Screening of short- and medium-chain chlorinated paraffins in selected riverine sediments and sludge from the Czech Republic

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Data on contamination of sediments from industrial areas fill the informational gap in the field of contamination of the Central Europe by chlorinated paraffins.

Abstract

Wide distribution of chlorinated paraffins in the environment has already been demonstrated in several studies; however, information about their levels in the Central Europe is still very limited. First study focused on the SCCP contamination of the Czech aquatic environment have been performed recently, and its results motivated the authors to analyze sediments from a wide set of the Czech rivers in order to obtain more detailed information. Thirty-six sediment samples from eleven rivers and five drainage vents neighboring the chemical factories were analyzed; special attention was paid to the industrial areas. For the first time in the Czech Republic, medium-chain in addition to short-chain chlorinated paraffins were analyzed using GC-ECNI-MS. Chlorinated paraffins were detected in sediment samples on the concentration levels up to 347 ng g^{-1} for short-chain chlorinated paraffins, and 5575 ng g^{-1} for medium-chain chlorinated paraffins. Average chlorination degree of SCCPs was 65%.
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1. Introduction

Chlorinated paraffins (CPs) are industrially produced mixtures of compounds with the general formula of $C_nH_{2n+2-z}Cl_z$. Based on the chain length, they are classified into three categories: short-chain (C_{10}—C_{13}; SCCPs), medium-chain (C_{14}—C_{17}; MCCPs), and long-chain ($C_{>17}$; LCCPs) chlorinated analogs of the straight-chain alkanes from which they are manufactured (Tomy et al., 1998). They can be further categorized according to the degree of chlorination: 40—50%, 50—60%, and 60—70%. Chlorinated paraffins have various

industrial applications: they are used in sealants, paints, metal-working fluids, leather treatment chemicals, carbon-less copy paper, as flame retardants or softeners in rubbers, textiles, polyvinylchloride (PVC) or other polymers (UNECE ad hoc Expert Group on POPs, 2003; Euro Chlor, 2006). SCCP mixtures with high chlorine content (60—70% in weight) are mostly used as flame-retardants. MCCPs, which usually do not reach such a high chlorination degree, are mainly used as softeners (plasticizers) while retaining an advantage of flame retarding properties (Euro Chlor, 2006).

The use of SCCPs in European Union decreased in the 1990s, and the estimated production is now lower than 15,000 tonnes per year (Ospar Commission, 2001). On the contrary, production of MCCPs has a growing trend in Europe, and it ranges from 45,000 to 160,000 tonnes per year (European Environmental Agency, 2002). In 2002, 32,000 tonnes

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of MCCPs was used just for PVC production in the European Union, while only 1000 tonnes of SCCPs was used as sealants, adhesives, softeners or flame-retardants in rubber and textiles industries (Euro Chlor, 2006). In Central Europe, short- and medium-chain chlorinated paraffins are still produced in the Slovak Republic (Novacke chemicke zavody), where dodecanes, pentadecanes, and pentacosane with chlorination degree between 40% and 64% are produced.

Chlorinated paraffins have a very low acute toxicity, they are classified as category 3 carcinogens, and they are considered to be toxic for aquatic environment. MCCPs have not yet been classified according to the Dangerous Substances Directive (67/548/EEC); however, they have recently been proposed for a new classification as dangerous for the environment, and the category 3 carcinogens (Euro Chlor, 2006).

