

Evaluation of persistent organochlorine pesticides and polychlorinated biphenyls in Umgeni River bank soil, KwaZulu-Natal, South Africa

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ABSTRACT

This study investigated the presence and distribution of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in soil collected along the banks of the Umgeni River, one of the largest rivers in the province of KwaZulu-Natal, South Africa. The analysis was performed using gas chromatography-mass spectrometry (GC-MS). The results showed that the levels of OCPs ranged from 3.58 ± 0.09 ng/g for hexachlorobenzene (HCB) to 82.65 ± 2.82 ng/g for HCH, with an individual mean concentration of 24.33 ± 2.00 ng/g dry weight (dw). The levels of PCBs ranged from 10.46 ng/g for PCB105 to 89.46 ng/g for PCB180, with an average PCB value of 25.47 ± 1.26 ng/g, dw. The highest levels of OCPs and PCBs were found at Northern Wastewater Treatment Plant (mean OCP: 32.39 ± 3.97 ng/g and PCB: 67.87 ± 1.67 ng/g). The two most abundant contaminants in the river were endrin and PCB180.

Keywords: Umgeni River, bank soil, OCPs, PCBs, gas chromatography mass spectrometry

INTRODUCTION

Organochlorine pesticides (OCPs), such as aldrin, endrin, dieldrin, HCB, heptachlor, chlordane, DDT and mirex, and polychlorinated biphenyls (PCBs), are among environmental contaminants included on the list of persistent organic pollutants (POPs) developed at the Stockholm Convention and signed in 2001. Most countries have restricted or eliminated their use, storage and manufacture since the 1970s (Voldner and Li, 1995; Zhu et al., 2014). Extensive use of OCPs for pest and disease control and mitigation started in the 1940s which explains their widespread presence in the environment (Tompson et al., 2017; Barrie et al., 1992; Bidleman et al., 1995; Dimond and Owen, 1996; Li et al., 1996; Li, 1999; Li et al., 2006). However, these contaminants are sources of various environmental and human health hazards due to their biomagnification through the food chain (Li and Macdonald, 2005; Jones and de Voogt, 1999).

PCBs were widely used as dielectric and coolant fluids in transformers and capacitors, in plasticisers, heat transfer fluids, hydraulic fluids, lubricating oils, additives in paints, adhesives and sealants. Even though termination of their production and usage has been implemented since the 1970s (Zhu et al., 2014), research has shown that the dismantling of electronic and electric waste still remains a significant source of PCBs in developing countries (Wang et al., 2011; Wong et al., 2007; Breivik et al., 2011).

Although the use and production of many OCPs and PCBs has been restricted or banned in many countries, their residues are still being detected in different environmental matrices such as water, soil, air and biota, and are a threat to human health in particular, and the environment in general (Tompson et al., 2017; Aigner et al., 1998; Li et al., 1996; Falandysz et al., 2001; Nakata et al., 2002; Ribes and Grimalt, 2002; Miglioranza et al., 2003; Gong et al., 2004; Barriada-Pereira

et al., 2005; Concha-Grana et al., 2006). OCPs and PCBs are able to partition between different matrices, and can volatilize from soil to the atmosphere; hence, contaminated soils can be considered as a substantial source of POPs to the atmosphere (Meijer et al., 2002; Wild and Jones, 1995; Harner et al., 2001).

Despite the fact that DDT is on the list of priority pollutants, it is still being used in a restricted form, for malaria control in certain parts of South Africa, due to its effectiveness in vector control (Maharaj et al., 2005). Research has shown that during the period 2000–2004 the indoor results spraying (IRS) with DDT reduced the number of confirmed malaria cases by 83% in South Africa in general and by 90% in KwaZulu-Natal in particular (Rohwer, 2012). During the above-mentioned period the number of confirmed malaria deaths were reduced by 65% in the country as a whole, compared to results obtained during the period 1996–1999 (WHO, 2010; Naud and Rohwer, 2012; Sadasivaiah et al., 2007). However studies have shown that DDT and its metabolites, DDD and DDE, were detected in blood samples taken from individuals exposed to DDT as a result of IRS (Bouwman et al., 1991). A study by Rollin also revealed the presence of high levels of DDT and its metabolites, particularly in the Indian Ocean coastal malaria sites and detectable levels of PCBs in the plasma of delivering women in 7 geographical regions of South Africa (Rollin et al., 2009).

Humans are exposed to OCPs and PCBs mainly through water and food consumption or the physical environment which may be contaminated. The Umgeni River is the main source of water supply in the province of KwaZulu-Natal in South Africa, which is used by many animals and informal settlements without any treatment. The Umgeni River level of contamination with regard to OCPs and PCBs is presently not known. Furthermore, work has been carried out on water and sediment of the Umgeni River but there is limited or outdated information on the presence of OCPs and PCBs in the soil along the banks of the river, which can be released into the waterways. The aim of this study was to evaluate the status of

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OCP and PCB contamination in soil from the Umgeni River. The results of this research will add knowledge on the presence and quantification of OCPs and PCBs in the Umgeni River soil. The structures of all the analytes investigated in this study are provided in Fig. 1. These particular PCBs were chosen because some of them are among the most toxic congeners and are recommended by the World Health Organisation for monitoring (PCB77, PCB105) while other PCBs were chosen for the study because they are indicator PCBs (PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180) and are recommended by the European Union for assessing PCB pollution (EC, 1999).

MATERIAL AND METHODS

Chemicals, standards and apparatus

High performance liquid chromatography (HPLC)-grade hexane, dichloromethane (DCM) and toluene, florisil

(MgO₃Si residue analysis grade, mesh 60-100, pore size 60Å), organochlorine pesticides and polychlorinated biphenyl standards, were all purchased from Sigma Aldrich in South Africa. Anhydrous sodium sulfate, (Na₂SO₄) gold line (CP) and silicon carbide boiling stones (CSi), were obtained from Associated Chemical Enterprises, (ACE, South Africa) and sulfuric acid (98%) was obtained from Promark Chemicals (UK). The test sieves (ss 200 mm φ × 100 μm to ss 200 mm φ × 600 μm) were obtained from DLD Scientific in South Africa.

Sample collection

Soil samples were collected from 15 to 17 July 2013 from the banks of the Umgeni River in the province of KwaZulu-Natal in South Africa. The samples were collected from 14 sites, including 12 sites selected along the river, from the source at Midmar Dam to the mouth at Blue Lagoon, where the Umgeni River drains into the Indian Ocean (Fig. 2). Two sites

