

CHLORINATED PARAFFINS IN HUMUS LAYERS FROM THE ALPS (MONARPOP)

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Abstract

Chlorinated paraffins (CPs) were determined in humus layer samples, which were taken within the Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants (MONARPOP). High resolution gas chromatography (HRGC) combined with electron ionisation tandem mass spectrometry (EI-MS/MS) was used for the total CP amount (sum of short, medium and long chain CPs). CPs were found in all samples. The total CP levels ranged from 7 to 199 ng/g dry weight. Concentrations were related to the altitude. Higher concentration levels could be observed between 700 and 900 m and between 1300 and 1500 m.

Introduction

Chlorinated paraffins (CPs) are polychlorinated straight-chain *n*-alkanes with a chlorination degree between 30 and 70%. They are produced since the 1930s and their global annual production is estimated to be about 300'000 t per year.¹ CPs are divided according to their carbon chain length into three main categories: short chain (SCCPs, C₁₀₋₁₃), medium chain (MCCPs, C₁₄₋₁₇) and long chain CPs (LCCPs, C_{>17}).¹ Over 200 CP formulations are in use for a wide range of industrial applications, such as flame retardants and plasticisers, and as additives in metal working fluids, in sealants, paints and coatings.² CPs are classified as persistent and their physical properties imply a high potential for bioaccumulation as well as for global long-range atmospheric transport.¹ Compared to other persistent organochlorine compounds like PCBs or toxaphenes, limited information is available about environmental CP concentrations.¹ Main reasons are the complex determination of CPs in environmental matrices and consequently the small number of laboratories, which are able to analyse CPs in environmental samples.³ A summary of available analytical methods set up during the past five years and their applicability to different matrices was presented by Zencak and Oehme.⁴

A permanent monitoring of CPs has become more and more important due to their ubiquitous presence in the environment including remote areas.⁵⁻⁹ For the first time, MONARPOP (Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants) will assess the input of POPs into the Alps.¹⁰ The Alps are a geographical and meteorological trap for airborne pollutants due to barrier effects, high precipitation, and low ambient temperature. This might also be the case for semivolatile organic compounds.¹¹ Within this project, humus was chosen as a suitable sample material since its high organic carbon content favours the accumulation of POPs.

This study presents CP levels in humus layer collected within the MONARPOP project. Instrumental analysis was performed using a triple quadrupole in the EI-MS/MS mode.¹² This method allows the determination of total CP concentration (sum of SCCPs, MCCPs, and LCCPs) within one fast measurement. This is a huge advantage compared with alternative quantification methods since they are both highly complex and time consuming or too expensive.

Materials and Methods

Chemicals. Solvents for the CP analysis are published in detail elsewhere and hence only the reference standards are described.¹³ SCCP (C₁₀₋₁₃, 55.5% chlorine content, solution in cyclohexane, 100 ng/μl) as well as ε-hexachlorocyclohexane (ε-HCH, solution in cyclohexane, 10 ng/μl) were purchased from Ehrenstorfer GmbH (Augsburg, Germany). ¹³C₁₀-*trans*-chlordan (100 ng/μl, solution in *n*-nonane, purity 99%) was supplied by Cambridge Isotope Laboratories (Andover, USA).

Humus samples. 33 humus samples from remote Norway spruce forests in the Alps were collected for the analysis of CPs and other persistent pollutants. Nine sampling sites were chosen, including seven altitude profiles, which consisted of four to five subplots to examine the vertical CP distribution (see Figure 1). The humus layer was taken within a 30 × 30 cm area. Sampling depth corresponded to the thickness of the humus layer. The material from seven to ten such pits along a 5 × 30 m rectangular grid was pooled for one sample.

