

**OCCURRENCE, DISTRIBUTION AND POTENTIAL SOURCE
OF ORGANOCHLORINE POLLUTANTS IN BOTTOM SEDIMENTS
OF THREE WATER RESERVOIRS, SLOVAKIA**

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Abstract

Bottom sediments are a specific type of water management waste. Mainly hydrophobic organic matter reported in sediments and particles with high surface area can leach more persistent organic pollutants. Thirty-four bottom sediments samples was collected from three water reservoirs – Zemplinska Sirava, Ruzin (at Hnilec and Hornad puller) and Velke Kozmalovce. 14 congeners of polychlorinated biphenyls and 10 organochlorinated pesticides (OCPs) were analyzed. The concentrations in dry weight samples of Σ PCB were in the ranges of 20,28 ng/g (Ruzin/ Hnilec) – 2530,00 ng/g (Zemplinska Sirava); of Σ DDT in the ranges 5,47 ng/g (Zemplinska Sirava) – 525,7 ng/g (Zemplinska Sirava). Hexachlorbenzene was reported in the ranges of 0,27 – 9,24 ng/g (Velke Kozmalovce). Lindan, Heptachlor and Mirex were under the detection limit. Sources of these OCPs are mainly agriculture and forestry in their catchments. The major source of PCBs is industrial wastewater and in the case of the Zemplinska Sirava water reservoir, land contamination caused by Chemko Strazske.

Key words

polychlorinated biphenyls, organochlorine pesticides, bottom sediments

Introduction

Persistent organic pollutants (POPs) are characterized by slow rates of environmental degradation, low water solubility, and high sorption to suspended particles. Once these chemicals are dispersed, they are capable of persisting for many years, with environmental half-lives often of the order of years to decades [1]. Long environmental half-lives and high particle sorption of POPs also mean that lake sediments are natural archives of these

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chemicals. Due to persistence and lipophilic properties, they are able to accumulate in the ecosystem. In addition to carcinogenetic / mutagenic potential, they may cause toxic effects on animal reproduction, development, and immunological functions [2]. Since POPs can enter fishponds and persist for a long period, they can be transferred into food chains, accumulated in fish, and finally reach human beings. In a biological system, several of these chemicals may also cause alterations in endocrine and nervous systems [3, 4, 5]. For these reasons, most countries have restricted or banned the use of PCBs and OCPs.

Polychlorinated biphenyls (PCB)

Chemically, PCBs are chlorinated, aromatic compounds. There are 209 congeners, containing from 1 to 10 chlorine (Cl) substituted on a biphenyl structure (monochlorobiphenyl to decachlorobiphenyl). Approximately 150 congeners are found in the environment [6]. PCBs are thermally stable and resistant to degradation by oxidation or chemical agents. PCBs also have excellent dielectric properties, which led to their widespread use as dielectric fluids in capacitors and transformers. They were also utilized as industrial fluids in various systems, in fire retardants, and in plasticizers used in adhesives, textiles, surface coatings sealants, printing and copy paper. The names of common PCB technical mixtures are Aroclor, Kanechlor, Clophen and Sovol [7]. The physico-chemical properties of chlorobiphenyl homologues are shown at Tab.1.

SELECTED PROPERTIES OF CHLOROBIPHENYL HOMOLOGUES [8]

Table 1

	IUPAC No.	Molecular weight (g.mol ⁻¹)	Water solubility (mg.l ⁻¹)	Vapour pressure (Pa)	log <i>K_{ow}</i>
Monochlorobiphenyl	1 – 3	188,7	1,21 – 5,5	0,9 – 2,5	4,3 – 4,6
Dichlorobiphenyl	4 – 15	223,1	0,06 – 2,0	0,008 – 0,60	4,9 – 5,3
Trichlorobiphenyl	16 – 39	257,5	0,015 – 0,4	0,003 – 0,22	5,5 – 5,9
Tetrachlorobiphenyl	40 – 81	292,0	0,043 – 0,010	0,002	5,5 – 6,3
Pentachlorobiphenyl	82 – 127	326,4	0,004 – 0,020	0,0023 – 0,051	6,0 – 6,5
Hexachlorobiphenyl	128 – 169	360,9	4,0.10 ⁻⁴ – 7,0.10 ⁻⁴	7.10 ⁻⁴ – 12.10 ⁻³	6,9 – 7,3
Heptachlorobiphenyl	170 – 193	395,3	4,5.10 ⁻⁵ – 2,0.10 ⁻⁴	2,5.10 ⁻⁴	6,7 – 7,0
Oktachlorobiphenyl	194 – 206	429,8	2,0.10 ⁻⁴ – 3,0.10 ⁻⁴	6.10 ⁻⁴	7,1 – 7,4
Nonachlorobiphenyl	207 – 208	464,2	1,8 .10 ⁻⁵ – 7,9.10 ⁻⁵	-	7,2 – 8,16
Dekachlorobiphenyl	209	498,7	1.10 ⁻⁶	3.10 ⁻⁵	8,26

