

**A SURVEY OF THE SPATIAL, ALTITUDINAL, AND  
TEMPORAL DISTRIBUTION OF CHLORINATED  
PARAFFINS IN THE ALPINE REGION**

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*Misura ciò che è misurabile,  
e rendi misurabile ciò che non lo è.*



Galileo Galilei (1564 – 1642)

Italian astronomer, philosopher, and physicist



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### PAPER II

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### PAPER III

Iozza, S., Müller, C. E., Schmid, P., Bogdal, C. and Oehme, M. “Historical Profiles of Chlorinated Paraffins and Polychlorinated Biphenyls in a Dated Sediment Core from Lake Thun (Switzerland)” **2008** *Environ. Sci. Technol.* 42, 1045-1050

## Further Publications

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PAPER I      Development of a comprehensive analytical method for the determination of chlorinated paraffins in spruce needles applied in passive air sampling

PAPER II     Altitude profiles of total chlorinated paraffins in humus and spruce needles from the Alps (MONARPOP)

PAPER III    Historical Profiles of Chlorinated Paraffins and Polychlorinated Biphenyls in a Dated Sediment Core from Lake Thun (Switzerland)

## Abbreviations

APCI	Atmospheric pressure chemical ionization	MONARPOP	Monitoring Network of the Alpine Region
BAF	Bioaccumulation factor	MS	Mass spectrometry
BC	Black carbon	MS/MS	Tandem mass spectrometry
BCF	Bioconcentration factor	NABO	Nationale Bodenbeobachtung (Swiss national soil monitoring)
CPs	Chlorinated paraffins	nHex	<i>n</i> -hexane
DCM	Dichloromethane	PBDEs	Polybrominated diphenylethers
DDT	1,1,1-trichloro-2,2- <i>bis</i> (4-chlorophenyl)-ethane	PCBs	Polychlorinated biphenyls
dw	Dry weight	PICI	Positive ion chemical ionization
ECD	Electron capture detector	POP	Persistent organic pollutant
ECNI	Electron capture negative ionization	PVC	Polyvinyl chloride
EI	Electron ionization	SCCPs	Short chain CPs
GC	Gas chromatography	SOC	Semivolatile organic compounds
GC×GC	Comprehensive GC	TOC	Total organic carbon
HLC	Henry's Law Constant	TOF-MS	Time-of-flight mass spectrometry
HR	High resolution	totCPs	Total CPs
LC	Liquid chromatography	ww	Wet weight
LCCPs	Long chain CPs		
LR	Low resolution		
<i>m/z</i>	Mass-to-charge ratio		
MCCPs	Medium chain CPs		
MDL	Method detection limit		



## Summary

Chlorinated paraffins (CPs) have been produced since 1930 and are still used in a wide variety of consumer products and industrial processes. In the last decades, CPs represented one of the largest group of chlorinated hydrocarbons produced in North America and Europe. In spite of the knowledge of their long-range transport, bioaccumulation, potential of carcinogen for rats and mice, and toxicity for aquatic organisms, information on the levels and fate of CPs in the environment is insufficient. This results from analytical difficulties associated with the quantification of CPs because of the complex composition of commercial formulations. Production and use of short chain CPs (SCCPs, C<sub>10-13</sub>) have been regulated in the European Community and in Switzerland due to their significant bioaccumulation and toxic potential. Furthermore, SCCPs are now under evaluation for inclusion into the Stockholm Convention on Persistent Organic Pollutants (POPs).

The aim of this work was to investigate several aspects of the environmental fate of CPs in Switzerland and in the Alps. For this purpose, available analytical methodologies for sediments and biota were adapted and improved for soil/humus, compost and conifer needles. Furthermore, a unified analytical approach suitable for the determination of CPs in various matrices is presented, which has the benefit of a standardized clean-up after a matrix specific extraction. The extraction and clean-up is kept as simple and efficient as possible in order to make this methodology applicable in routine laboratories environment. The very selective clean-up allowed to eliminate interferences and enables the use of low resolution mass spectrometry (LRMS).

Gas chromatography combined with electron ionization tandem mass spectrometry (EI-MS/MS) was used for the determination of total CPs (sum of short, medium (MCCPs, C<sub>14-17</sub>), and long chain CPs (LCCPs C<sub>>17</sub>)). SCCP and MCCP levels as well as congener group patterns (*n*-alkane chain length, chlorine content) could be evaluated by electron capture negative ionization low resolution mass spectrometry (ECNI-LRMS).

The alpine region was the target area, since the Alps are surrounded by regions with significant industrial activities and a high population density. Due to barrier effects, high precipitation rates and low ambient temperatures, the Alps are supposed to act as a geographical and meteorological trap for atmospheric pollutants including semivolatile organic compounds.

The first study presents altitude profiles and the spatial distribution of CP levels in humus layers and spruce needles collected within the Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants (MONARPOP) project. CPs were present in all samples; their concentrations varied between 7 and 199 ng g<sup>-1</sup> dry weight (dw) and from 26 to 450 ng g<sup>-1</sup> dw in humus and needle samples, respectively. Elevated concentrations were observed for altitude profiles in humus samples taken between 700 and 900 m as well as between 1300 and 1500 m. A clear vertical tendency could not be ascertained for the individual altitude profiles. No correlation could be observed in the needle samples due to higher variations of the data. Data for environmental airborne CPs on spruce needles are presented for the first time providing evidence that spruce needles are a suitable passive sampling system for the monitoring of atmospheric CPs.

CP levels were determined in ten soil samples from reference sites of the Swiss national soil monitoring network (NABO). The aim of this study was to achieve the load of CPs in Switzerland. For this purpose, EI-MS/MS was used for the determination of total CP amounts. Total CP concentrations were between 34 and 151 ng g<sup>-1</sup> dw. These concentrations are comparable to soil concentrations from the MONARPOP project. ECNI-LRMS measurements revealed SCCP concentrations of 2-51 ng g<sup>-1</sup> dw and MCCP concentrations of 15-85 ng g<sup>-1</sup> dw.

Furthermore, three compost samples from Switzerland were analyzed. EI-MS/MS analysis revealed concentrations of 182-614 ng g<sup>-1</sup> dw for total CPs and ECNI-LRMS measurements of 57-140 ng g<sup>-1</sup> dw for SCCPs and 29-245 ng g<sup>-1</sup> dw for MCCPs.

A dated sediment core from Lake Thun covering the last 120 years was analyzed to get an overview of the historical trend of the CP deposition. Studies of dated sediment cores are an excellent way to investigate concentration trends over decades. Total CP concentrations showed a steep increase in the 1980s and a more or less stable level of 50 ng g<sup>-1</sup> dw since then. The concentration-time profile was in good agreement with the available information on global production data. