

POLYCHLORINATED NAPHTHALENES AND CHLORINATED PARAFFINS IN THE AIR AND SOIL SAMPLES FROM THE CZECH REPUBLIC

Příbylová P, Kukučka P, Klánová J, Holoubek I

RECETOX - Research Centre for Environmental Chemistry and Ecotoxicology, Masaryk University, Kamenice 3/126, 625 00 Brno, Czech Republic

Introduction

Polychlorinated naphthalenes (PCNs) and chlorinated paraffins (CPs) are the groups of persistent organic pollutants (POPs) prone to the long-range atmospheric transport and deposition. The global extent of the POP pollution became apparent when they were detected in the areas, where they have never been used or produced at levels posing risks to the wildlife.

Polychlorinated naphthalenes are formed by a chlorine substitution of naphthalene. PCNs contain one to eight chlorine atoms per naphthalene molecule, and they form complex mixtures of 75 congeners.¹ The general formula is $C_{10}H_{8-n}Cl_n$. PCNs are hydrophobic compounds with a high chemical and thermal stability, good weather resistance, good electrical insulating properties, and low flammability. They were used as preservatives, intermediates for paints, additives to machine oils or rubber products, and flame retardants. The technical mixtures of PCNs are known mainly under the trade names as Halowaxes, Nibren waxes or Seekay Waxes. The production of PCNs decreased in the late 1970s. Incineration, copper ore roasting, and aluminum reclamation can cause the PCN pollution as well. Other known sources are the technical PCB formulations since PCNs are known to be common impurities found in the technical PCB mixtures.²

Chlorinated paraffins are produced by chlorination of *n*-alkane feedstock using molecular chlorine yielding extremely complex mixtures of the optical isomers and congeners. CPs are the complex mixtures with a chlorination degree between 30 – 70%, and carbon chain lengths of C_{10} - C_{13} (short-chain CPs), C_{14} - C_{17} (medium-chain CPs) or $C_{>17}$ (long-chain CPs). The general formula of chlorinated paraffins is $C_nH_{2n+2-z}Cl_z$. Physicochemical properties of CPs are similar to PCNs and PCBs. Chlorinated paraffins are used commonly as the high temperature lubricants in metal working industry, and as the flame-retardant plasticizers.³

Both PCNs and CPs are persistent, and they can be accumulated in the living organisms. PCNs are more or less planar, and several investigated congeners exhibited a high dioxin-like toxicity.⁴ Short chain chlorinated paraffins were classified as the Category 3 carcinogens.⁵ PCNs and CPs have been detected in a wide range of environmental compartments.

New fractionation method enabling the simultaneous determination of polychlorinated biphenyls, organochlorinated pesticides, polychlorinated naphthalenes, and chlorinated paraffins is presented here. This method was applied in the study focused on contamination of the air and soil in the Czech Republic by less frequent types of persistent substances. Recent data about the PCN and CP contamination of this region is presented here.

Methods and Material

Sample collection

Air and soil samples were taken in 2005. Passive air samplers (PAS) based on the polyurethane foam (PUF) as a sampling medium were used. Air samples were collected from 33 sampling sites representing industrial, urban, rural, and background locations. Six sampling campaigns of 28 days were performed on each site, and each set of six samples from the same site was pooled to obtain the POP levels higher than detection limits. Soil samples were obtained from the same sampling sites.

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Extraction and clean up

Exposed polyurethane foam filters as well as soil samples were extracted for 60 minutes by a hot solvent extraction (Soxtec-Büchi, Switzerland) using 120 mL of dichloromethane. Interfering compounds such as lipids were removed by a column chromatography on the sulfuric acid modified silica gel. PCBs, PCNs and CPs were eluted by 30 mL of dichloromethane-hexane (1:1) mixture.

The first fractionation was achieved on the silica gel deactivated by addition of 3% (w/w) of water; PCNs were eluted quantitatively in the first *n*-hexane fraction (40 mL), CPs were eluted in the second fraction by dichloromethane-hexane (1:1) mixture. γ -HCH as an internal standard was added to the CP fraction before the final analysis on the GC-ECNI-MS ion trap.⁶

Further separation of the PCN fraction was achieved on a mini-column containing activated charcoal with silica gel (1:20). 100 mg of this mixture was sandwiched between two layers (50 mg) of silica gel in a Pasteur pipette. The column was prewashed with 5 mL of toluene followed by 5 mL of 30% dichloromethane in cyclohexane. The first fraction was eluted with 5 mL of 30% dichloromethane in cyclohexane. The second, PCNs containing fraction was eluted with 5 mL of toluene. PCN fraction was transferred to cyclohexane, and PCB 121 was added as an internal standard prior to final analysis.