PCBs were also produced as Delor (Delotherm, Hydeler) by Chemko Strážske in eastern Slovakia (Michalovce District in the former Czechoslovakia) from 1959 to 1984. The production of Delor 106 was started in 1959 for use in a paint factory. In 1967 and 1968, the production of Delors 103 and 105 was initiated for use in transformers and capacitors. Delor 103 was used as a dielectric fluid in capacitors and Delor 105 was used in transformers manufactured in the Czech Republic. It has been estimated that Chemko produced 21 500 metric tons of PCBs. About 46% of the PCBs were exported to the former East Germany, whereas the rest were used in the territory of former Czechoslovakia. High concentrations of PCBs have been found in humans and wildlife sampled in the area of former PCB manufacture in Slovakia [9,10]. The production of Delors was based on the direct catalytic (FeCl₃) chlorination of pure biphenyl, which was manufactured by Chemko through the high-temperature pyrolysis of benzene. When the expected stage of chlorination was achieved, the

reaction mixture was neutralized with sodium hydroxide and vacuum distilled. Less chlorinated compounds were distilled out of the mixture using steam-jet air pumps. Distilled residues contained highly chlorinated biphenyls and terphenyls. Because the residues were heated at high temperatures (500°C), formation of PCDFs and other dioxin-like compounds could be expected [11]. The compositions of chlorobiphenyl homologues in Delor mixtures in comparison with those in Aroclors PCB mixtures are shown in Figure 1.

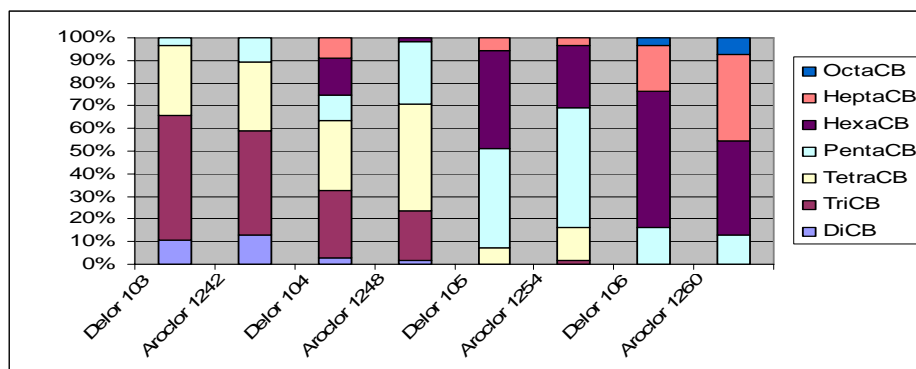


Fig. 1. Composition (%) of chlorobiphenyl homologues in PCB commercial mixtures [11]

DDT

DDT has been widely used throughout the world to control arthropod disease-vectors and agricultural pests. As a result DDT residues are widely distributed and are persistent environmental contaminants. Although DDT is banned in developed nations it is still being used in developing nations [12] due to its cost effectiveness and broad-spectrum activity. In Slovakia it was manufactured in a Bratislava chemical plant in the 60's and 70's. Its use for agriculture was banned in 1976, however, in spite of that fact it was used until the depletion of DDT stockpiles. For example, in 1970 about 140 t of active ingredient was used. Currently, there is almost no information on obsolete DDT stockpiles in Slovakia. One can expect that limited amounts of obsolete DDT could be still stored at cooperative farms and by individuals. A certain amount is in the landfill site of the former producer outside Bratislava [13]. Commercial grade DDT generally contains 75% p,p'-DDT, 15% o,p'-DDT, 5% p,p'-DDE, <0,5% p,p'-DDD, <0,5% o,p'-DDD, <0,5% o,p'-DDE and <0,5% unidentified compounds [14]. DDE and DDD are the two major metabolites of DDT usually present together with their parent compound in DDT-contaminated soils and sediments. It is a common notion that DDT is biodegraded to DDE under aerobic conditions or to DDD under anaerobic conditions in the environment. Combined with the fact that DDT (sum of p,p'-DDT and o,p'-DDT) accounts for more than 90% of the technical DDT formulation, the ratio of DDT/(DDE+ DDD) is often used to indicate whether fresh technical DDT input is viable [15]. In addition, o,p'-DDT/p,p'-DDT is close to 7 in dicofol and 0,2 in technical DDT mixture; hence, a ratio of o,p'-/p,p'-DDT close to 7 suggests the likelihood of dicofol-related inputs [16].