Chlorinated paraffins could reach the environment through production, storage, transportation or industrial use, and also by leaching, runoff and volatilization from contaminated environmental compartments. There have been several studies focused on the CP contamination of sediments around the globe. Data from United Kingdom showed heavy contamination of sediments by short- and medium-chain CPs; the sum of MCCPs found in sediment was up to $65\ \mu g\ g^{-1}$ (Nicholls et al., 2001). SCCP levels in sediments from Norway were determined to be $19\ \mu g\ g^{-1}$ of the wet weight, and MCCP levels up to $11\ \mu g\ g^{-1}$ of the wet weight (Borgen et al., 2003). In Japanese sediments concentrations of CPs (CP_{10-30}) were up to $10\ \mu g\ g^{-1}$. In other countries, contamination of freshwater sediment was generally lower: MCCP levels lower than $5\ ng\ g^{-1}$ were measured in Lake Zürich, Switzerland, and they stayed bellow $700\ ng\ g^{-1}$ in the River Lech, Germany (Tomy et al., 1998). CP concentrations in sediments from Lake Fox, Canada were up to $257\ ng\ g^{-1}$ (Tomy et al., 1998, 1999), in sediments from Lake Ontario researchers found the average SCCP concentration of $49\ ng\ g^{-1}$ (Marvin et al., 2003), and $1–11\ ng\ g^{-1}$ of CPs were detected in Sugar Creek, USA. For the sea sediments, $112\ ng\ g^{-1}$ of SCCPs and $146\ ng\ g^{-1}$ of MCCPs were found in German Bight, North Sea (Hüttig et al., 2004), and highest concentrations in Baltic Sea sediments reached 377 and $499\ ng\ g^{-1}$ for SCCPs and MCCPs, respectively (Hüttig et al., 2004). Concentration levels up to $65\ \mu g\ g^{-1}$ were measured in sewage sludge from industrial areas in Germany; while $30\ \mu g\ g^{-1}$ was the CP concentration in sewage sludge from Switzerland. Also, the samples from drainage ditches of a CP manufacturing facility in the USA showed concentrations up to $40\ \mu g\ g^{-1}$ for SCCPs and $50\ \mu g\ g^{-1}$ for MCCPs (Table 1).

In spite of the fact that short- and medium-chain chlorinated paraffins are still manufactured in Slovakia, there is a lack of data about CP contamination of the Central European environment. There has only been one paper focused on two industrial areas in the Czech Republic with the aim of determining whether the contamination of aquatic environment by short-chain chlorinated paraffins (SCCPs) is an issue deserving more attention (Štejnarová et al., 2005). The highest concentration of SCCPs was detected in sediment from Drevnice river, Zlin region (up to $181\ ng\ g^{-1}$ of dry sediment

Table 1
Chlorinated paraffins in the sediment and sludge samples

Country	Concentration in sediment/sludge ($\mu g\ g^{-1}$) $\sum$SCCPs	$\sum$MCCPs	$\sum$CPs
United Kingdom		65	
Germany (sludge)		65	
Germany (River Lech)		0.7	
German Bight, North See	0.112	0.146	
Baltic Sea	0.377	0.499	
Switzerland (sludge)			30
Switzerland (Lake Zurich)		0.005	
Norway	19	11	
Japanese			10
USA (sludge)	40	50	
USA (Sugar Creek)			0.011
Canada (Lake Fox)			0.257
Canada (Lake Ontario)	0.049		

weight). Results of the study as well as the recent regulation of the Czech government concerning monitoring of SCCPs in aquatic ecosystem motivated the authors to perform the here presented screening study of sediment samples from all bigger Czech rivers.

2. Materials and methods

2.1. Chemicals

n-Hexane (Supersolv; Merck, Darmstadt, Germany), tetrahydrofuran, dichloromethane (Pestiscan; Labscan, Dublin, Ireland), sulfuric acid (Pro analysis; Merck, Darmstadt, Germany), hydrochloric acid (Pro analysis; Lachema, Brno, Czech Republic) were used as received. Powder copper (Fluka, Seelze, Germany) was activated before application by addition of hydrochloric acid, and washed with deionized water. Silica gel (63–200 mesh, Merck, Darmstadt, Germany) was cleaned by dichloromethane for 8 h, activated at 150 °C for 12 h, and deactivated by addition of 3% (w/w) deionized water. Helium and nitrogen in 5.5 quality were supplied by Siad (Braňany u Mostu, Czech Republic). Methane in 5.5 quality was supplied by Linde (Brno, Czech Republic). Standards of chlorinated paraffins—SCCPs with various chain lengths ($CP_{10,\ 11,\ 12,\ 13}$) and chlorination degree of each chain (45%, 50%, 55%, 60%, 65%, 70%)—and MCCPs ($CP_{14.47}$; $CP_{16.50}$; $CP_{17.46}$) were synthesized, and kindly provided by the group of Professor Dr. H. Parlar, Technical University of Munich (Germany). Synthesis of chlorinated paraffins was described elsewhere (Coelhan et al., 2000). Cereclor 63L (technical mixture $CP_{10-13.63}$) was supplied by Imperial Chemicals (UK). Lindane was used as an internal standard (Supelco, Bellefonte, PA, USA).