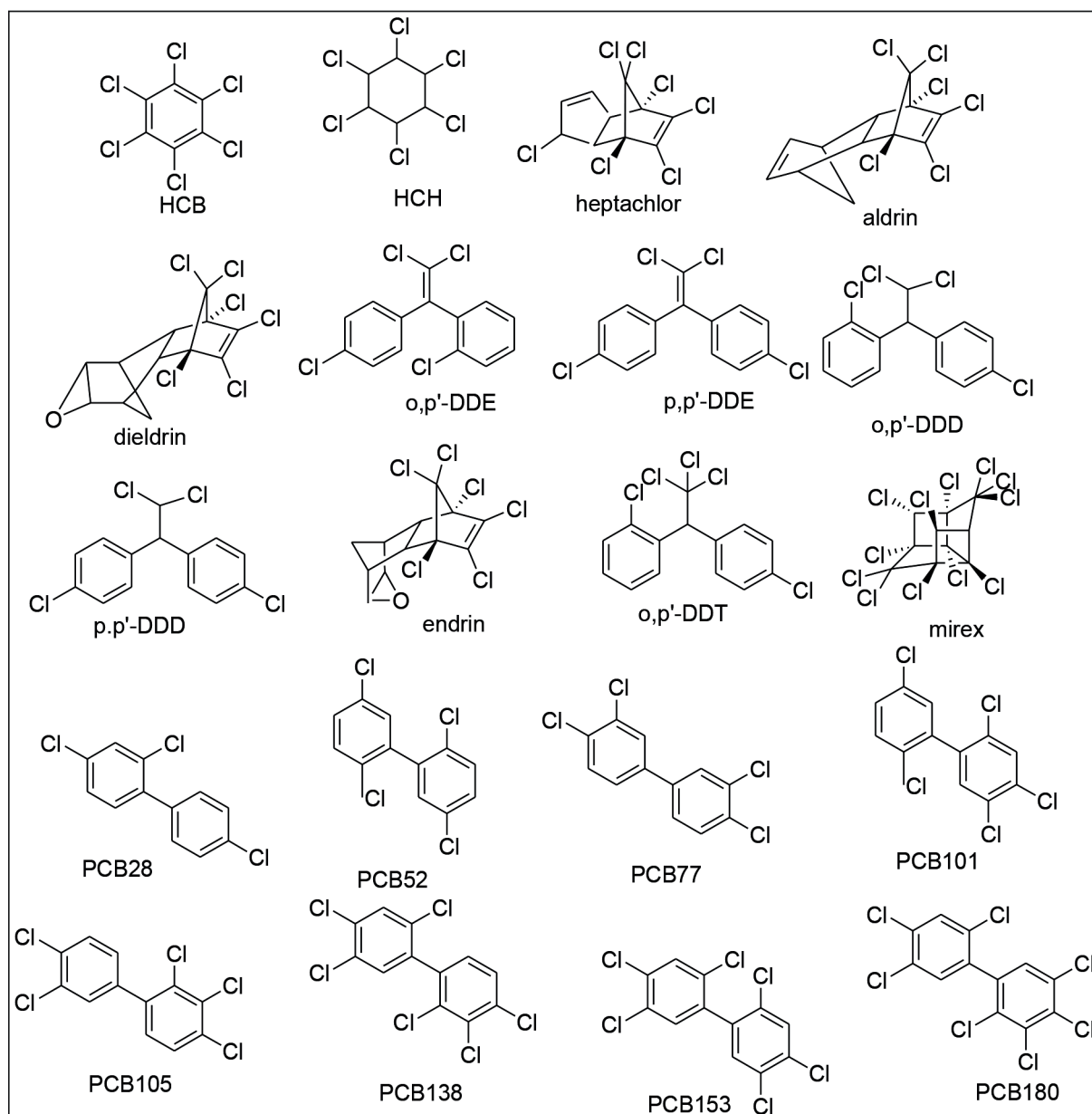


Figure 1. Structures of OCPs and PCBs investigated

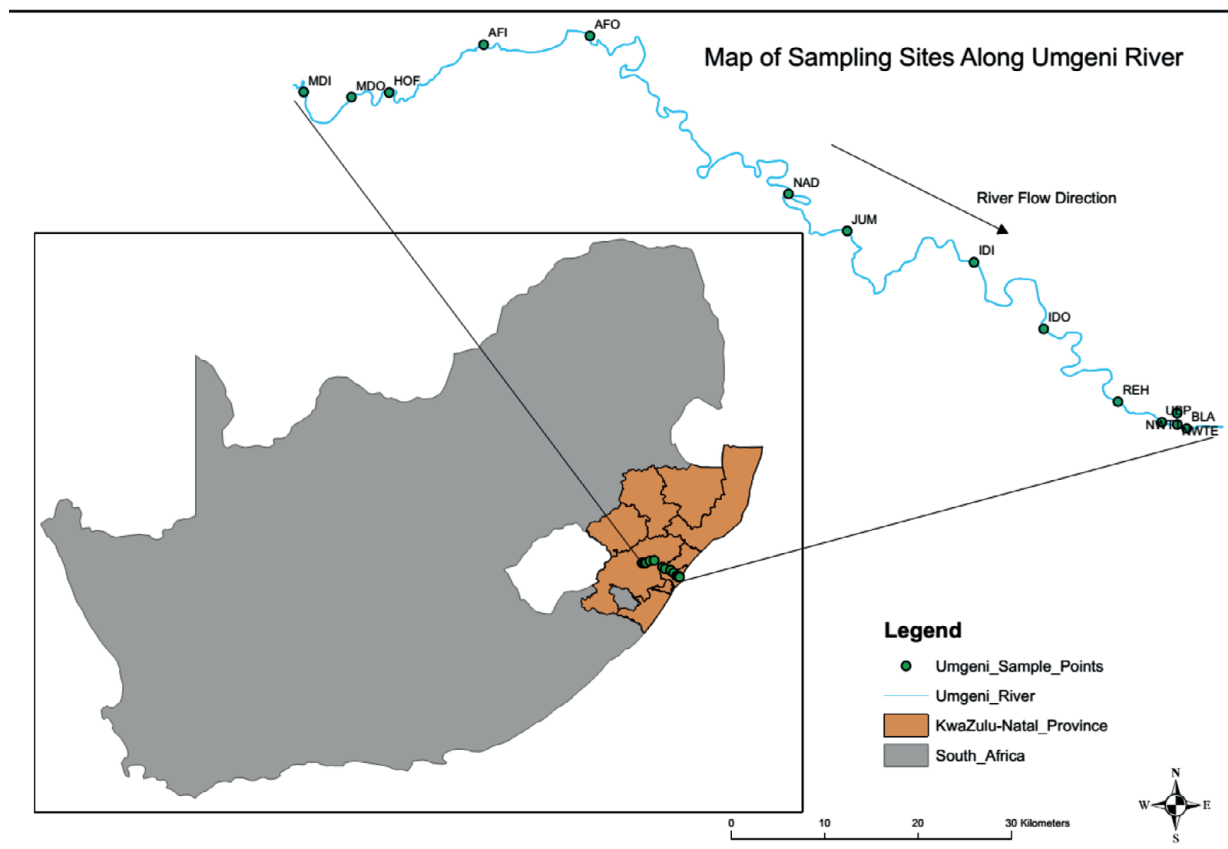


Figure 2. Map showing the sampling sites along the Umgeni River (map was generated from GPS coordinates using ArcGIS 10.2)

at the Northern Wastewater Treatment Works, which treats residential and industrial wastewater from the surrounding Durban city, were also included. The sampling sites and their geographical coordinates are shown in Table 1.

Soil samples were collected using an auger and were stored in 150 mL glass bottles previously washed with hot water and detergent and thereafter rinsed with sulfuric acid, deionized water and river water from the site to be sampled. The bottle caps were lined with aluminium foil. Once the samples were collected, they were kept in a portable ice chest containing ice and transported to the analytical research laboratory.

Sample preparation and treatment

The soil samples were air dried in the laboratory for several days (approximately 14 days) before being ground using a pestle and mortar and thereafter sieved (ss 200 mm \times 100 μ m to ss 200 mm \times 600 μ m). Portions of dried soil (60 g) were accurately measured and transferred into a cellulose extraction thimble which was inserted into a Soxhlet assembly fitted with a 500 mL round bottom flask. The extraction was carried out using 300 mL of HPLC-grade toluene for 24 h (EPA method 3540c) (USEPA, 1996). Toluene was identified as the

Table 1. Location of the sampling sites in the downstream direction and their description

Sample code	Sample name	Coordinates		Site description
		South	East	
MDI	Midmar Dam inlet	29°29'16.05"	30° 09' 23.10"	Dam for water supply inlet
MDO	Midmar Dam outlet	29°29'34.02"	30° 12' 09.13"	Dam for water supply outlet
HOF	Howick Falls	29°29'18.18"	30° 14' 19.70"	Waterfall
AFI	Albert Falls inlet	29°26'31.94"	30° 19' 47.10"	Dam for water supply inlet
AFO	Albert Falls outlet	29°26'01.81"	30° 25' 55.76"	Dam for water supply outlet
NAD	Nagle Dam	29°35'08.42"	30° 37' 23.94"	Dam water
JUM	Joining point Umgeni/Msunduzi	29°37'16.61"	30° 40' 46.59"	River banks
IDI	Inanda Dam inlet	29°39'05.20"	30° 48' 06.24"	Dam for water supply inlet
IDO	Inanda Dam outlet	29°42'55.74"	30° 52' 07.69"	Dam for water supply outlet
REH	Reservoir Hills	29°47'08.05"	30° 56' 25.51"	River banks
UBP	Umgeni business park	29°48'19.05"	30° 58' 58.08"	River banks
NWTT	Northern Wastewater Treatment after treatment	29°47'47.02"	30° 59' 50.06"	Pond containing treated water
NWTE	Northern Wastewater Treatment effluent	29°48'27.01"	30° 59' 51.05"	Discharge of treated water to the river
BLA	Blue Lagoon	29°48'41.03"	31° 02' 12.05"	Discharge of the river water to the Indian ocean

most suitable solvent for extraction of aromatic ring bearing compounds such as organochlorine pesticides and PCBs (Oleszek-Kudlak et al., 2007). The extracts were concentrated using a rotary evaporator to about 5 mL and subsequently cleaned-up.

The extracts were cleaned-up using florisil (activated at 130°C for 12 h) containing a top layer of anhydrous Na₂SO₄ (10 g). Sequential elutions were carried out with a solvent system consisting of hexane-dichloromethane (DCM) (20 mL) (94:6), (85:15), (50:50) and 100% DCM (modified EPA method 3620-C) (USEPA, 2007a). The obtained fractions were combined and concentrated with a rotavap to 5 mL, air-dried and reconstituted to 2 mL and analysed using GC-MS.

Instrumental analysis

The sample analyses for OCPs and PCBs were carried out separately to avoid overlapping of peaks (Figs A1 and A2 in Appendix). The gas chromatography system (Agilent 6890 series) coupled to a mass spectrometer detector (MSD 5973) and equipped with a ZB-5MS (Hewlett Packard; Houston, TX) capillary column (length: 30 m, 0.25 mm, internal diameter: 0.25 μm). Helium was used as the carrier gas at a constant flow rate (1 mL/min). The oven temperature started at 120°C (initial hold of 2 min) and increased to 290°C at a ramping rate of 14°C/min and held for 2 min. A 2 μL injection volume was used in splitless mode with a 4 min solvent delay. The MS source and Quad were operated at 250°C and 200°C, respectively. The electron energy was 70 eV. The MS was operated in selected ion monitoring (SIM) mode and 3 ions were monitored for each target analyte (Table 2, Figs A3 and A4, Appendix).