SELECTED PROPERTIES OF CHOSEN ORGANOCHLORINE PESTICIDES [8]

Table 2

	IUPAC name	Molecular weight (g.mol ⁻¹)	Water solubility 25°C (mg.l ⁻¹)	Vapour pressure	log <i>K_{OW}</i>
o,p'-DDT	1,1,1-trichloro-2,2-bis (p-chlorophenyl)ethane	354,49	0,085	1,1.10 ⁻⁷ torr (20°C)	6,79
o,p'-DDE	1,1-dichloro-2,2-bis (p-chlorophenyl)ethylene	318,03	0,14	6,2.10 ⁻⁶ torr (25°C)	6,00
o,p'-DDD	1,1-dichloro-2,2-bis (p-chlorophenyl)ethane	320,05	0,1	1,94.10 ⁻⁶ torr(30°C)	5,87
HCB	hexachlorobenzene	284,78	0,006	1,09.10 ⁻⁵ mmHg (20°C)	5,73
Alpha HCH	alpha-1,2,3,4,5,6-hexachlorocyclohexane	290,83	10	4,5.10 ⁻⁵ mmHg (25°C)	3,8
Beta HCH	1-alpha, 2-beta, 3-alpha, 4-beta, 5-alpha, 6-beta-hexachlorocyclohexane	290,83	5	3,6.10 ⁻⁷ mmHg (20°C)	3,78
Gamma HCH	1-alpha, 2-alpha, 3-beta, 4-alpha, 5-alpha, 6-beta-hexachlorocyclohexane;	290,83	17	4,2.10 ⁻⁵ mmHg (20°C)	3,2
Delta HCH	1-alpha,2-alpha,3-alpha, 4-beta, 5-alpha, 6-beta-hexachlorocyclohexane	290,83	10	3,5.10 ⁻⁵ mmHg (25°C)	4,14
Heptachlor	1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	372,32	0,05	3.10 ⁻⁴ mmHg (20°C)	6,10
Mirex	1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	372,32	0,05	3.10 ⁻⁴ mmHg (20°C)	6,10

Hexachlorobenzene (HCB)

This compound does not occur naturally. It is formed as a by-product during the manufacture of chemicals used as solvents (substances used to dissolve other substances), other chlorine-containing compounds, and pesticides. Small amounts of hexachlorobenzene can also be produced during combustion processes such as burning of city wastes. It may also be produced as a by-product in waste streams of chlor-alkali and wood-preserving plants. It was also used to make fireworks, ammunition, and synthetic rubber [17]. Hexachlorobenzene was widely used as a pesticide until 1965. In Slovakia HCB was manufactured in a Bratislava chemical plant in the 60's and 70's. It was used mainly as a pesticide until its use was banned in 1976. For example, in 1971 about 4.5 t of active ingredient was used in agriculture [13].

Hexachlorocyclohexane (HCH)

An insecticide on fruit, vegetables, and forest crops, and animals and animal premises - hexachlorocyclohexane (HCH) is a synthetic chemical that exists in eight chemical forms called isomers. The different isomers are named according to the position of the hydrogen atoms in the structure of the chemical [18]. Amongst the hexachlorocyclohexane isomers, lindane (gamma HCH) was consistently present in higher concentrations than alpha- and beta-HCH. This suggests that lindane has been used instead of technical HCH, a mixture that contains several HCH isomers, generally with high percentages of alpha-HCH [19]. Commercial HCH contains 55–80% alpha-HCH, 5–14% beta-HCH, 12–15% gamma-HCH, 2–10% delta-HCH and other chloroorganic compounds [20]. In soils, the average half-life of

delta-HCH is 20–50 days, while that for alpha-HCH is 20 weeks [19]. Because the ratio of alpha-HCH/gamma-HCH (4–7 in commercial grade HCH) is relatively stable, it can be used as an indicator of the level of degradation or use of HCHs [20].

Heptachlor

Heptachlor is a manufactured chemical and doesn't occur naturally. It is produced via the Diels-Alder reaction of hexachlorocyclopentadiene and cyclopentadiene. The resulting adduct is brominated followed by treatment with hydrogen chloride in nitromethane in the presence of aluminum trichloride or with iodine monochloride. Pure heptachlor is a white powder that smells like camphor (mothballs). Heptachlor was used extensively in the past for killing insects in homes, buildings, and on food crops, especially corn. These uses stopped in 1988. Currently it can only be used for fire ant control in power transformers [21].