2.2. Instrumentation

A centrifuge Jouan BR4 (Jouan Technology for life, Winchester, VA, USA) was used. Chromatographic separation was carried out on a gas chromatograph Finnigan Q-GC connected with a Finnigan GCQ mass spectrometer (Thermo Electron, San Jose, CA, USA). A gas chromatograph was equipped with a split/splitless injector (Finnigan 2200) and a silica capillary column (30 m, 0.25 mm i.d.) coated with 0.25 μm film of DB5-MS stationary phase (5% phenyl/95% methylpolysiloxane, J&W Scientific, Folsom, CA, USA).

2.3. Samples

Sediment samples from 11 rivers (Labe, Bilina, Ohre, Vltava, Jihlava, Dyje, Svitava, Morava, Becva, Mala Becva, and Drevnice), and five drainage vents in the Czech Republic were taken. Sampling sites were selected with

a special attention to potential industrial sources of contamination. Details about the sampling sites are given in Fig. 2 and Table 2. Top-layer (<10 cm) sediment was sampled by dredging during several sampling campaigns in 2003 and 2004 (see Table 2). Samples were transported to the laboratory in glass boxes and air-dried at the room temperature. Dry samples were homogenized and total organic carbon was determined in each sample.

2.4. Extraction and clean-up

Ten grams of dry sediment sample was extracted by hot solvent extraction (Soxtec-Büchi, Switzerland) with dichloromethane (120 ml) for 60 min. Interfering compounds were removed by addition of sulfuric acid (3 ml): extracts changed to hexane were heated with sulfuric acid addition (in the oven at 60 °C, 60 min) and centrifuged. After centrifugation at 1500 rpm for 5 min, the hexane fraction was taken and evaporated to 500 μL with a nitrogen stream. Activated copper was used for sulfur removal. A glass column (30 cm length, 1 cm i.d.) filled with 5 g of silica gel (activated overnight at 150 °C, and deactivated by addition of 3% w/w of deionized water) was used for fractionation. The first fraction was eluted by *n*-hexane (40 ml), the second (CPs containing) fraction by DCM:*n*-hexane (1:1) (30 ml). Clean-up procedure was described in detail elsewhere (Štejnarová et al., 2005). γ-HCH as an internal standard was added to all samples before analysis on gas chromatography-electron capture negative ion trap mass spectrometry (GC-ECNI-IT-MS) to get the final concentration of 2 ng μL^{-1}.

2.5. Gas chromatography and mass spectrometry

CPs were determined in sample extracts using gas chromatography with mass spectrometric detection working in electron capture negative ionization mode (GC-ECNI-MS) on a Thermo Electron GCQ benchtop ion trap instrument. Chromatographic separation was achieved on a gas chromatograph Finnigan Q-GC with a capillary column (DB5-MS, 30 m × 0.25 mm × 0.25 μm) and following parameters of chromatographic separation: splitless injection, injector temperature 250 °C, injection volume 1 μl, He at a constant linear velocity of 36 cm s^{-1}; temperature program started at 100 °C, held for 1 min., raised at 30 °C min^{-1} to 160 °C, held for 5 min, raised at 30 °C min^{-1} to 310 °C, final hold time 22 min. Total time of analyses was 35 min.

Methane was used as a reagent gas for an ion trap GCQ. Full spectra were taken under the full scan conditions in the mass range of 240–550 amu. Negative mode chemical ionization was optimized to give the highest response for the peak m/z 414 of the internal calibration compound [FC-43, perfluorotributylamine]. The electron beam energy was 70 eV. Transfer line temperature was 275 °C and ion source temperature was 200 °C. Lenses were auto tuned to 12, 125, and 16 V for lens 1, lens 2, and lens 3, respectively. The trap offset was set manually to 7.0 V.