Gas chromatography

PCN determination was performed on GC-MS (GC HP 5890 Series II, MS 5973 and MS 5975 inert XL MSD, Agilent Technologies) equipped with a 60 m DB5-MS column. Spectra were taken in a SIM mode. PCNs were quantified using the standard mixture PCN-MXB (Wellington, USA).

CP determination was achieved on GC-ECNI-MS (Thermo-Quest GCQ benchtop ion-trap with methane as a reagent gas) equipped with a 30 m DB5-MS column. Full scan spectra were taken in ECNI mode. CPs were quantified using the mixtures CP_{10.65}; CP_{11.65}; CP_{12.65}; CP_{13.65}; CP_{14.47}; CP_{15.50}; CP_{16.46} (Technical University of Munich, Germany).

QA/QC

The recoveries were $78 \pm 6\%$ for PCNs, $97 \pm 9\%$ for SCCPs, $63 \pm 4\%$ for MCCPs. Laboratory blanks were analyzed with each set of samples.

Results and Discussion

Polychlorinated naphthalenes

Air samples: PCN levels were determined in 33 air samples from industrial, urban, and background sites. The results are presented as an average amount in pg per filter. In general, the PCN concentrations in the air samples are low (2, respectively 4 orders of magnitude lower when compared to PCBs and PAHs). This is mostly due to the lack of primary sources of PCNs in the environment. PCNs are not currently used in the Czech Republic, they were never produced, and only small amounts were applied in the history. However, PCNs are the trace impurities in the technical PCB mixtures which were both, produced and frequently applied in former Czechoslovakia. Various thermal processes involving chlorinated compounds can be a source of PCN contamination as well.

The average amount of PCNs (18 congeners, mono- to octachlorinated) sequestered in the passive filter exposed for 28 days (between the spring and the summer) ranged from 114 to 519 pg/filter. The lowest concentrations were found in the samples from rural and background sites (215 pg/filter average), highest at urban (278 pg/filter average), and industrial (356 pg/filter average) sites. Homologue profile was dominated by mono- and dichloronaphthalenes at rural and background sites. At urban and industrial sites, tri- to pentachloronaphthalenes were also detected. No hexa- to octachloronaphthalenes were detected in any of the air samples. Lighter PCN congeners (mono- to tetrachloronaphthalenes) are more volatile than the heavier congeners (penta- to octachloronaphthalenes), and they are more readily a subject to revolatilization and atmospheric transport.

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Soil samples: PCN concentration in the soil samples ranged from 37 to 1 120 pg g^{-1} (PCNs were not detected at several sites). Lowest PCN concentrations were found at rural and background sites (35 pg g^{-1} d. w. average, highest - similarly to the air samples - at urban (96 pg g^{-1} d. w.) and industrial (170 pg g^{-1} d. w.) sites. Mono- to octachlorinated congeners were found in the soil samples, the homologue profiles significantly varied among individual locations. PCN concentration in the soils was 2-3 orders of magnitude lower when compared to PCBs. Most probable source of PCNs in the soils is the historical use of PCB technical mixtures at industrial sites, and the atmospheric deposition at the background areas. Figure 1 shows the relation between PCN concentrations in the air and in the soil at individual locations.