Mirex

Mirex is not known to occur in the environment as a natural product. Mirex was produced as a result of the dimerization of hexachlorocyclopentadiene in the presence of an aluminum chloride catalyst. Technical grade preparations of mirex contained 95,18% mirex, with chlordecone as a contaminant. Mirex was most commonly used in the 1960s as an insecticide. Because it is nonflammable, mirex was marketed primarily as a flame retardant additive for use in various coatings, plastics, rubber, paint, paper, and electrical supplies [22].

Samples and methods

Sample collection

Thirty-four samples of surface sediments were collected from three water reservoirs – Zemplínska Sirava, Ruzin (at Hnilec and Hornád puller) and Velke Kozmalovce in July – September 2003. Details of the sampling sites are shown in Fig. 2. These sampling sites were recorded using the global position system (GPS). The sediments of the Ruzin water reservoir were collected using a stainless steel box corer (developed by Czech Geology Survey, Brno). Other sediments were collected using UWITEC sediment sampling equipment (Austria). Sediment samples were stored in glass bottles, capped with aluminum foil and transported inside ice-chest boxes to the laboratory at the Czech Geology Survey, Brno. They were dried, ground, homogenized and stored to prior analysis. Detailed information is reported in Hiller et al. [23].

Extraction and analysis

Extractable organic matter (EOM) was extracted by agitation with a mixture of n-hexane and acetone (1 : 1, v/v), supported by an ultrasound. Evaporation residues of EOM were used for the determination of the organochlorinated pollutants of interest (PCB, OCP). Hexane leachates of EOM evaporation residues were chromatographically purified on a column with silica gel, impregnated with concentrated H₂SO₄, NaOH and AgNO₃. Pentane eluates, concentrated using the TurboVap evaporator (Zymark, USA), were analysed on an HP 5890 (Hewlett-Packard, USA) gas chromatograph equipped with an electron capture detector

(ECD) and HP ChemStation software package. The basic parameters of the HRGC experimental arrangement for analysis of halogenated substances were: capillary column HP-5 (length 60 m, inner diameter 0,25 mm, phase film thickness 0,25 μm), hydrogen as carrier gas, automated pulsed splitless sample injection. This way, altogether 14 components (congeners) of PCB and 8 components of OCP were determined, with LOD values of about 0,1 ng/g for the majority of the analyzed analytes with relative standard deviations of about 15 %.