This method is capable of distinguishing between short- and medium-chain chlorinated paraffins in one sample, since the retention times are evaluated as an important parameter enabling the SCCP and MCCP identification. However, the complete separation is not possible. Typical chromatogram of CPs is shown in Fig. 1. Due to the small differences in the mass between some SCCP and MCCP fragments, only a limited number of ions were selected for the quantification of each group of equal chain length (Štejnarová et al., 2005): 313/381/417 (C_{10}), 329/361/395 (C_{11}), 341/375/409 (C_{12}), 355/389/423 (C_{13}), 403/439/471 (C_{14}), 383/417/451/489 (C_{15}), and 465/499/535 (C_{16}). Interference of some SCCP and MCCP masses had to be taken into consideration (Reth and Oehme, 2004). The masses of chlorinated undecanes (395/431/465), for instance, interfere in spectra with those of chlorinated hexadecanes. Similarly, the masses of chlorinated decanes interfere with those of chlorinated pentadecanes.

The standard closely matching the fingerprint of a real contaminant present in the sample was selected for quantification of each carbon chain (standards CP_{10}, CP_{11}, CP_{12}, CP_{13} with 45%, 50%, 55%, 60%, 65%, 70% chlorination degree, and $CP_{14.47}$, $CP_{15.50}$, $CP_{16.46}$ were available for SCCPs and MCCPs, respectively). In case of the Czech river sediments, the standards $CP_{10.65}$, $CP_{11.65}$, $CP_{12.65}$, and $CP_{13.65}$ were applied since the average percentage of chlorination of SCCPs present in the river sediment samples was determined

to be 65%. Medium-chain chlorinated paraffins were quantified using the only available standards $CP_{14.47}$, $CP_{15.50}$, and $CP_{16.46}$.

2.6. Quality assurance and quality control

Surrogate recoveries of the analytical procedure (including extraction, sulfuric acid treatment, and adsorption column chromatography) were performed by analysis of CP free sediment samples enriched with Cereclor 63L and MCCP mixture to get the final concentration of 1000 and 100 ng g^{-1} (dry weight). Recoveries were determined to be $103 \pm 8\%$ ($n = 12$) for low, and $92 \pm 11\%$ ($n = 5$) for high concentration of SCCPs. Recoveries for MCCPs after the same procedures were $57 \pm 3\%$ ($n = 4$) for low, and $68 \pm 4\%$ ($n = 4$) for high concentration.

The detector response was linear in the tested range of 2 and 1000 ng μL^{-1}, and it depended on a chlorination degree and a chain length in case of chlorinated paraffins. Five-point calibration was prepared using individual mixtures of SCCPs and MCCPs in the concentration range of 2 and 500 ng μL^{-1}. Linear regression confidence values R^2 varied from 0.951 for $CP_{10.65}$ to 0.9983 for $CP_{13.65}$. The analytical detection limit for the sum of CPs was 2 ng μL^{-1}. The signal to noise quantification ratio was set to be higher than 10. The limit of quantification for the real sediment samples was based on the lowest concentration of CPs that could be calculated. The limit of quantification for the sediment samples was 10 ng g^{-1} (dry weight). Laboratory blanks were analyzed (one with each 10 real samples), and they gave no signal that could interfere with CP detection. Repeatability of the GC-MS measurement was tested. Relative standard deviation was calculated to be 6% ($n = 10$).

3. Results and discussion

The Czech Republic has historically been highly industrialized country with coal mining, metalworking, engineering, chemical, rubber, textile and other industries. In the 1990s, production was restricted in many branches, but there are still several environmentally stressed regions with a high concentration of industry. Sediment samples from Ohre (sampling sites no. 10–12, Table 2, Fig. 2), and Bilina (6–9) rivers were collected in northwestern part of the country with biggest chemical companies (Chemopetrol Zaluzi, Spolchemie Usti, Eastman Sokolov). In addition to the river sediments, several sewage sludge samples were taken from drainage vents of Chemopetrol (8), and Spolchemie (33–36) companies. Sediments from Labe (1–5), and Vltava (13) rivers were sampled in the central part of the country where chemical company Spolana Neratovice is considered to be the most serious point source of contamination besides some engineering companies. Metalworking, engineering, chemical, rubber, leather, and paint industries dominate in the eastern part of the country. Morava river (19–27) with its tributaries Becva (28–30), Mala Becva (31), Drevnice (32), and Dyje (15–17) are the main water bodies of this region, and they were all included in the sampling design of the study.