Target analytes were quantified using an external calibration method based on peak areas. The six calibration levels used for both OCPs and PCBs were 0.25; 0.5; 1; 2; 4 and 8 ng/mL. The identification of specific target compounds was achieved by analysis of mass spectra against that found in the NIST library as well as comparison of retention times of sample analytes with those of reference standards.

Quality control and assurance

The procedures used for the analysis of selected OCPs and PCBs were monitored with appropriate quality control and assurance measures. Procedural blanks were used in all the extraction, clean-up and analysis steps along with sample preparation and analysis to determine if there was any possible input from external sources during analysis. There were no detectable levels of target contaminants in blank samples composed of toluene and DCM. Solvent blanks (DCM) were regularly run after each batch of 10 injections through the GC-MS column. A 0.5 ng/mL reference standard of OCPs and PCBs was run intermittently to ensure that variation from the initial calibration standards were as minimal as possible. Target analyte recoveries were performed by spiking real soil subsamples with separate OCP and PCB standards before extraction, as well as leaving one subsample unspiked. The difference between the concentrations of spiked subsamples (X_s) and non-spiked subsamples (X_u) was divided by the known concentration of the spike in the sample (X_k) and multiplied by 100 to obtain the percentage recoveries (%R) (Eq. 1, Harry et al., 2008). The recovery and actual sample analyses were carried out in triplicate to ensure the reproducibility and precision of the method used. The limits of detection (LOD) were calculated as 3 times the signal-to-noise ratio using the standard deviation of three calibration intercepts divided by the slope, whereas the limit of quantification (LOQ) was 10 times this ratio (Eqs 2, 3 and 4) (Shrivastava and Gupta, 2011).

$$\%R = \frac{X_s - X_u}{X_k} \times 100 \quad (1)$$

$$y = mx + b \quad (2)$$

$$LOD = \frac{3S}{m} \quad (3)$$

Table 2. Ions monitored, % recovery, limits of detection (LOD) and quantification (LOQ) in ng/g

Analytes	Ions monitored	% recovery	LOD	LOQ
OCPs				
HCB	284, 249, 142	68.1±0.058	0.50	1.66
HCH	219, 183, 147	108.4±3.81	0.50	1.66
Heptachlor	374, 272, 237	103.7±7.24	0.50	1.62
Aldrin	327, 293, 263	53.16±10.37	0.78	2.59
o,p-DDE	318, 284, 246	87.66±4.77	0.96	3.20
p,p'-DDE	318, 281, 246	51.67±1.62	0.62	2.07
o,p'-DDD/dieldrin	320/380, 235/263, 165/147	87.37±2.08	1.04	3.45
Endrin	317, 263, 207	84.69±6.04	1.02	3.41
p,p'-DDD/o,p-DDT	320/235, 235/199, 165/165	89.13±2.61	1.23	4.11
Mirex	402, 272, 237	111.9±12.84	0.63	2.07
PCBs				
PCB28	256, 186, 150	60.68±0.97	0.76	2.52
PCB52	292, 220, 150	78.73±0.58	0.21	0.71
PCB77	292, 255, 220	64.74±1.47	0.92	3.06
PCB101	326, 291, 254	72.63±0.86	0.30	0.99
PCB105	326, 254, 184	71.88±0.74	0.28	1.12
PCB138	360, 290, 145	72.69±1.38	0.22	0.75
PCB153	360, 290, 145	74.74±1.95	0.31	1.03
PCB180	394, 324, 162	77.80±2.55	0.19	0.66

$$LOQ = \frac{10S}{m} \quad (4)$$

where S = standard deviation of the response, m = the slope of the calibration curve, b = y -intercept

The concentrations of various analytes (C_a) were calculated using the following equation (USEPA, 2007b; USEPA, 2008).

$$C_a = \frac{C_{ex} \times V_{ex}}{W_s} \quad (5)$$

where C_a = concentration of the analyte in ng/g, C_{ex} = concentration of the analyte in the extract in ng/mL, V_{ex} = the extracted volume in mL, W_s = the sample weight (dry weight) in g.

RESULTS AND DISCUSSION

Organochlorine pesticides (OCPs) in riverbank soil

Levels of OCPs in the soil collected from the banks of the Umgeni River are shown in Table 3 and Fig. A5 (Appendix). All the OCPs investigated were detected at all the sampling sites and their concentrations ranged from 3.58 to 82.65 ng/g. Endrin (37.08–70.18 ng/g) was the most abundant OCP in all the sites investigated, except NWTE where the OCP in highest concentration was HCH (Fig. 3 and Fig. A6, Appendix). This was attributed to endrin's low mobility in soil and its long half-life. Once released in soil, endrin remains for a long period of time, up to more than 14 years (USEPA, 2009). Its leaching into groundwater and evaporation to air is very limited due to its very strong adsorption to soil particles ($\log K_{oc} = 4.53$) and low vapour pressure, respectively (USEPA, 2009). Other OCPs such as DDDs and DDEs were also detected in substantial amounts. The higher concentrations of residues of these breakdown products of DDT may be an indication of its extensive use in the past. DDT is still in use in certain areas of South Africa for malaria control, especially in high-risk areas such as northern KwaZulu-Natal, Limpopo and Mpumalanga where its use is monitored by the government to avoid its widespread and uncontrolled use (Rother and Jacobs, 2008; Naud and Rohwer, 2012; Van Dyk et al., 2010).

The total concentrations of OCPs were higher at 4 different sites, namely, Howick Falls (HOF) (284.09 ng/g), Inanda Dam inlet (IDI) (284.82 ng/g) and at NWTT (323.92 ng/g) and NWTE (320.60 ng/g) (Fig. 4 and Table 3). The high concentrations at HOF were probably due to its location in an urban environment and it may be influenced by urban activities. There may also be runoff of agricultural pesticides from surrounding farms, mainly sugar cane and wood plantations

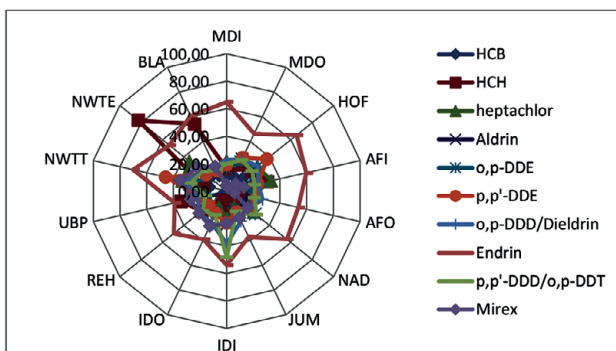


Figure 3. Distribution of OCPs across the various sampling sites

Table 3. Concentration of OCPs in bank soil of Umgeni River

Site	Concentration (ng/g ± SD) of OCPs in river bank soil										Σ OCPs
	HCB	HCH	Heptachlor	Aldrin	o,p-DDE	p,p'-DDE	o,p-DDD/Dieldrin	Endrin	p,p'-DDD/o,p-DDT	Mirex	
MDI	10.42±0.10	16.35±0.42	21.95±3.06	15.72±1.24	16.15±0.33	19.17±0.10	22.71±0.33	64.90±1.42	20.02±0.30	4.43±2.86	211.82±10.15
MDO	11.97±3.38	21.17±1.20	26.00±1.37	26.02±0.70	23.71±1.28	27.17±0.60	25.90±1.62	46.36±3.52	25.20±1.27	2.52±2.05	236.01±16.97
HOF	15.08±1.10	23.73±4.32	28.75±2.35	24.48±4.62	27.91±1.42	37.57±0.23	29.17±4.95	65.33±3.53	23.70±0.44	8.36±7.20	284.09±30.18
AFI	14.79±0.98	30.69±6.53	33.51±2.11	18.14±1.95	16.84±0.67	23.33±1.82	23.66±0.97	59.71±3.00	20.91±0.82	12.81±2.77	254.40±21.62
AFO	7.45±1.70	10.07±0.48	17.43±0.10	15.75±2.07	19.75±0.75	22.53±0.86	26.87±0.57	53.77±1.12	20.89±0.75	5.93±3.35	200.44±11.76
NAD	18.63±0.86	7.51±0.33	24.78±1.08	15.20±1.49	26.66±0.63	21.26±0.59	19.83±0.89	56.30±4.99	27.70±0.76	19.61±2.35	237.48±13.97
JUM	5.81±0.50	19.21±0.77	12.90±0.73	15.31±1.56	14.22±0.45	16.77±0.57	24.13±0.72	37.08±7.72	16.41±0.40	21.54±0.37	183.38±13.79
IDI	11.82±0.56	18.18±0.79	19.84±3.07	24.29±1.91	23.75±0.84	23.15±1.24	38.46±0.70	53.87±2.52	48.00±0.75	23.46±2.69	284.82±15.09
IDO	4.24±0.38	7.41±0.61	13.12±0.63	15.99±1.07	16.61±0.85	18.05±0.70	25.56±0.81	39.10±2.37	19.40±0.72	28.29±4.13	187.76±12.27
REH	3.58±0.09	23.27±2.07	14.88±0.85	18.30±2.81	14.43±0.87	16.45±0.80	25.60±1.10	49.41±4.20	22.50±2.00	25.85±3.90	214.27±18.68
UBP	18.19±0.87	34.24±1.24	16.02±1.09	14.96±4.39	14.94±1.24	19.61±0.52	21.29±0.14	38.97±5.98	15.86±0.38	27.12±3.12	221.21±18.97
NWTT	13.00±0.68	17.26±3.14	33.35±2.47	26.48±6.76	25.76±6.23	45.78±3.85	30.53±0.97	70.18±11.54	26.76±1.78	34.82±2.24	323.92±39.66
NWTE	15.55±0.86	82.65±2.82	34.93±7.77	23.52±5.63	16.67±0.72	19.28±1.33	23.72±0.71	53.65±9.12	22.98±1.34	27.65±3.15	320.60±33.45
BLA	12.32±0.63	54.15±0.99	16.87±3.41	13.09±3.11	15.86±0.72	16.44±1.11	19.62±1.45	60.81±8.43	17.37±1.81	20.06±1.98	246.58±23.65
Σ OCPs	162.84±12.69	365.91±25.71	314.33±30.08	267.27±39.32	273.25±17.01	326.55±14.32	357.04±15.94	749.42±69.46	327.70±13.50	262.47±3.01	3406.78±28.20
Min	3.58±0.09	7.41±0.61	12.90±0.73	13.09±3.11	14.22±0.45	16.44±1.11	19.62±1.45	37.08±7.72	15.86±0.38	2.52±2.05	183.38±13.79
Mean	11.63±0.91	26.14±1.84	22.45±2.15	19.09±2.81	19.52±1.21	23.33±1.02	25.50±1.14	53.53±4.96	23.41±0.96	18.75±3.01	243.34±20.01
Max	18.63±0.86	82.65±2.82	34.93±7.77	26.48±6.76	27.91±1.42	45.78±3.85	38.46±0.70	70.18±11.54	48.00±0.75	34.82±2.24	323.92±39.66