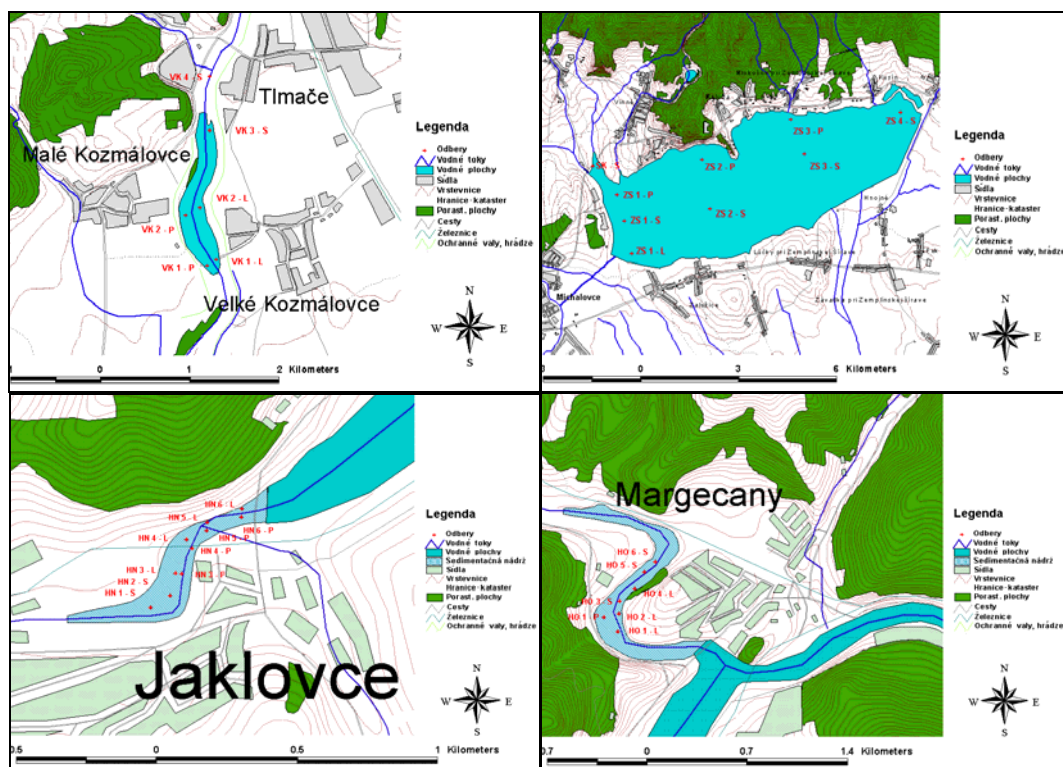


Fig. 2. Map of sampling sites



Fig. 3. The sampling equipment

Results and discussion

PCB concentrations and source identification

CONCENTRATIONS OF PCBs (ng/g DRY WEIGHT) IN BOTTOM SEDIMENTS Table 3

	Velke Kozmalovce				Zemplinska Sirava				Ruzin / Hnilec				Ruzin / Hornad			
	min.	max.	mean	med.	min.	max.	mean	med.	min.	max.	mean	med.	min.	max.	mean	med.
CB8	0,29	1,10	0,88	0,93	0,96	181,00	44,53	30,00	0,38	1,83	1,41	1,02	0,22	1,20	0,42	0,24
CB18	0,81	2,87	2,03	2,05	1,31	209,00	54,16	30,50	1,19	5,11	4,64	3,75	0,52	4,90	1,29	0,58
CB28	1,59	4,66	3,66	3,88	3,35	501,00	137,76	87,50	2,50	8,42	8,61	7,83	1,33	8,20	2,55	1,45
CB31	1,34	3,95	3,14	3,30	2,18	378,00	95,62	65,00	1,80	6,27	6,04	5,56	0,89	6,00	1,82	1,04
CB44	1,01	2,69	1,95	1,93	1,19	113,00	39,59	31,90	1,27	4,10	3,77	3,84	0,54	3,70	1,10	0,63
CB52	1,52	3,51	2,64	2,66	2,12	205,00	68,69	57,90	1,64	4,91	4,44	4,55	0,93	4,20	1,52	1,04
CB101	2,77	5,67	4,16	4,13	2,27	149,00	58,93	52,80	1,59	4,36	3,20	3,27	2,14	3,10	2,63	2,78
CB118	1,17	2,16	1,68	1,71	1,04	85,10	31,88	27,50	0,64	1,77	1,39	1,42	0,68	1,20	0,87	0,83
CB138	4,32	6,79	5,95	6,18	2,61	176,00	69,32	63,20	2,27	7,00	4,09	4,02	3,70	6,78	5,19	5,42
CB149	3,39	6,00	4,98	5,07	2,51	165,00	63,87	54,90	2,00	5,40	3,43	3,49	3,20	5,37	4,31	4,60
CB153	4,48	7,19	6,28	6,53	2,79	197,00	72,44	63,90	2,47	7,26	4,42	4,40	4,10	7,14	5,58	5,86
CB180	3,20	4,99	4,15	4,12	1,65	121,00	48,22	40,60	1,70	5,29	3,11	2,98	3,20	5,24	4,07	4,08
CB194	0,66	1,03	0,82	0,78	0,41	25,40	11,07	9,96	0,46	1,03	0,64	0,61	0,66	0,99	0,80	0,75
CB203	0,76	1,02	0,87	0,84	0,51	24,50	10,86	9,32	0,37	1,05	0,75	0,75	0,72	1,10	0,91	0,90
SUM PCB	27,31	53,63	43,20	44,07	24,90	2530,00	806,94	624,98	20,28	63,80	49,95	47,45	22,83	59,12	33,05	30,21