Chemopetrol Zaluzi (8) was selected to be one of the sites where the sludge was analyzed since this company is the main producer of ethylene (supplied to Spolana Neratovice, where PVC is manufactured), and propylene (supplied to Eastmen Sokolov) in the country. However, there were no CPs detected in the sewage sludge from Chemopetrol. On the contrary, the CP levels in the sludge from Spolchemie Usti (33–36) ranged from 205 ng g^{-1} to 396 ng g^{-1}, and from 736 ng g^{-1} to 2301 ng g^{-1} for SCCPs and MCCPs, respectively. In

Table 2
Chlorinated paraffin levels in the Czech river sediment and sludge

Sampling site number	Matrix	River	Sampling site	Sampling date	TOC (%)	Concentration ng g^{-1} (dry weight)									
						$\sum C_{10}$	$\sum C_{11}$	$\sum C_{12}$	$\sum C_{13}$	$\sum C_{14}$	$\sum C_{15}$	$\sum C_{16}$	$\sum$SCCPs	$\sum$MCCPs	$\sum$CPs
1	Sed	Labe	Valy	30.7.2003	n.a.	0.1	1.8	0.8	3.6	4.1	7.0	6.9	6	18	24
2	Sed	Labe	Obristvi	29.7.2003	n.a.	0.2	6.9	0.9	3.9	6.5	14.8	51.7	12	73	85
3	Sed	Labe	Srnojedy 1	19.11.2003	<0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4	Sed	Labe	Srnojedy 2	19.11.2003	<0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	Sed	Libis−Labe	Neratovice	2003	n.a.	16.1	65.9	126.7	138.7	277.7	206.1	1114.6	347	1598	1946
6	Sed	Bilina	Usti nad Labem	16.8.2001	n.a.	0.6	6.9	2.5	7.1	4.4	10.7	16.0	17	31	48
7	Sed	Bilina	Most upstream	22.5.2004	7.96	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8	Sludge	Drainage−Bilina	Chemopetrol Zaluzi	22.5.2004	10.10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
9	Sed	Bilina	Most downstream	22.5.2004	1.53	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10	Sed	Ohre	Kynsperk	22.5.2004	4.61	3.1	18.4	24.3	43.2	1098.2	1394.6	3082.7	89	5575	5665
11	Sed	Ohre	Sokolov upstream	22.5.2004	2.91	1.5	4.6	5.3	20.8	92.1	193.4	314.6	32	600	632
12	Sed	Ohre	Sokolov downstream	22.5.2004	1.06	0.9	2.7	2.6	8.3	61.4	93.6	152.5	15	308	322
13	Sed	Vltava	Zelcin	28.7.2003	<0.05	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
14	Sed	Jihlava	Jihlava	5.2004	3.36	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
15	Sed	Dyje	Znojmo	5.2004	5.43	2.1	4.5	5.2	16.4	195.9	250.3	311.1	28	757	785
16	Sed	Dyje	Postorna	5.2004	0.59	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
17	Sed	Dyje	Moravska Nova Ves	5.2004	0.33	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
18	Sed	Svitava	Svitavy	5.2004	<0.05	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
19	Sed	Morava	Zabreh	5.2004	<0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
20	Sed	Morava	Olomouc	5.2004	1.15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
21	Sed	Morava	Kromeriz	5.2004	1.93	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
22	Sed	Morava	Kromeriz confluence Mala Becva	4.6.2004	0.82	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
23	Sed	Morava	Otrokovice	5.2004	0.81	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
24	Sed	Morava	Uherske Hradiste	4.6.2004	2.49	1.1	4.1	5.5	17.0	93.7	138.1	184.5	28	416	444
25	Sed	Morava	Chropyne	4.6.2004	1.65	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
26	Sed	Morava	Spytihnev	4.6.2004	0.22	2.5	16.0	64.2	67.0	36.8	32.4	124.1	150	193	343
27	Sed	Morava	Lanzhot	5.2004	1.81	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
28	Sed	Becva	Prerov	5.2004	<0.05	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
29	Sed	Becva	Valasske Mezirici	5.2004	2.21	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
30	Sed	Becva	Zubri	4.6.2004	0.61	0.5	1.7	17.7	26.6	10.4	9.9	99.9	60	120	180
31	Sed	Mala Becva	Za Plesovcem	4.6.2004	0.32	0.3	0.8	0.6	2.0	33.5	35.9	43.7	4	113	117
32	Sed	Drevnice	Malenovice	4.6.2004	0.54	1.5	6.3	9.9	36.5	154.1	317.8	420.8	54	893	947
33	Sludge	Drainage	Spolchemie Usti	14.1.2004	24.40	31.3	68.6	109.7	132.7	192.1	225.0	395.8	342	813	1155
34		Drainage	Spolchemie Usti	14.1.2004	25.90	24.9	42.9	63.1	74.8	116.5	235.6	384.2	206	736	942
35		Drainage	Spolchemie Usti	28.1.2004	25.60	33.6	74.7	112.9	175.7	366.3	547.9	1387.1	397	2301	2698
36		Drainage	Spolchemie Usti	28.1.2004	24.50	31.2	54.3	86.5	110.0	165.2	230.5	408.7	282	804	1086