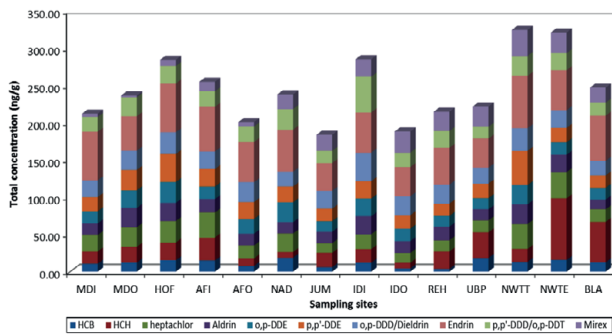


Figure 4. Total concentration of OCPs in Umgeni River bank soil at each site

around Howick. In the case of IDI, the higher concentrations in soil may be due to agricultural runoff and regular spraying of a mixture of herbicides to avoid weed growth around the dam, as was observed during sampling trips. This spraying was observed during the sampling period. The higher levels of contaminants at NWTT and NWTE were expected since the wastewater treatment works receives residential and industrial waste which may contain many of these contaminants. The samples collected from these sites were mainly comprised of bio-solids which may have accumulated more contaminants than soils obtained from the banks of the river.

Polychlorinated biphenyls (PCBs) in river bank soil

Selected PCBs, the most toxic and indicator PCBs, were investigated in soil obtained from the banks of the Umgeni River and their concentrations varied from 10.46 to 89.46 ng/g (Table 4). Figures 5 and A7 (Appendix) revealed that HOF had high levels of total PCBs (275.09 ng/g). This could be attributed to its location in Howick town and the contamination by industrial wastes which may contain substantial amounts of contaminants, including PCBs. A high total PCB concentration was also detected in the bio-solids collected from the NWTT (542.95 ng/g) due to industrial and residential waste. The most abundant PCB congener in the river bank soil was found to be PCB180 (17.08–89.46 ng/g) with a mean concentration of 39.17 ng/g (Table 4 and Fig. 5). This is probably due to its strong affinity for organic carbon ($\log K_{oc} = 5.78-6.9$) in soil to which it strongly adsorbs (Preda et al., 2010). Furthermore, its complexity of having 7 chlorine atoms in its structure makes it relatively stable and resistant to degradation and

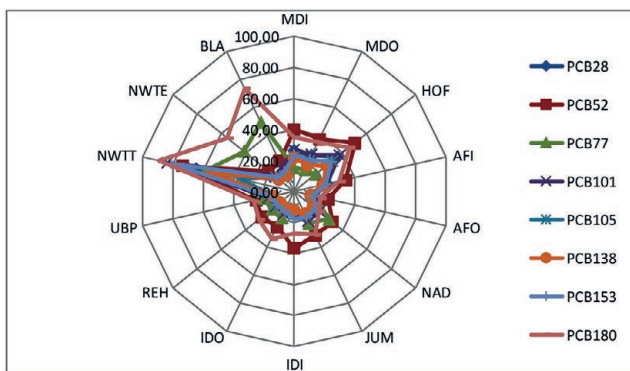


Figure 5. Distribution of PCB congeners at different sites

Table 4. Concentrations of PCBs in Umgeni River bank soil

Site	Concentrations of PCBs in bank soil in ng/g								ΣPCB
	PCB28	PCB52	PCB77	PCB101	PCB105	PCB138	PCB153	PCB180	
MDI	26.13±1.28	39.83±3.14	15.27±0.25	26.96±2.31	22.24±1.96	21.65±1.60	23.68±2.59	35.03±2.01	210.78±15.12
MDO	25.70±1.49	37.55±2.30	15.76±0.20	26.17±1.19	21.69±1.73	19.26±1.38	22.76±1.65	35.25±3.17	204.15±13.83
HOF	36.09±1.61	49.95±2.90	17.52±1.25	37.60±1.87	31.69±1.58	26.49±1.63	30.49±1.71	45.27±1.23	275.09±14.77
AFI	21.98±1.81	33.98±2.40	19.09±1.88	20.00±8.00	18.53±1.79	18.90±0.61	20.87±2.11	29.79±1.33	183.13±19.93
AFO	12.02±1.00	22.50±1.57	13.43±1.28	13.64±1.34	10.60±0.84	11.05±1.84	12.48±1.01	17.08±2.24	112.79±11.12
NAD	18.66±1.20	31.49±1.46	28.61±0.14	20.54±1.28	17.25±1.10	15.35±0.60	18.02±1.12	20.43±0.23	170.35±8.14
JUM	19.09±0.05	31.31±0.32	22.58±0.26	21.05±0.22	16.67±0.24	16.02±0.12	18.45±0.40	30.62±0.07	175.79±1.67
IDI	13.59±0.31	36.59±0.13	12.20±0.42	15.09±0.21	10.79±0.29	11.62±0.34	17.70±0.15	27.15±0.90	144.73±2.76
IDO	13.99±0.97	25.35±1.04	18.56±0.69	15.93±0.58	11.85±0.53	11.85±0.25	14.08±0.41	33.68±0.55	145.29±5.03
REH	13.90±0.72	26.54±0.70	18.38±0.91	15.35±0.51	11.96±0.32	11.68±0.38	14.11±0.39	29.01±0.38	140.93±4.62
UBP	15.70±1.41	25.10±0.89	19.87±0.91	16.95±1.15	12.64±0.60	14.19±0.87	15.22±0.59	26.67±0.85	146.34±6.58
NWTT	64.56±0.72	73.66±2.96	59.36±0.86	83.59±0.82	36.73±1.18	54.49±1.81	81.11±2.52	89.46±1.78	542.95±13.36
NWTE	12.54±1.41	21.64±1.02	41.25±1.63	15.87±1.01	15.23±1.57	12.8±21.27	14.38±0.48	55.19±2.57	188.91±10.03
BLA	12.32±0.46	21.75±2.25	49.31±3.11	17.79±3.28	10.46±1.11	11.41±0.31	14.23±1.16	73.77±2.46	211.03±14.09
ΣPCB	306.26±0.42	477.23±23.09	351.19±14.80	346.51±24.50	248.34±14.85	256.76±13.01	317.58±16.27	548.40±20.77	2852.28±141.04
Min	12.02±1.00	21.64±1.02	12.20±0.42	13.64±1.34	10.46±1.11	11.05±1.84	12.48±1.01	17.08±2.24	112.79±11.12
Mean	21.88±0.98	34.09±1.65	25.08±0.06	24.75±1.75	17.74±1.06	18.34±0.93	22.68±1.16	39.17±1.48	203.73±10.07
Max	64.56±0.72	73.66±2.96	59.36±0.86	83.59±0.82	36.73±1.18	54.49±1.81	81.11±2.52	89.46±1.78	542.95±13.36

volatilisation from soil to air, compared to other investigated congeners (De Voogt et al., 1990; Vesna et al., 2006). The second most abundant congener was PCB52 (21.64–73.66 ng/g). The 2',5,5'-Tetrachlorobiphenyl (PCB52) is of lower complexity having only 4 chlorine atoms and, together with its relatively lower ($K_{oc} = 5.91$) value, tends to adsorb less strongly to soil and would therefore have relatively lower concentrations in the soil. Therefore, the higher than expected concentrations suggest a possible input of this congener into the river. The other congeners were also present in significant amounts: PCB28 (12.02–64.56 ng/g), PCB77 (12.20–59.36 ng/g), PCB101 (13.64–83.59 ng/g), PCB105 (10.46–36.73 ng/g), PCB153 (12.48–81.11 ng/g) and PCB138 (11.05–54.49 ng/g) (Table 4).

