

Chlorinated paraffins in the sediment from the Czech Republic

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Introduction

Chlorinated paraffins originate from anthropogenic activities and are introduced to environment as complex technical mixtures with different carbon and chlorine composition. Carbon chain length and chlorination degree depends on the field of use. Generally, chlorinated paraffins are classified into three categories: short chain C₁₀-C₁₃ (SCCPs), medium chain C₁₄-C₁₇ (MCCPs) and long chain C_{>17} (LCCPs). The degree of chlorination varies between 10 and 72%. Technical mixtures contain several thousands molecules, and large number of isomers and homologues, which complicates analytical determination of chlorinated paraffins.

Chlorinated paraffins are used in various applications, mainly as metalworking fluids, sealants, in paints and coatings, flame retardants and softeners in rubber, textiles, PVC and other polymers.¹ In the last decade, annual world-wide production of CPs has been estimated to 300 kilotons.² Estimated production of SCCPs in Europe is up to 15 kilotons per year.¹ While SCCPs production is decreasing, the production of MCCPs in Europe has a growing trend.³ In 2002, the main use of MCCPs was in PVC production (32 kilotons/year in the European Union), and the main use of SCCPs in sealants and adhesive, as a softener/flame retardant in rubber and textiles (1 kiloton/year together in the EU).³ Chlorinated paraffins could get into environment during their production, storage, transportation, and industrial use of manufactured product, leaching, runoff and volatilization from contaminated parts of the environment. CPs are very persistent and not biodegradable. They adsorb strongly to sludge and sediments. They are therefore very prone to bioaccumulation.³ Especially SCCPs have been suggested to be toxic compounds for aquatic organisms.^{4, 5}

There were several studies performed in the field of CP contamination of environment until now, and it was demonstrated that short and medium chain chlorinated paraffins are distributed in the environment, especially in aquatic and terrestrial compartments.⁶⁻⁸ Nevertheless, information about environmental contamination and behavior of CPs is still limited. The absence of available instruments and methods in the Central and Eastern Europe cause the real information gap in the field of CP contamination in those regions. CPs are broadly produced in Slovak Republic (one part of former Czechoslovakia) and they are probably still in use in the Czech Republic. However, the amounts that are used today, as well as level of potential environmental contamination, are practically unknown. Monitoring of SCCPs in water was ordered by Ministry of Environment of the Czech Republic recently.⁹ Information about SCCP contamination of the Czech sediments measured on GC-MS using short column are presented here. Short chain chlorinated paraffins were detected in the samples from all tested sites at the level up to 181 ng g⁻¹. These results confirmed the presence of CPs in the Czech environment and it inspired further development of analytical methods and performance of more detail studies. Emphasis was posed on optimization tests of clean up procedures and optimization of final analysis using GC-ECNI-MS equipped with ion trap mass analyzer and 30 m chromatographic column. This method was tested on enriched sediment samples, and it is now employed for the project of CP screening of the Czech environment. This work is a contribution to the ongoing national POPs inventory in the Czech Republic that is focused on the new types of persistent industrial substances.

Materials and Methods

Sample collection

Top layer sediment samples were taken from the rivers by dredging at different times from 2001 to 2004. Sampling locations were chosen with the aspect of investigation of regions with various industrial discharges. Košetice

location was chosen as background area in the Czech Republic. Sampling sites are shown in Figure 1. Sediment samples were dried at the room temperature for 1 month, and homogenized.

Extraction and clean up

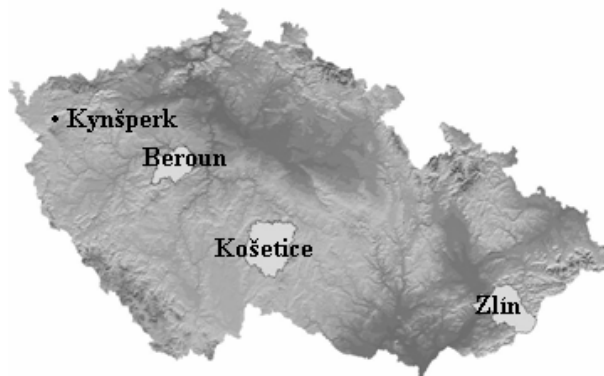
Ten grams of dry sediment sample was extracted by hot solvent extraction (Soxtec-Büchi, Switzerland) with addition of 120 mL dichloromethane for 60 minutes. Interfering compounds such as lipids, unstable interferents, PCBs, and organochlorinated pesticides were removed using sulfuric acid treatment, activated copper, silica gel chromatography column, and gel permeation chromatography. During optimization tests, GPC on Phenogel was accepted as optional step for the samples with toxaphene contamination. γ -HCH in concentration $2 \text{ ng } \mu\text{L}^{-1}$ was added into the samples before the final analysis on GC-ECNI-MS ion trap. It was not possible to use the internal standard in short column GC-MS instrument.

Gas chromatography

SCGC-ECNI-MS: GC was equipped with the short quartz capillary column (1.3 m x 0.15 mm I.D.) without a stationary phase. Gas chromatograph was coupled to a Finnigan Mat 8200 MS) instrument. Methane was a reagent gas. Full scan spectra were taken in ECNI mode.

GC-ECNI-MS: Optimization tests were performed on GC-ECNI-MS on a Thermo-Quest GCQ benchtop ion-trap instrument with methane as reagent gas. GC was equipped with 30 m column DB5-MS. Full scan spectra were taken in ECNI mode.