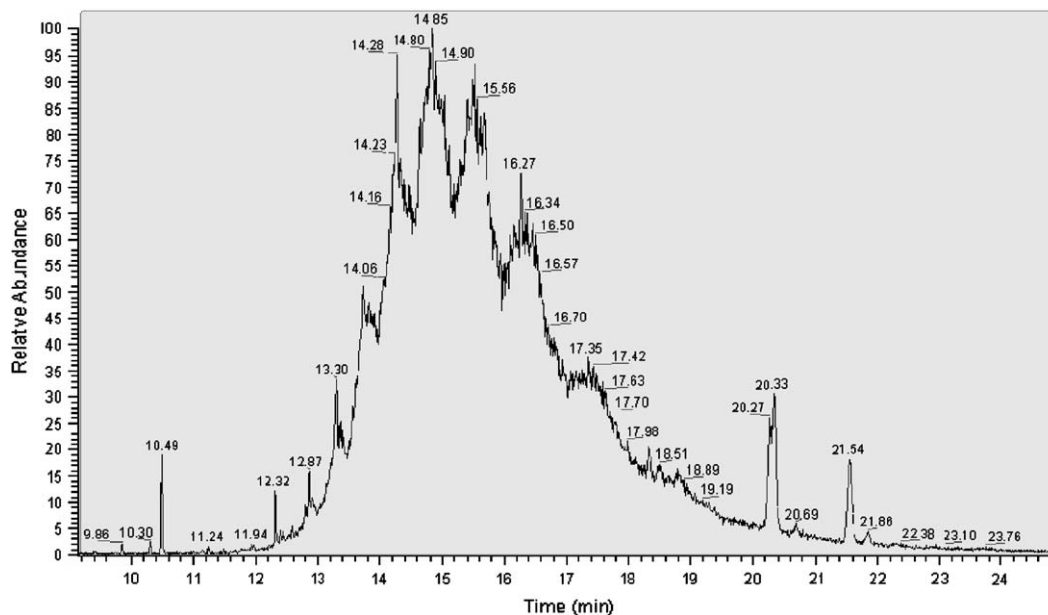Sed, sediment; n.a., not analyzed; n.d., not detected; LOD, limit of detection.

Fig. 1. Chromatogram of CPs from the sediment sample.

Spolchemie, organic paints and pigments are produced, and application of CPs as adhesives can be a source of significant contamination of the sludge. Relatively high concentrations of SCCPs (up to one third of the sum of CPs, Table 2) support this assumption.