The most contaminated site was NWTT (Fig. 6 and Fig. A8, Appendix). This was attributed to the accumulation of contaminants from wastewater since the site stores wastewater before it is discharged into the river. Being a store of wastewater and having an excess of plant life as a result of eutrophication, this site (NWTT) may contain more organic carbon than other sites. This may allow for partitioning of more PCBs and may be the reason for the high concentrations found at this site. A study of fate and persistence of PCBs in soil revealed that their persistence was greater in soil with higher organic carbon content (Ayris and Harrad, 1999).

Comparison of levels of PCBs and OCPs in soil from various locations globally

The levels of PCBs detected in the present study were compared to the levels of PCBs detected in various locations around the world (Table 5). The total PCB concentration ranged from 112.79 to 542.95 ng/g, with mean of 203.73 ng/g (Table 4). The PCB concentrations detected were lower than the results obtained by Yuan and co-workers who found total PCB concentrations in topsoils of Beijing in China ranging from 47.04 to 3 883.77 ng/g, with a mean of 679.62 ng/g (Yuan et al., 2014). Levels of PCBs in eastern Romania were determined by Dragan and co-workers who found this to range between 34 and 1 132 ng/g, with a mean of 278 ng/g (Dragan et al., 2006). The total concentrations of OCPs in topsoil of Beijing in China were found to vary from 2.38 to 933.12 ng/g, with a mean of 68.76 ng/g (Yuan et al., 2014). Table 5 summarizes the results obtained from different regions of the globe. The results obtained in this study were far below those reported by Yuan and co-workers in the top-soil of a typical urban area in Beijing, China, where the levels of OCPs ranged from 2.4 to 3 883.8 ng/g (Yuan et al., 2014), as well as those detected in South East Romanian soil (58–1662 ng/g) (Ene et al., 2012)

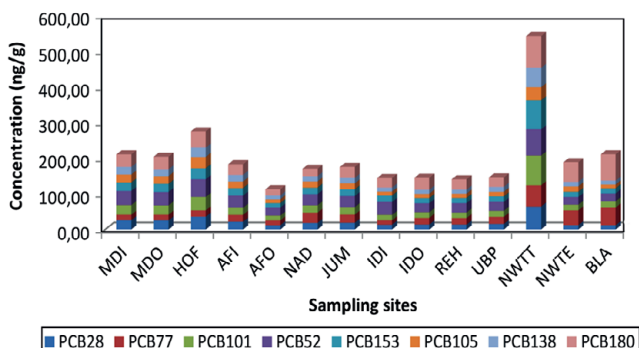


Figure 6. Trend of concentration of individual PCB congeners across all sites

Table 5. Comparison of results of this study and PCB concentrations in soil reported in different locations in the world

Country/location	Site descriptions	No. of congeners	ΣPCBs (ng/g)	Sampling date	References
South-Africa	Bank of the river, industrial, urban residential, agricultural	8	112.79–542.95	Jul 2013	This study
China/Beijing	Urban	25	47.04–3 883.77	Jul 2011	Yuan et al., 2014
United Kingdom	Urban	7	1.00–750.00	Apr 2009	Vane et al., 2014
China	Contaminated area	32	317.85–927.30	Feb 2012	Gao et al., 2015
Russia/Moscow	Background	33	5.50–79.00	1996–2003	Wilcke et al., 2006
Russia	Arboretum of botanical garden	-	300.00–24 250.0	2012	Agapkina et al., 2012
Eastern Romania	Vicinity of waste disposal site	21	34.00–1 132.00	2002	Dragan et al., 2006
Bulgaria	Urban	6	7.20–17.20	2013	Dimitrova et al., 2013

and those detected at Patagonia in Argentinian soil (38 100–46 500 ng/g) (Gonzaleza et al., 2010). However, the Umgeni River OCP levels were higher than the levels investigated in the Chao River soil in China (0.8145–16.8524 ng/g) (Yu et al., 2014).

Being ubiquitous, the organochlorine pesticides occur everywhere in any environmental compartment in different parts of the globe. Table 6 shows the comparison of the results of the present study with those of other investigations carried out worldwide.

CONCLUSION

In this study, assessment of the levels and distribution of OCPs and PCBs in soil collected from the banks of the Umgeni River was carried out. All the contaminants investigated were detected at all sites. The distribution of OCPs and PCBs in the soil from the banks of the Umgeni River was ubiquitous because of different potential sources, such as agricultural runoff, industries, wastewater treatment plants and non-point sources. Considering the levels of OCPs and PCBs detected in this study, the bank soil from the Umgeni River is contaminated, which may leach into the river. Therefore, serious measures must be taken by the local government to reduce the contamination effects of the river water and protect the environment. This was the first study on the presence of organic pollutants in the soil of the Umgeni River which has added to the present limited knowledge of their environmental distribution in bank river soils from KwaZulu-Natal in South Africa.

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Table 6. Comparison of results of this study and OCP concentrations in soil reported in different locations in the world

Country/location	Site descriptions	No. of OCPs	ΣOCPs (ng/g)	Sampling date	References
South Africa	Bank river, urban, residential,	12	183.38–323.92	15–17 Jul 2013	This study
India	Industrial, agricultural, residential	22	129–1 001	-	Manohar et al., 2014
China/Beijing	Urban	23	2.38–933.12	Jul 2011	Yuan et al., 2014
China	Paddy soil	14	35–3 669	2014	Wang et al., 2007
Pakistan	Surface soil	-	216–541	Sep–Oct 2013	Sultana et al., 2014
China	Along the Chao River	24	0.8145–16.8524	2013	Yu et al., 2014
South East Romanian	Agriculture, industrial	15	58–1 662	Apr 2009	Ene et al., 2012
Western China	Surface soil	10	0.51–181.63	March–July 2011	Liu et al., 2013
North-Eastern Romania	Surface soil	-	4.4–95	Aug–Sep 2005	Doina et al., 2013
Tajikistan	High mountain soil	-	52.83–247.98	2012	Zhonghua et al., 2013
Poland	Arable, agricultural and industrial	8	0.35–453.20	2005	Maliszewsk-Kordybach et al., 2014
Argentina	Agricultural area	15	38 100–46 500	-	Gonzaleza et al., 2010

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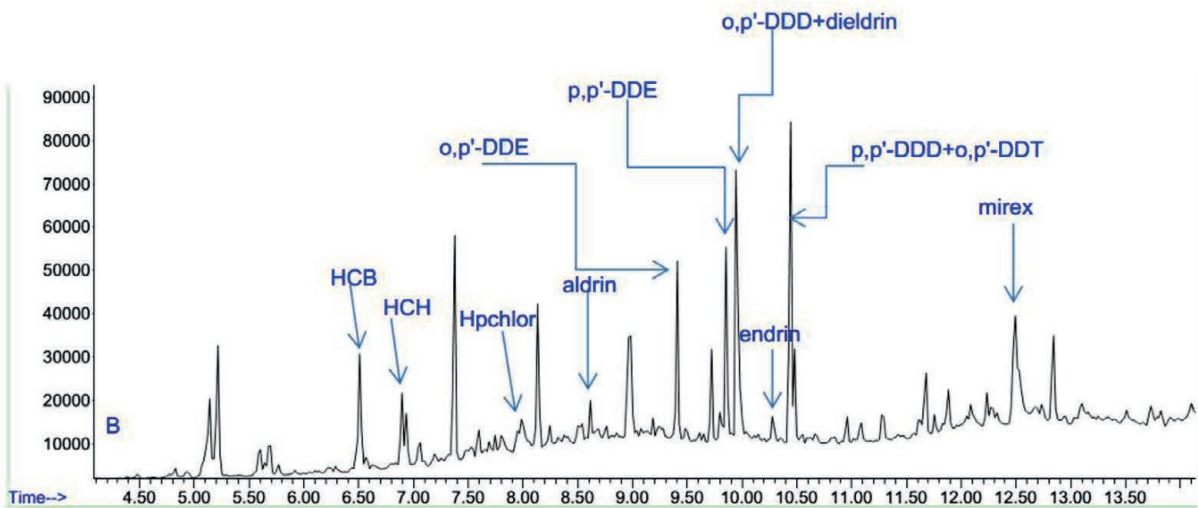
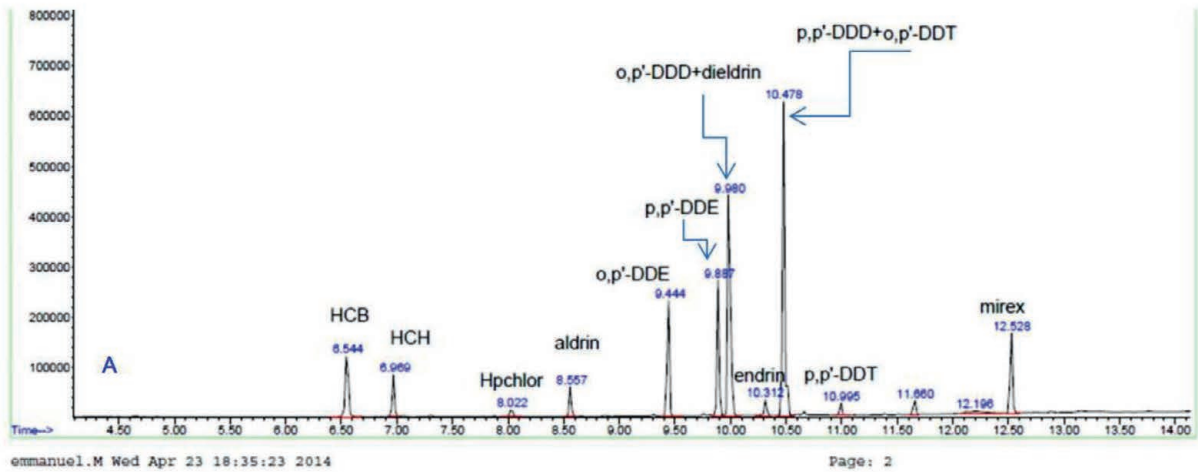