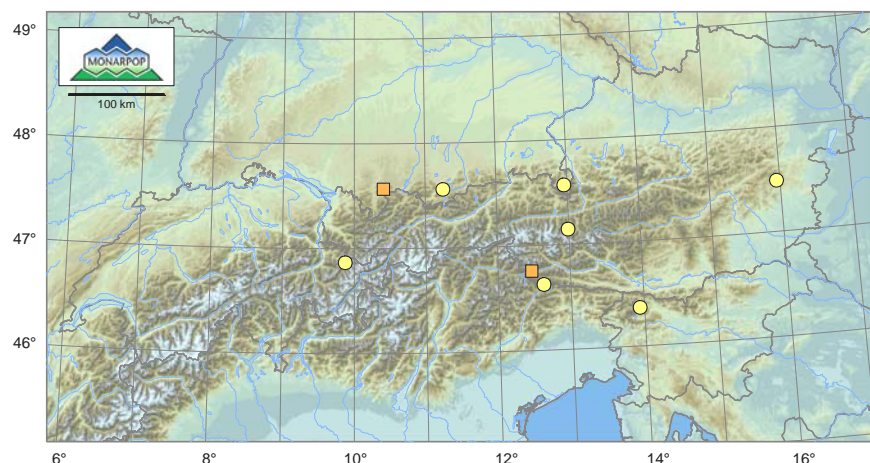


Figure 1 Map of nine MONARPOP sampling locations in the European Alps. Yellow dots: Sampling locations with altitude profiles.

Sample clean-up. Further details of the applied clean-up procedure are given elsewhere and hence only briefly described.¹³ 20 g of dried and homogenised samples were spiked with the internal standards (10 ng of ¹³C₁₀-*trans*-chlordane) and then Soxhlet extracted with 200 ml of dichloromethane and *n*-hexane (DCM/*n*Hex, 1+1, v/v) for 8 hours. Activated copper powder was added to eliminate sulphur. After solvent evaporation, sample matrix not persistent to sulphuric acid was removed by column chromatography on 20 g of silica gel impregnated with concentrated sulphuric acid (44%). CPs were eluted with 70 ml of DCM/*n*Hex (1+1, v/v). Further fractionation was carried out on 16 g of Florisil® (1.5% water content) eluted with 75 ml of *n*Hex and 5 ml of DCM (first fraction) and 60 ml of DCM (second fraction). The latter fraction contained all CPs and was concentrated to 0.5 ml and the solvent was changed to cyclohexane. Finally, the extract was reduced to 100 µl and 10 ng of ε-HCH in 10 µl of cyclohexane were added as recovery standard.

Instrumentation. Parameters for the GC-EI-MS/MS analysis are published in detail elsewhere and hence only briefly described.¹² Instrumental analysis was performed on a gas chromatograph CP-3800 coupled with a 1200L triple quadrupole mass spectrometer (Varian, Walnut Creek, USA). The gas chromatograph was equipped with a split/splitless injector and a fused silica capillary column (15 m, 0.25 mm i.d.) coated with 0.25 µm of crosslinked 5% phenyl-methylpolysiloxane (DB5-MS, J&W Scientific, Folsom, USA). Helium (99.999%, Carbagas, Basel, Switzerland) was employed as carrier gas at a constant flow of 2 ml/min. The injector temperature was set to 275 °C. Splitless injections (3.0 min) of 2.5 µl volume were carried out with a Combi Pal autosampler (CTC Analytics, Zwingen, Switzerland). The temperature program was as follows: 1 min isothermal at 100 °C, increased at 50 °C/min to 300 °C, then isothermal for 4 min. The transfer line temperature was set at 280 °C and the ion source temperature at 200 °C. The EI mass spectra were acquired at 70 eV electron energy with a filament emission current of 150 µA and a scan time of 0.5 s/scan. CID gas pressure (Argon) was set to 133 mPa. The following fragmentations and collision energies were applied for the determination of the total CP amount: *m/z* 91 → *m/z* 53 (collision energy: -10 V), *m/z* 102 → *m/z* 67 (-10 V) and *m/z* 104 → *m/z* 67 (-10 V). The precursor ion *m/z* 383 and the product ion *m/z* 276 were selected for the internal standard ¹³C₁₀-*trans*-chlordane (-28 V).

Quality assurance. Extreme care was used to avoid contamination and background. Therefore, glassware was washed in a glassware washer and inserted in a glass alkaline bath (5% RBS@35 concentrate, Fluka). After the washing procedure, glassware and glass fiber thimbles (30 × 100 mm, 603G, Wathman®, Schleicher & Schuell, Meidsone, England) were solvent rinsed and heated at 450 °C overnight. Florisil®, sodium sulphate, and silica gel were dried over night at 220 °C.

Method blanks were analysed with the same extraction and clean-up procedure. The method detection limit (MDL) was determined as the sum of the mean concentration in the blank and three times the standard deviation of five measurements. Hereby, blank concentrations were calculated on a fictive mean sample weight of 20 g dry weight (dw).

Results and Discussion

CPs were detected in all analysed samples. Recoveries ranged between 58 and 110% (mean 74%). Total CP levels are summarised in Table 1 and in Figure 2. CP concentrations ranged between 7-199 ng/g dry weight (dw) (mean 40 ng/g dw). The levels were approx ten times higher compared to reported total PCB concentrations (sum of PCB 28, 52, 101, 138, 153 and 180) in this region (mean 4.5 µg/kg dw).¹⁴

Table 1 Total CP concentrations in Alpine humus layers (n = 33) by GC-EI-MS/MS.

	min	max	mean	SD	5 th P	10 th P	25 th P	50 th P	75 th P	90 th P	MDL
Total CP concentration [ng/g dw]	7	199	41	37	13	14	15	31	49	78	3

dw: dry weight; SD: standard deviation; P: percentile; MDL: method detection limit

Most of the samples (n = 25) had a concentration between 10 and 50 ng/g dw as shown in Figure 2.

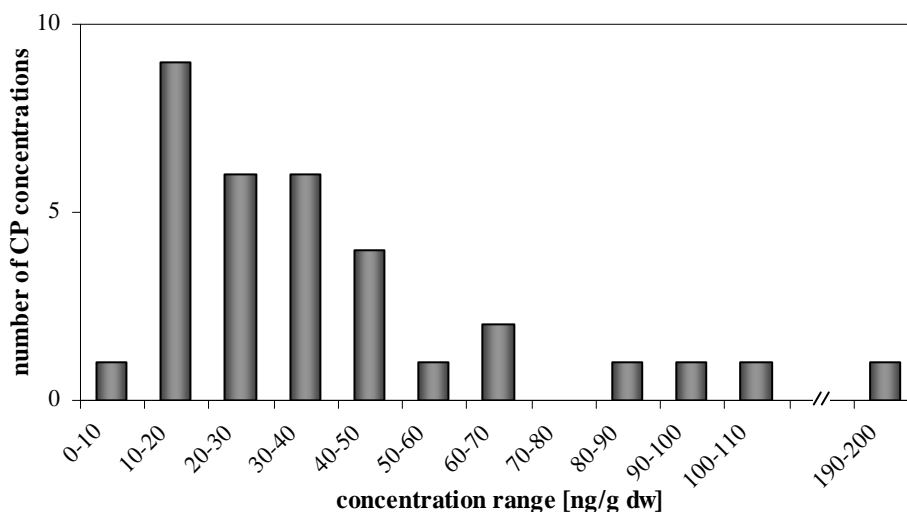


Figure 2 Frequency histogram of total CP levels in humus layers from the Alps obtained by GC-EI-MS/MS.

Figure 3 shows the correlation between CP levels and altitude. Higher CP concentrations were determined at low altitudes (700-900 m). A tendency of a Gaussian distribution was observed between 900 to 1900 m altitude with a maximum between 1300 and 1500 m.

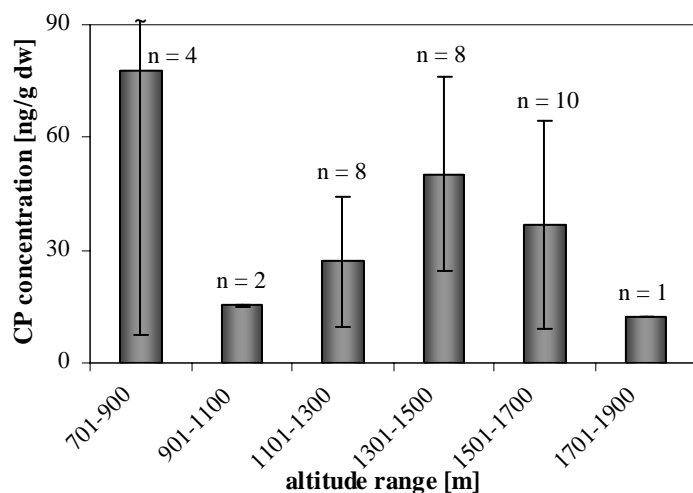


Figure 3 Histogram of total CP levels in humus layers from the Alps related to altitude. Error bars indicate the standard deviations.

Conclusion. CPs were detected in all analysed humus samples from remote forest sites in the Alps. A relation could be observed between the CP concentration and the altitude:

- Concentrations are higher at lowest altitudes.
- A slight concentration maximum is observed between 1300 and 1500 m.

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