Figure 1: Sampling locations in the Czech Republic



Results and Discussion

QA/QC

Recoveries were determined by spiking CPs free sediment samples with Cereclor 63L and MCCPs mixture to get final concentrations 1000 and 100 ng g^{-1} (dry weight). Recoveries of SCCPs were $103 \pm 8\%$ ($n = 8$) for low, and $92 \pm 11\%$ ($n = 8$) for high concentration of SCCPs. Recoveries

for MCCPs were $62 \pm 7\%$ ($n = 9$) in spiked sediment samples, after the same procedure. In the case of Czech sediment, standards $\text{CP}_{10.65}$, $\text{CP}_{11.65}$, $\text{CP}_{12.65}$, and $\text{CP}_{13.65}$ were applied for quantification, because of the highest similarity of the pattern in real samples. Medium chain chlorinated paraffins were quantified using the only available standards $\text{CP}_{14.47}$, $\text{CP}_{15.50}$, $\text{CP}_{16.46}$ in the optimization tests.

SCGC-ECNI-MS: The certainty of measurement using this method was determined to be 98% ($n = 5$ injections/one sample). The limit of quantification was 0.5 ng g^{-1} (dry weight) for the sediment samples. The analytical detection limit for the Cereclor 63L solution was $100 \text{ pg } \mu\text{L}^{-1}$.

GC-ECNI-MS: Repeatability of the GC-MS (with ion trap) measurement of CPs was tested, too. The certainty of measurement using this method was calculated to be 94% ($n = 10$ injections/one sample). The analytical detection limit for the sum of CPs was $2 \text{ ng } \mu\text{L}^{-1}$. Signal to noise ratio for quantification was set to be higher than 10.

Environmental data

The Czech Republic is a country with advanced industry; however, industrial production in many branches was restricted in 90's of the last century. Engineering, metalworking, chemical, rubber, coal mining, as well as textile industries could represent the main industrial branches in the Czech Republic.

Presence of chlorinated paraffins in the Czech sediments was proved by this study. Chlorinated paraffins were detected in all studied areas. The SCCPs were detected in most of the samples from the Košetice and Zlín locations, and in five samples from Beroun area. Environmental levels of total C₁₀-C₁₃ SCCPs in sediment samples from these regions varied between 4.6–180.8 ng g⁻¹ (dry weight). The degree of chlorination of the SCCPs in these samples was deduced from the mass spectra to be 60-70%. Chlorinated decanes were less abundant compounds; the most abundant compounds were chlorinated undecanes.

In the Košetice area, samples were taken in the years 2001 and 2002 from the same location each time. The sum of C₁₁-C₁₃ SCCPs varied in the range of 24.0–45.8 ng g⁻¹ dry weight (n = 14) (Table 1). The sampling locations are mainly in forested areas, quite far from any industry. It can be assumed that the chlorinated paraffins in this location were transferred primarily *via* atmospheric transport and deposition from the industrial, highly developed western or northwestern parts of Bohemia, or from Western Europe. The highest concentration levels of chlorinated paraffins were found in Zlín location. In Zlín, the rubber, tanning, and textiles industries are located. The concentrations were higher than 100 ng g⁻¹ (dry weight) in six cases (n = 10). The concentration range in the samples from this location varied between 16.3–180.8 ng g⁻¹ dw in 2001. Concentrations in the samples from the following year were: 87.9–143.6 ng g⁻¹ (dry weight). In Beroun, the location where the cement, engineering, glass factories are located, contamination by chlorinated paraffins was not as high as in the Zlín area. CPs were not detected in the most cases. SCCPs were present in five samples (n = 13). Concentrations of decanes, undecanes, dodecanes and tridecanes were near the detection limit or lower. Σ C₁₀-C₁₃ levels were in the range of 4.6–34.0 ng g⁻¹ (dry weight).

| Location | Σ SCCPs |
|---------------|----------------|
| Košetice 2001 | 26.6–45.8 |
| Košetice 2002 | 24.0–40.2 |
| Zlín 2001 | 16.3–180.8 |
| Zlín 2002 | 87.9–143.6 |
| Beroun 2001 | 4.6–34.0 |

Table 1: Chlorinated paraffins levels in the sediment samples (ng g⁻¹dw)

Short column GC was used to obtain the first information about contamination of the Czech environment by short chain chlorinated paraffins. Medium chain CPs were not measured. The advantages of this method for CP analysis are very short times of analyses, increased sensitivity, and the possibility of identifying CPs in the full scan mode. The complete elimination of all interferences is essential for SCCPs analysis. This, as well as the interference of MCCP can make interpreting the mass spectrum quite difficult. The task of removing these compounds should not be underestimated.

Analysis of CPs using GC-MS with ion trap mass analyzer and 30 m chromatography column was tested on enriched environmental samples and employed for screening of CP levels in the Czech environment. This method proved to be simple and effective tool for CP determination in abiotic as well as biotic samples and could be implemented to the routine analyses. This analytical method allowed to determine medium chain chlorinated paraffins abreast of short chain ones. This method is now used in the screening studies of the Czech rivers contamination (sampled 2003-2004). North-western part of Bohemia and Zlín region seem to be the most contaminated areas. Medium chain CPs highly prevailed over the short chain ones. The highest concentrations were found in Ohře river in Kynšperk in the western Bohemia (MCCPs 5575.5 ng g⁻¹, SCCPs 89.1 ng g⁻¹), and in Dřevnice river in Zlín area (MCCPs 892.7 ng g⁻¹, SCCPs 54.2 ng g⁻¹).

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