Short- and medium-chain chlorinated paraffins were detected in several sediment samples as well; all studied rivers except for Jihlava (14), Svitava (19), and Vltava (13) were contaminated at least at some of the sampling sites (Table 2). Ohre river (northwest) on its upper stream in Kynsperk (10) was the most contaminated site in this study, with SCCP concentration of 89 ng g^{-1} but that of MCCPs as high

as 5575 ng g^{-1}. This sampling site was probably strongly affected by a local factory (GPH, a Nexans company) where a range of crimping connectors and lugs for aluminum or copper cables are produced. A sale and service of hydraulic and mechanic equipments for electrical engineering was confirmed at the same facility as well. Metal working and hydraulic fluids could increase the CP contamination of Ohre river as well. Eastmen Sokolov, the chemical factory where waterbased dispersions and polymers are produced, is located down the same river (Ohre). Two sampling sites up (11) and down (12) the stream from this company have not shown such a heavy contamination (14 ng g^{-1} and 32 ng g^{-1} for SCCPs, 307 ng g^{-1}
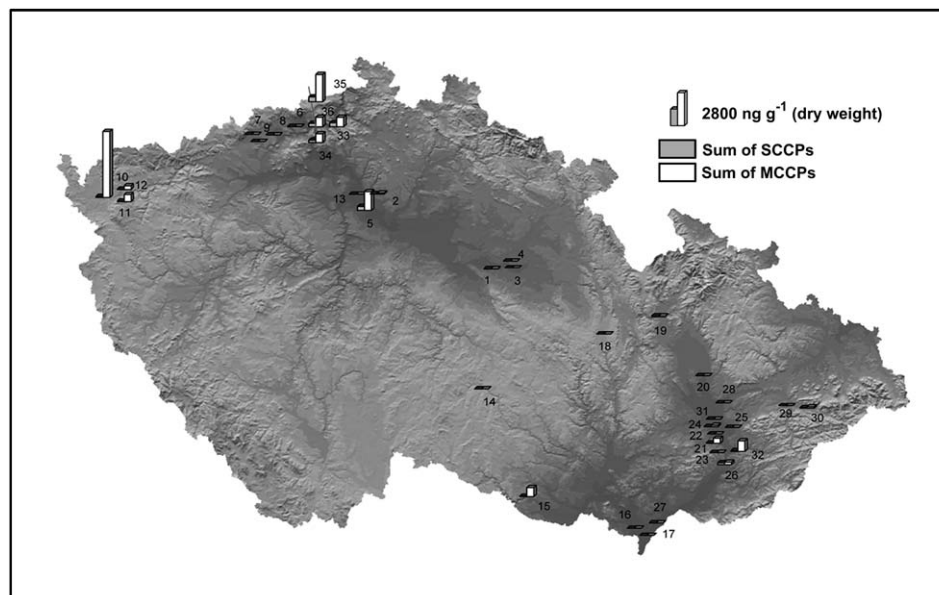

Fig. 2. Map of the sampling sites showing detected levels of CP contamination.

and 600 ng g^{-1} for MCCPs, with higher upstream levels). It can be concluded that CPs released to the aquatic ecosystem are quickly bound to the sediment and remain in the close proximity of their source causing significant local contamination. Similar results were obtained for Bilina river: CPs were detected in river sediment in Usti (6) near Spolchemie, where they were also found in high concentrations in the sewage sludge. On the contrary, CPs were not detected in sediments further down the stream of Bilina river in Most (7 and 9).

The second highest CP concentration was found in sediments from Labe river (central region) in Libis (5) near Spolana Neratovice (347 ng g^{-1} for SCCPs, 1598 ng g^{-1} for MCCPs). It is not surprising since PVC production has been known to be a major CP application and a potential source of CP contamination, and Spolana is a main producer of PVC. All the other sediment samples from Labe river (1–4) had low or none concentrations with maximum of 12 ng g^{-1} for SCCPs and 73 ng g^{-1} for MCCPs.

In the eastern part of the country, Drevnice river (a tributary to Morava) with 54 ng g^{-1} of SCCPs, and 892 ng g^{-1} of MCCPs in sediment was the most contaminated site probably due to the rubber, leather, and engineering industries. Dyje in Znojmo (28 ng g^{-1} of SCCPs, 757 ng g^{-1} of MCCPs), Becva in Zubri (59 ng g^{-1} of SCCPs, 120 ng g^{-1} of MCCPs), and Mala Becva (3 ng g^{-1} of SCCPs, 113 ng g^{-1} of MCCPs) were other Morava tributaries where CPs were found, but there were just two sites with limited CP contamination found in Morava river itself: Uherske Hradiste (27 ng g^{-1} of SCCPs, 416 ng g^{-1} of MCCPs, probably due to the long history of the paint industry) and Spytihnev (149 ng g^{-1} of SCCPs, 193 ng g^{-1} of MCCPs); all the others were CP free.