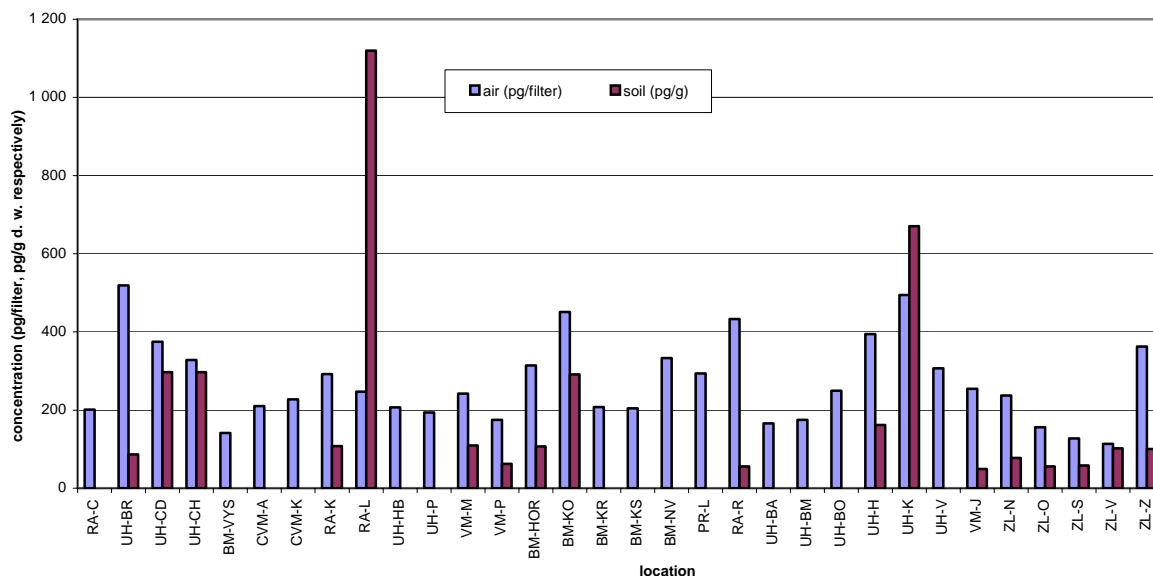


Figure 1. Concentration of PCNs in the air and soil samples at individual sampling sites

Chlorinated paraffins

Soil samples: Short-chain and medium-chain chlorinated paraffins were detected at several sampling sites mostly from industrial parts of the Czech Republic. Concentration levels for the sum of chlorinated paraffins varied between 11 ng g^{-1} d. w. (urban) and 339 ng g^{-1} d. w. (industrial) (Figure 2). Highest CP level found at urban sites was 39 ng g^{-1} d. w. Medium chain chlorinated paraffins prevailed in all samples except for the sampling site in the paint production factory. The composition of the CP technical mixtures used in this factory is not known, however, chlorinated paraffin mixtures are probably still used in the factory. Generally, CPs were found at low levels in the local soils mainly in the vicinity of CP using industry.⁶ This finding corresponds with the former information about the CP contamination of the Czech environment.

Air samples: Chlorinated paraffins were not detected in the passive air samples from the Czech Republic. Low volatility potential of CPs from the soils as well as low CP concentrations detected in the soils from the same sampling sites are the most probable reasons.

PCNs/CPs relation

Polychlorinated naphthalenes and chlorinated paraffins were detected at the low levels in the soil samples, PCNs – unlike CPs – were found in the passive air samples as well. CP contamination does not correspond with the PCN contamination which suggests different environmental sources of those two types of

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pollutants. However, PCN contamination does correlate with the PCB levels suggesting that the PCB technical mixtures are probably the main source of PCNs in the environment.

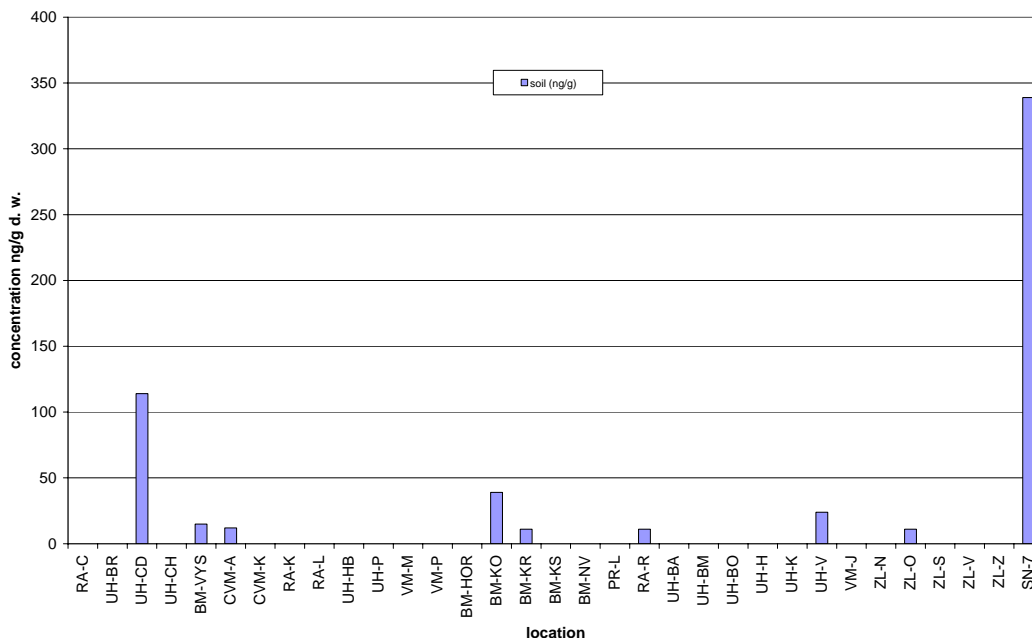


Figure 2. Concentration of CPs in the soil samples

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