeners were predominant, followed by tri-, tetra- and hepta-CBs (figure 5), suggesting the use of formulations similar to Aroclor 1254. However, it is difficult to correlate the congener profiles with the sources, especially when there is more than one source.

In general, DDT concentrations in Bahlui sediments in this study were relatively low and ranged from 16 to 78 ng g^{-1} dry weight (table 2). The occurrence of DDT isomers is predominant in the following order: p,p'-DDD > p,p'-DDT > p,p'-DDE > o,p-DDT (figure 3). The p,p'-DDD contributed with 46% of the total DDT in sediments in accordance with the anaerobic degradation pathway of p,p-DDT [25]. The mean ratio p,p'-DDT/p,p'-DDE was 1.2, suggesting a recent input of DDT in the river. Highly significant correlations between the concentration of DDT analogues and PCB153 suggest similar trends in pollution inputs and distribution for the two classes of pollutants (figure 6). The data are consistent with previous findings for other rivers [17]. The β-HCH was the predominant HCH isomer (67%), followed by α-HCH (20%) and γ-HCH (13%) (figure 2). Together with a ratio α-HCH/γ-HCH > 1, this suggests a predominant contamination through the use of technical lindane in the river's basin.

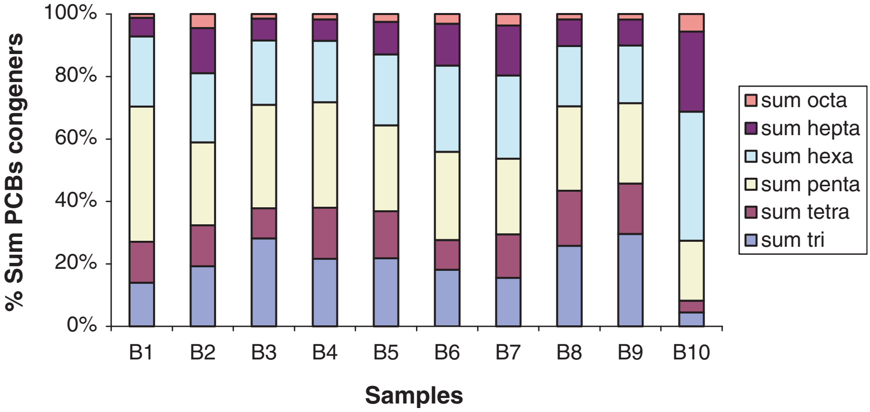

Figure 5. Percentage distribution of the sum of PCB congeners in sediments from Eastern Romania.

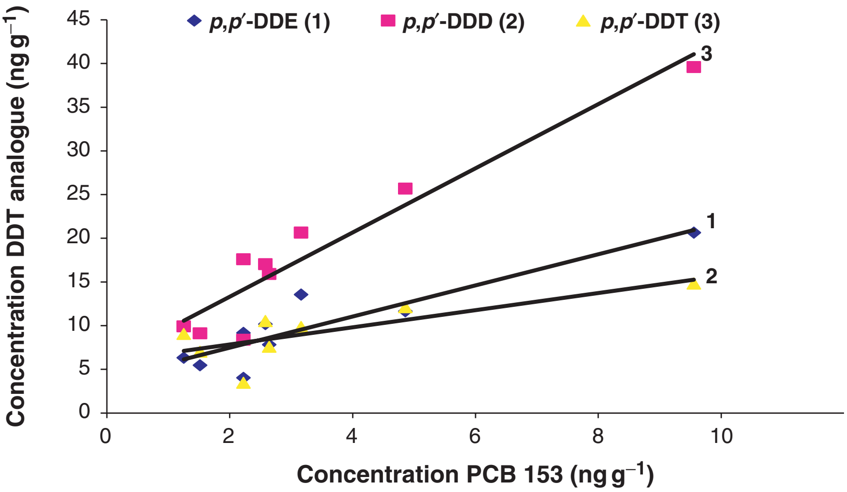

Figure 6. Correlation between concentration of DDT analogues and PCB 153 in sediment samples (for p,p'-DDE: $y = 1.8x + 3.9$, $r^2 = 0.81$; p,p'-DDD: $y = 3.7x + 5.9$, $r^2 = 0.91$; p,p'-DDT: $y = 0.9x + 5.9$, $r^2 = 0.59$).

4. Conclusions

OCPs and PCBs were detected in soil samples from the forest zone, and a waste-disposal site and in sediments from the Bahlui River. Atmospheric transport and direct contamination of soils and sediments have been indicated as possible contamination mechanisms for these samples. The presence of POPs in high amounts at most sites (especially at the waste-disposal site) may constitute a potential health hazard. Therefore, the systematic monitoring of abiotic and biotic compartments, especially of those related to human food production, is desirable.

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