Medium-chain chlorinated paraffins prevailed in all samples, which is in agreement with data demonstrating trends in production and use of SCCPs and MCCPs. In most of the sampling sites, MCCP levels were more than one order of magnitude higher than those of SCCPs (Table 2).

Highest concentration of SCCPs was found in the sewage sludge from Spolchemie Usti (205–396 ng g^{-1}); a similar level was detected in Libis drain (347 ng g^{-1}) near Spolana Neratovice. This probably indicates the use of SCCPs as adhesives in paints, as softeners or flame retardants in polymer production. Levels of MCCPs in these samples were only 2–5 times higher than those of SCCPs. In the remaining samples, SCCPs were detected in tens of nanograms per gram only, while concentrations of MCCPs were 1–2 orders of magnitude higher. In all samples, chlorinated undecanes and tridecanes were the most abundant molecules in the SCCP mixture (Table 2). The average chlorination degree of short-chain chlorinated paraffins was 65% in all collected samples.

Medium-chain chlorinated paraffins were found in hundreds of nanograms per gram of sediment in most of the sites. However, in the sediment from Ohre river in Kynsperk, their level reached 5575 ng g^{-1} and was higher than in any sewage sludge (804–2301 ng g^{-1} in Spolchemie Usti). MCCP concentration in this sample was 60 times higher than the concentration of SCCPs. Medium-chain chlorinated paraffin concentration varied between 18 and 5575 ng g^{-1}, and chlorinated hexadecanes were the most abundant.

Polychlorinated biphenyls (PCBs), organochlorinated pesticides (OCPs), and polyaromatic hydrocarbons (PAHs) were determined in most of the samples from this study as well. PCBs ranged between 7 and 134 ng g^{-1}, DDTs between 2 and 43 ng g^{-1}, HCHs between 0.5 and 11 ng g^{-1}, and PAHs between 2 and 66 μg g^{-1}. There was no correlation observed between these persistent organic pollutants and detected CP levels. On the contrary, neither the sample with highest PCB (134 ng g^{-1}) or highest PAH (66 μg g^{-1}) levels (both from Bilina river) showed any CP contamination. Similarly, the sites with highest levels of CPs in sediment showed only very low PCB, OCP or PAH concentrations.

Total organic carbon was measured in all sediment samples. No significant correlation between the organic carbon content and CP concentration in the sediment was found using Spearman correlation analysis. The sewage sludge samples were excluded from the statistical analysis.

4. Conclusion

Results from GC-ECNI-IT-MS analysis of 36 sediments from 11 Czech rivers confirmed the assumption that chlorinated paraffins are widely distributed in the Czech aquatic environment. The highest concentrations of chlorinated paraffins were detected in river sediments close to the chemical and electro engineering industries (GPH, a Nexans company, Kynsperk, Spolana Neratovice, Spolchemie Usti). Detected maxima up to 2698 ng g^{-1} for the sum of CPs in the sewage sludge, and 5664 ng g^{-1} for the sum of CPs in river sediments correspond to the data about the CP contamination of European rivers published recently.

Medium-chain chlorinated paraffins highly prevailed in all samples, which is in agreement with the known trends in production and use of SCCPs and MCCPs, but in contrast with other data previously published. There have only been very few papers concerned with both, SCCP and MCCP concentrations in sediments; according to available data, however, their levels were comparable. It is obvious that MCCP/SCCP ratio is source specific and cannot be simply correlated with a level of contamination or a distance from the source. Both low and high ratios were found in contaminated areas close to the sources as well as in remote areas. More detailed study with a row of samples along the river with various point sources is obviously needed to evaluate the changes in ratio, and to estimate the mobility of SCCPs and MCCPs in aquatic environment. This is a subject of our future work.

This project has been carried out as a contribution to the ongoing national POPs inventory in the Czech Republic, which is focused on the new types of persistent industrial substances.

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