Figure A1. A: chromatogram of a 0.25 ppm standard mixture of OCPs. B: chromatogram of clean water extract fortified with 0.125 ppm standard

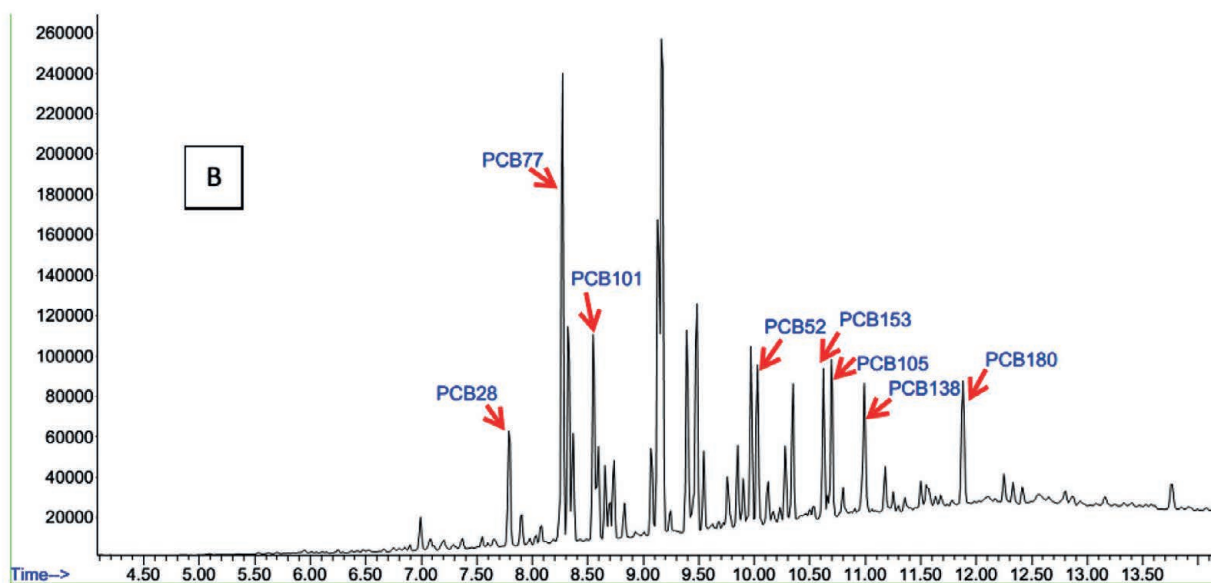
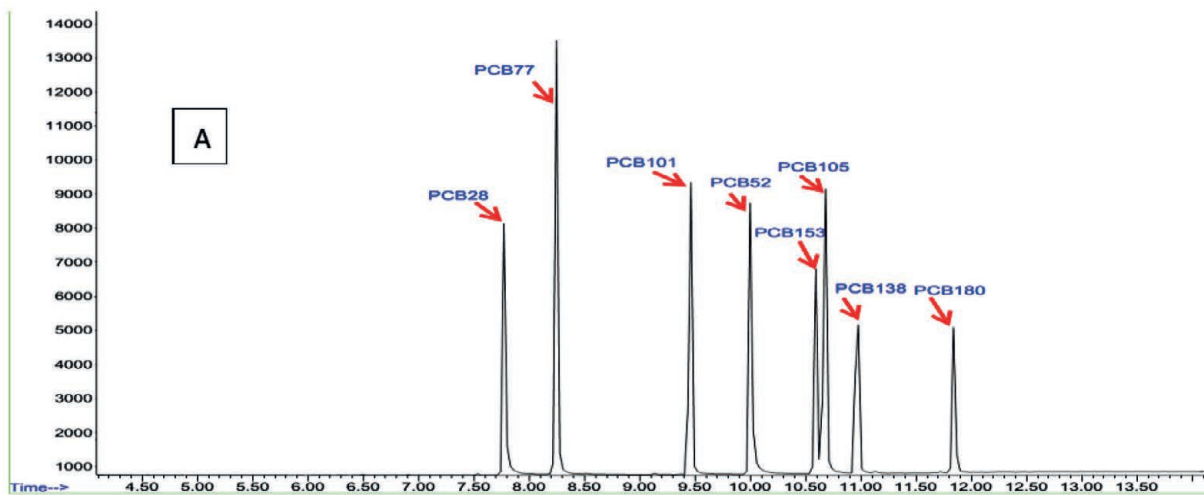


Figure A2. A: chromatogram of a mixture of 0.5 ppm of 8 PCBs. B: chromatogram of cleaned-up soil extract fortified with a 0.125 ppm standard

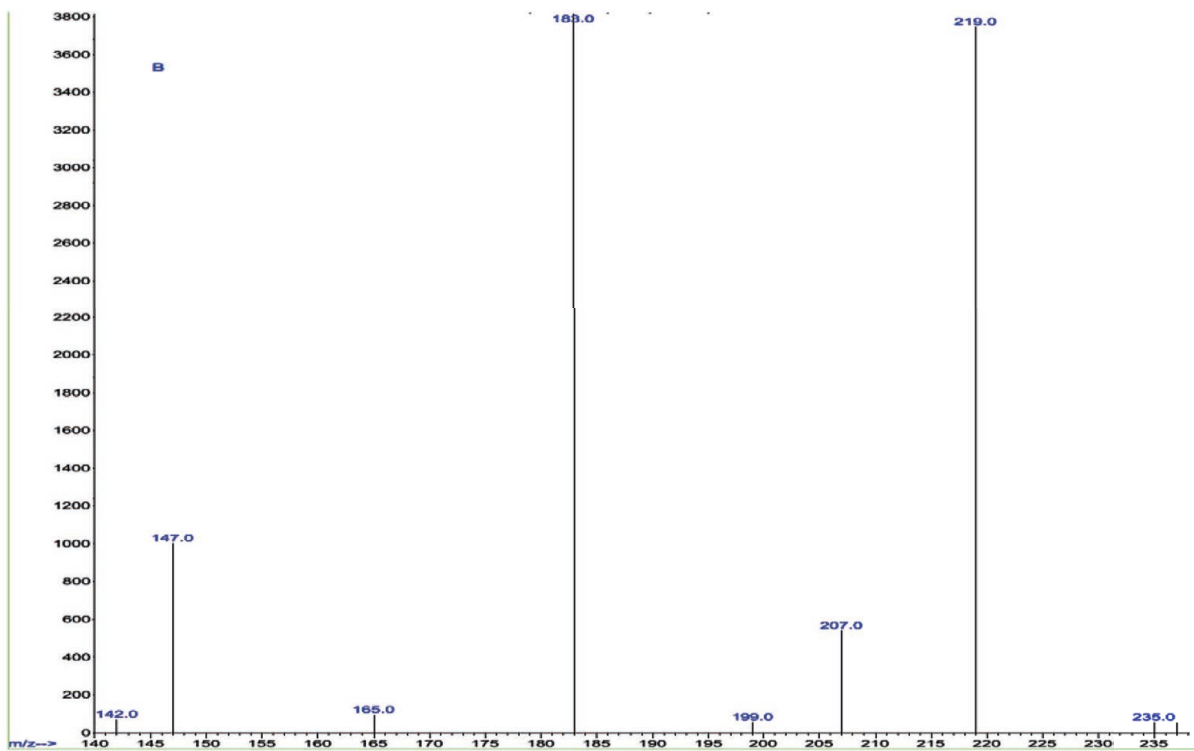
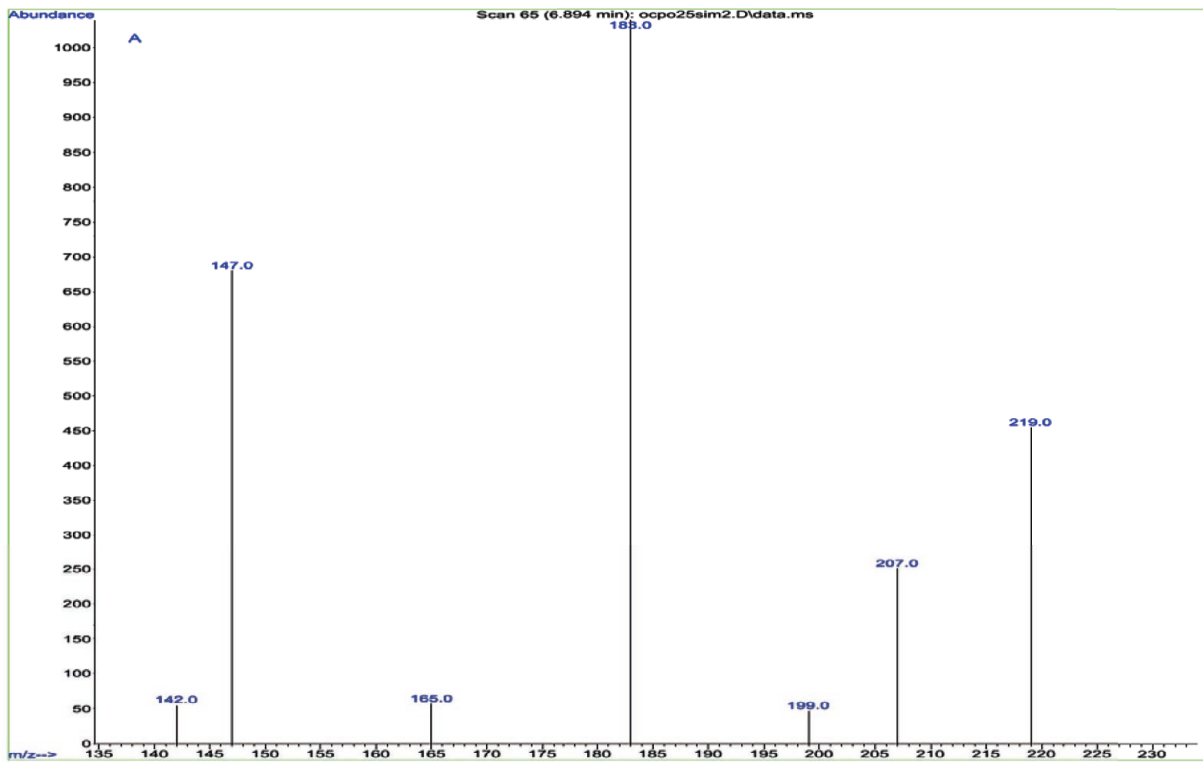