The concentrations of Σ PCB (the sum of measured 14 congeners) in the bottom sediments from three Slovak water reservoirs ranged from 20,28 ng/g (Ruzin/Hnilec) to 2530,00 ng/g dry weight (Zemplinska Sirava) with a mean value 233,28 ng/g. The highest concentration of Σ PCB was found at site ZS2 – S, and the second highest at site ZS3 – S (1135,60 ng/g). The source of these higher concentrations is Chemko Strazske. In sediment samples, the most abundant PCB congeners were 28, 31, 153,138 comprising up to 46,35% of the total amount of PCB. The PCB concentrations in sediments from three Slovak water reservoirs were found to be lower than the maximum of those in the sediments of other lakes and rivers in Slovakia. In 1997 – 1998 the Institute of Preventive and Clinical Medicine (IPCM) in Bratislava analyzed 53 samples of stream and lake sediments taken from the surroundings of the chemical plant Chemko Strážske. All results were positive. The maximum sum value of PCBs was registered in the waste canal from the chemical plant with PCB concentrations achieving 4100 ng/g. The State Hydrometeorological Institute analyzed PCBs in sediments from the Slovak rivers Danube, Hron, Ipel and Vah in 2001. Altogether 21 samples were analyzed. Positive values were discovered in 4 samples from the Danube and 1 sample from the Vah [13]. In comparison to other regions and countries, Kang et al. [24] reported Σ PCB 11,5 – 485 ng/g dry weight from the Perl River Estuary, South China, Xing et al. [25] 15,1 – 58 ng/g dry weight from Minjiang River, Southeast China and 0,62 – 337 ng/g dry weight from Songhua River, Northeast China. Hartmann et al. [26] reported Σ PCB 20,8 - 1760 ng/g dry weight from Narragansett bay, USA, Barakat et al. [27] 0,9-1210 ng/g dry weight from Alexandria harbour, Egypt, Sprovieri et al [28] 10 - 899 ng/g dry weight from Neaple harbour, Southern Italy. He et al. [29] reported Σ PCB nd – 6,0 ng/g dry weight from the mid- and down-stream of the Yellow River, North China and Shen et al. [30] 0,92 – 9,7 ng/g dry weight from the lower reaches of the Yangtze River, East China.

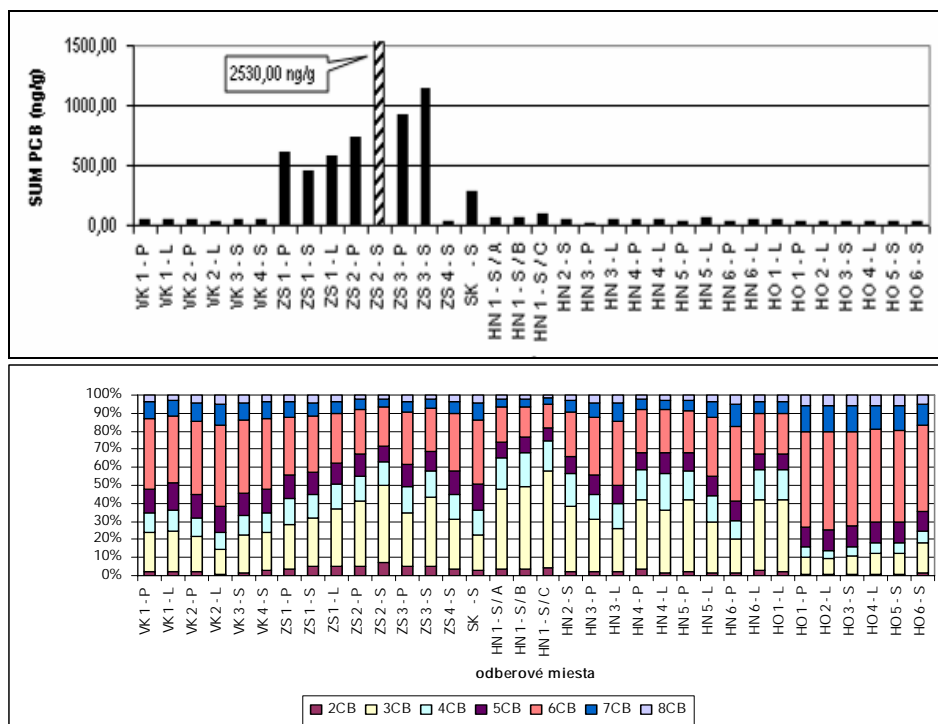


Fig. 4a) Concentrations of Σ PCB (ng/g dry weight) and **4b)** percentage compositions of PCBs in sediments

Our sediment investigation revealed the general prevalence of lower molecular weight PCBs. The proportion of different PCBs in sediment samples from Zemplinska Sirava and Ruzin / Hnilec decreased in the following order: trichlorobiphenyls, hexachlorobiphenyls, tetrachlorobiphenyls, pentachlorobiphenyls, heptachlorobiphenyls, di- and octachlorobiphenyls in Zemplinska Sirava / octa- and dichlorobiphenyls in Hnilec. The dominant congeners in Velke Kozmalovce and Ruzin / Hornad are hexachlorobiphenyls, trichlorobiphenyls and pentachlorobiphenyls. A number of previous studies show the production of low molecular weight PCBs during steel manufacturing processes. This is due to the presence of PCBs in fly ash generated from burning coal during the iron ore sintering process [31, 32]. A relatively higher percentage of high chlorinated congeners, such as heptachlorobiphenyl and octachlorobiphenyl in our sediments indicates near-source emissions of PCBs from industrial wastewater and domestic sewage. Congener composition indicates that the PCBs in sediments originated from sources like Delor 106 (used mainly as paint additive) or Delor 103 retrospectively (used primarily in power capacitors as dielectricum). The result is also consistent with the fact that the heavier PCBs are deposited nearer the source while lower chlorinated PCBs are more mobile and easily biodegraded [33, 34, 35].