Figure A3. Main fragment ions monitored in SIM mode m/z 147, m/z 183, m/z 219: A-HCH standard ions. B-soil HCH ions

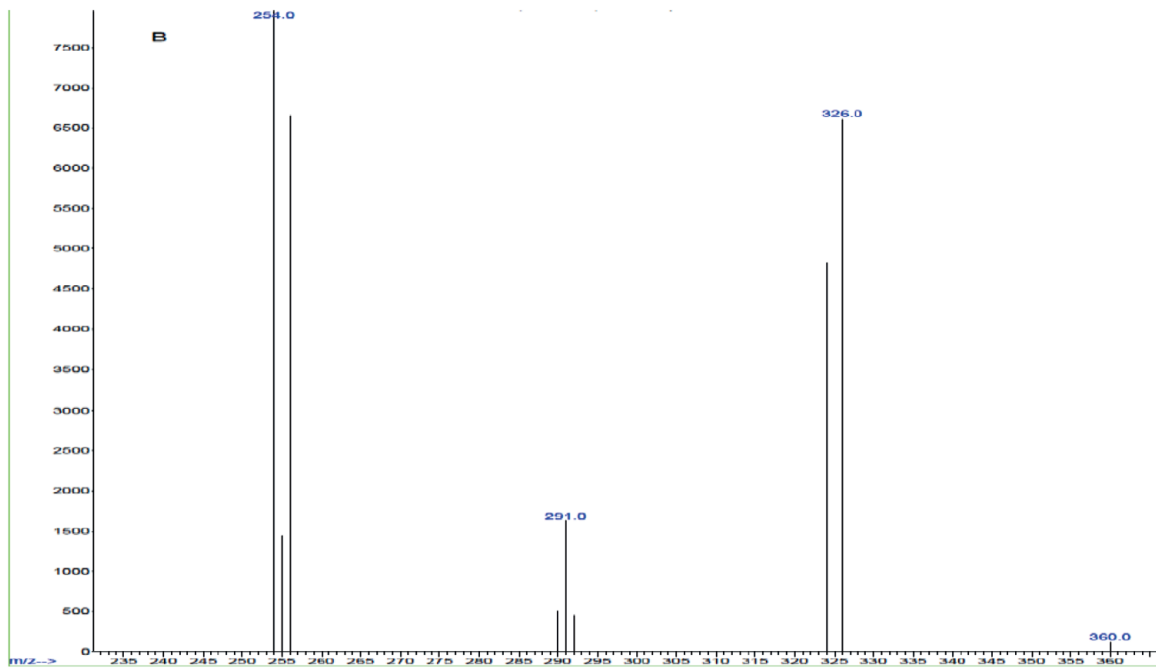
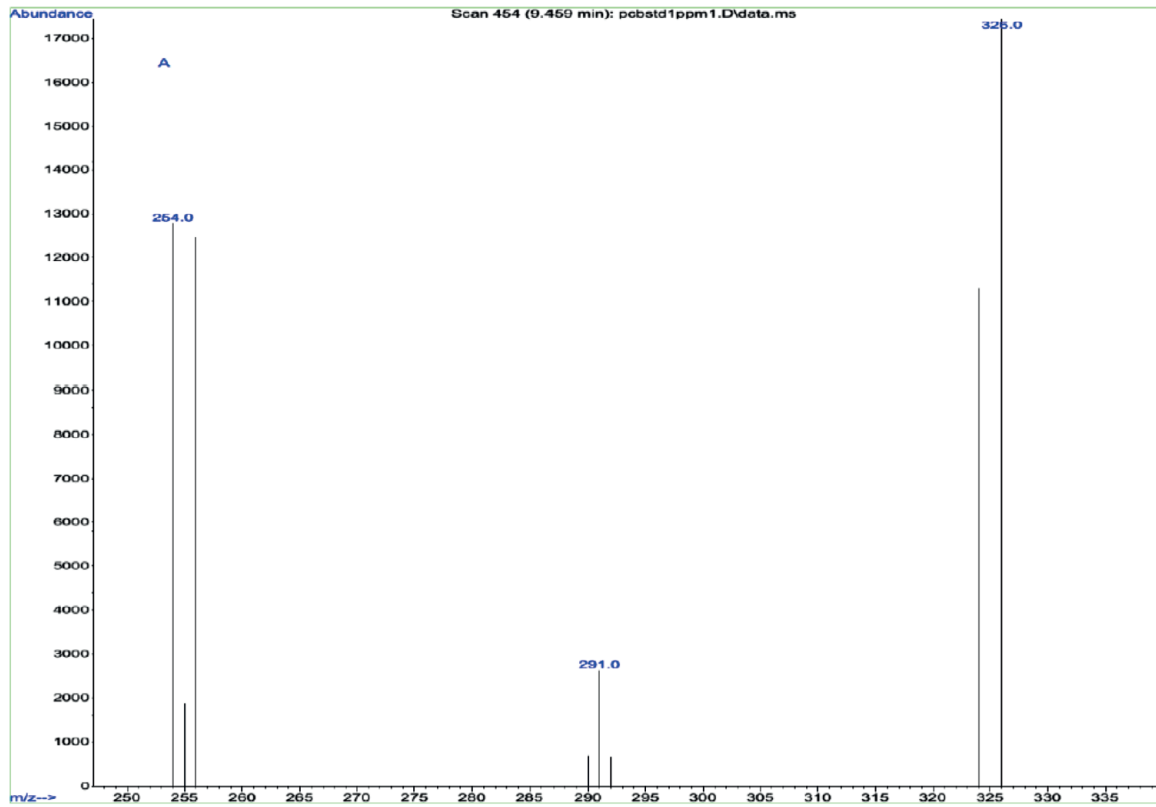


Figure A4. Main fragment ions monitored in SIM mode m/z 254, m/z 291, m/z 326: A-PCB101 standard ions. B-soil PCB ions

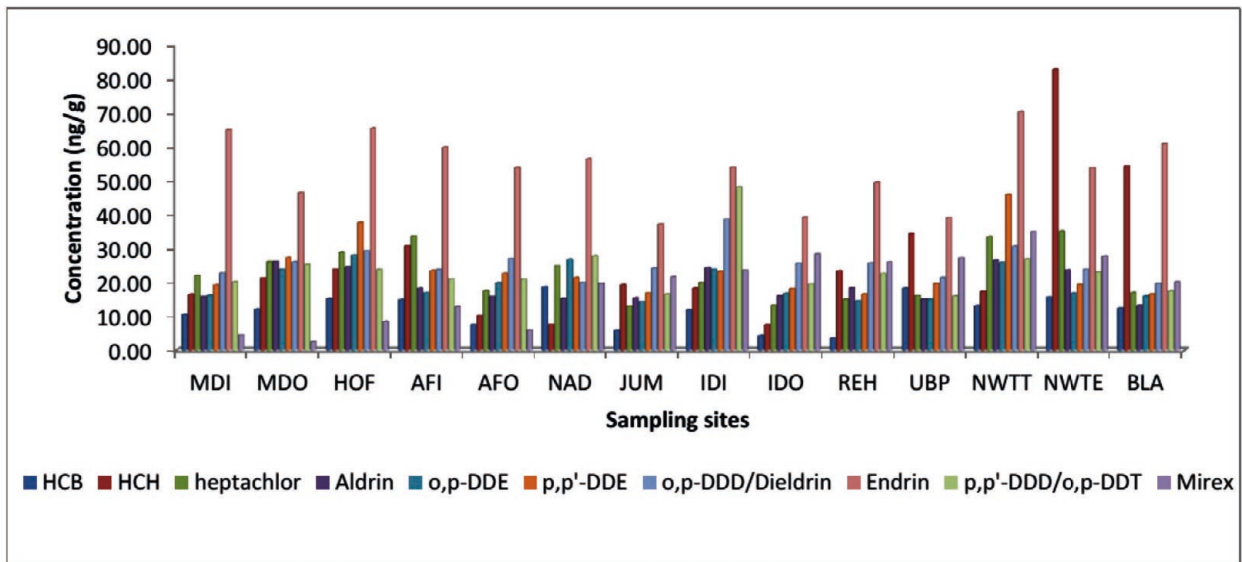


Figure A5. Individual concentrations of OCPs in river bank soil

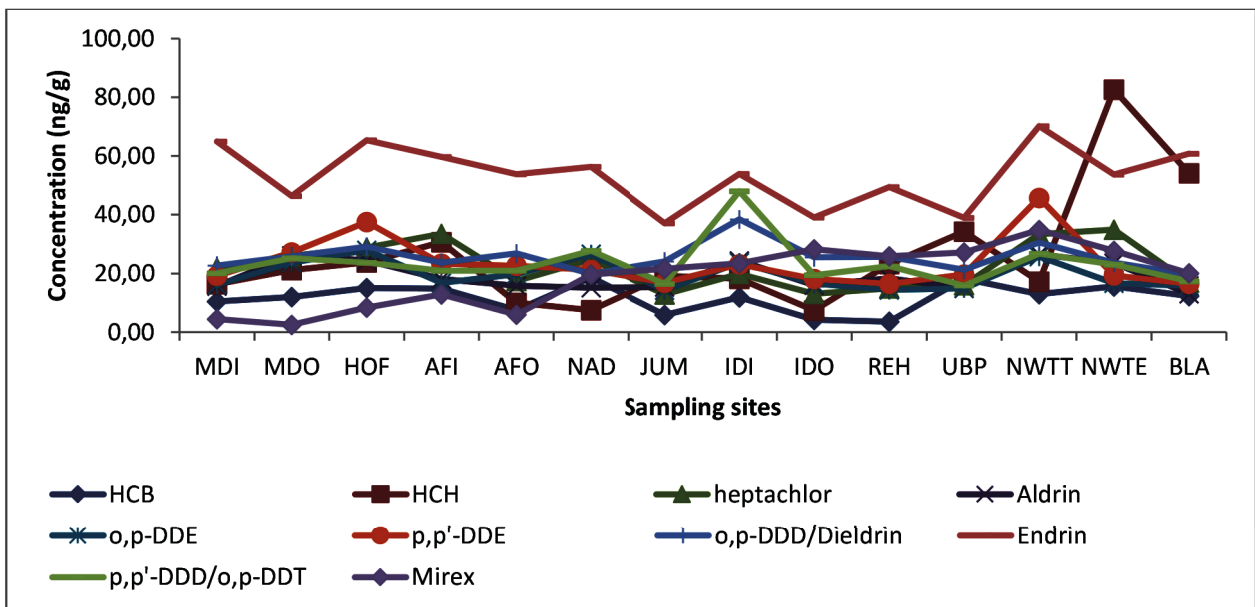


Figure A6. Trend of concentrations of individual OCPs along the river

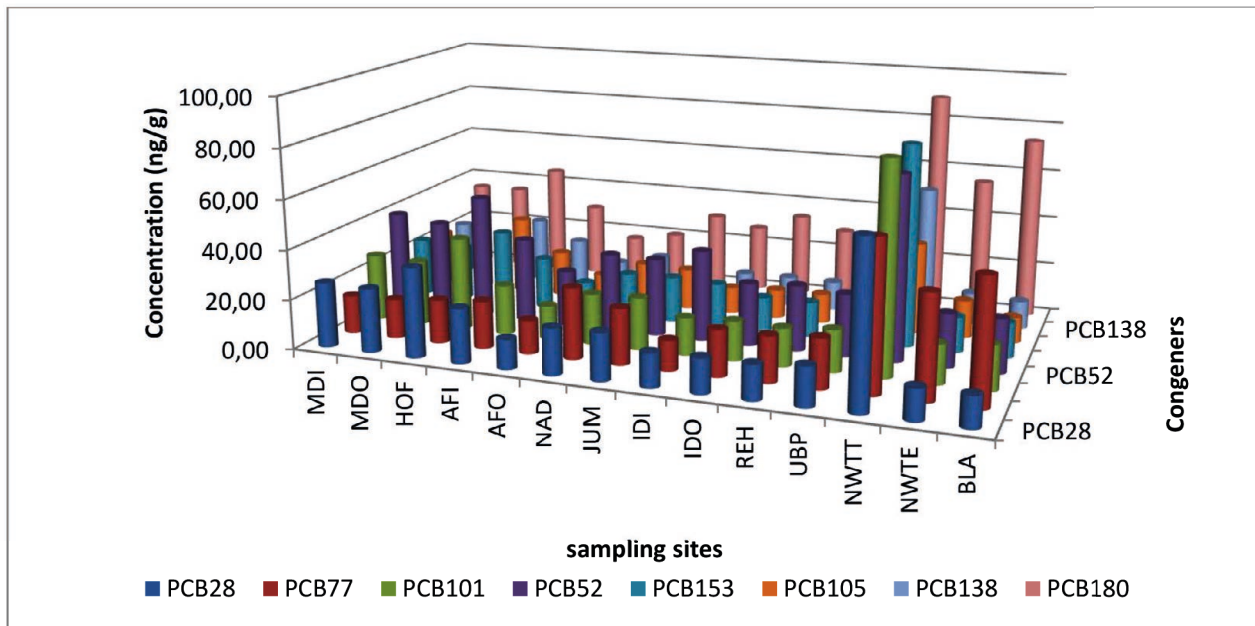


Figure A7. Individual concentrations of PCBs in river bank soil

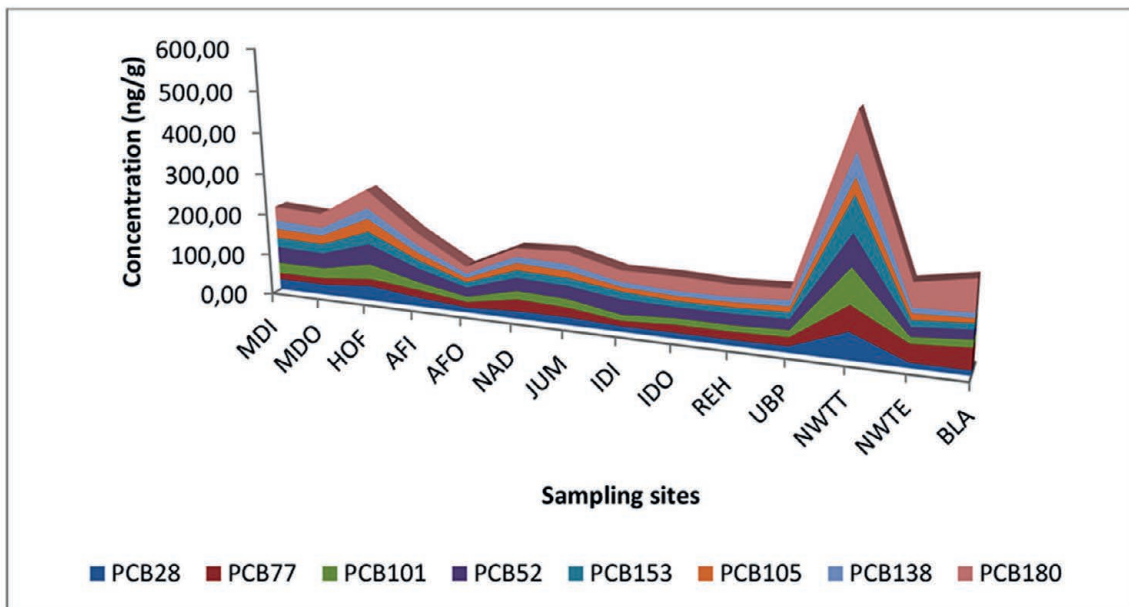


Figure A8. Trend of concentrations of individual and total PCBs along the river