OCP concentrations and source identification

CONCENTRATIONS OF OCPS (NG/G DRY WEIGHT) IN BOTTOM SEDIMENTS

Table 4

	Velke Kozmalovce				Zemplinska Sirava				Ruzin / Hnilec				Ruzin / Hornad			
	min.	max.	mean	med.	min.	max.	mean	med.	min.	max.	mean	med.	min.	max.	mean	med.
p,p'-DDT	2,25	13,00	6,58	4,35	0,40	8,50	3,38	3,00	0,40	1,70	0,69	0,50	0,40	15,10	2,77	0,50
o,p'-DDT	0,38	0,92	0,69	0,73	0,50	5,30	1,03	0,50	0,30	0,30	0,43	0,30	0,30	0,70	0,36	0,30
p,p'-DDE	5,51	9,79	8,47	8,95	1,27	410,00	54,46	9,92	2,36	8,60	6,35	6,88	4,60	13,20	10,18	10,70
o,p'-DDE	0,20	0,22	0,21	0,21	1,00	7,57	1,73	1,00	0,17	0,23	0,21	0,21	0,20	0,54	0,32	0,29
p,p'-DDD	0,31	1,29	0,60	0,47	0,30	53,30	6,58	0,70	0,30	0,50	0,32	0,30	0,30	6,00	1,57	0,50
o,p'-DDD	2,00	2,00	2,00	2,00	2,00	41,20	6,36	2,00	2,00	2,00	2,00	2,00	2,00	2,00	2,00	2,00
HCB	0,66	9,24	3,44	2,59	0,27	2,64	1,09	1,01	0,53	9,00	1,73	1,06	0,90	2,80	2,29	2,51
Lindan	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50
Hepta chlor	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50
Mirex	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40

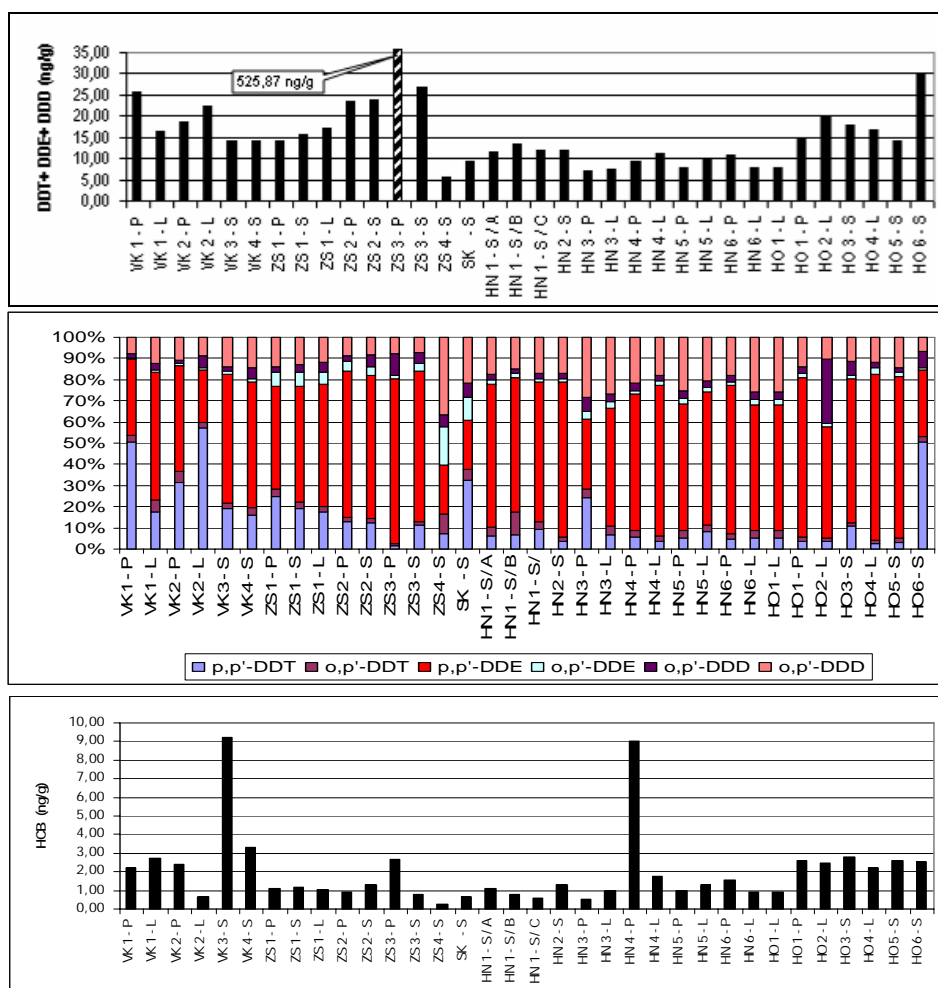


Fig. 5a) Concentrations of Σ DDT (ng/g dry weight), **5b)** percentage compositions of DDT and its metabolites **5c)** Concentrations of hexachlorbenzene in sediments

It is still possible to prove the presence of DDT in the environment together with the DDT degradation products DDE and DDD. The total concentrations of DDTs (sum p,p'-DDT, o,p'-DDT, p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDD) ranged from 5,47 to 525,7 ng/g dry weight, with a mean of 29,81 ng/g. The highest concentration of DDTs was found at site ZS3 – P and the lowest concentration was detected at ZS4 – S (Zemplinska Sirava). In comparison to other reports, the DDT pollution was relatively comparable. Amongst 73 samples taken in the Spiš-Gemer Mountains, 7 were positive - with the maximum concentration of 208 ng/g. Samples of water sediments were taken in the frame of the project TIBREG in districts Sobrance, Vranov, Michalovce and Trebisov. The content of DDT in the sediments was low even though agricultural activities are widespread in this region. Of 125 samples, only 2 were above the detection limit - 90 and 20 ng/g. The highest DDT concentration was discovered in the district of Levice: 940 ng/kg in the sample taken near the village Horsa [13]. May et al. [36] reported Σ DDT 35,1 – 91,1 ng/g dry weight from Zhujiang River, China, 22,9 – 40,41 ng/g dry weight from Shiziyang River, China, 5,0 – 16,6 1 ng/g dry weight from Xijiang, China, and 26 – 115,6 1 ng/g dry weight from Lingding Bay, China.

Among DDT and its metabolites in our sediment samples, p,p'-DDE was most dominant and its concentrations were in the range of 1,27 – 410 ng/g dry weight with a mean value 20,25 ng/g dry weight, accounting for 68% of the total DDTs. o, p'-DDD was the second highest. This composition indicated an aerobic pathway of metabolism of DDT, probably after its application on agricultural soil. Evaluating the o,p'-DDT/p,p'-DDT ratio in all samples, there were used a technical DDT mixture, and using the DDT/(DDE+ DDD) ratio we can determine historical application.

Hexachlorbenzene (HCB) was detected in all soil samples collected, and the concentrations ranged from 0,27 (Zemplinska Sirava) to 9,24 ng/g dry weight (Velke Kozmalovce) with a mean 1,98 ng/g. The higher concentrations were detected in the sediment samples VK3 – S (9,24) and HN3-L (9,0). Some previous studies reported the existence of HCB in sediments near the Chemko Strazske chemical plant, in the water reservoirs of Domaša, Sirava, Laborec and Ondava. The highest concentrations were found in the western part of the water reservoir Sírava: 1100 mg/kg, in the central part of Zemplinska Sirava: 100 mg/kg, Domaša – Turany nad Ondavou: 1100 mg/kg, Domaša-Bžany 2500 mg/kg. The content of HCB in other samples was below 1 mg/kg. [13] By comparison with other countries, our levels of HCB were similar to or higher than those of others studies as follows: Han river (main stream): 1,43 ng/g, Bukhan river: 1,74 ng/g and Namhan river: 1,34 ng/g [37]

Lindan, heptachlor and Mirex was analyzed in all sediment samples, but their concentrations were under the concentration limit.

Conclusions

The present study examined the occurrence, distribution and possible sources of 14 congeners of PCBs and 10 OCPs in bottom sediments from three Slovak water reservoirs. Although the use of these POPs is banned, it is still possible to prove their presence in the environment. The most frequently occurring POPs in three Slovak water reservoirs – Zemplinska Sirava, Velke Kozmalovce and Ruzin are PCBs, DDT and hexachlorobenzene.

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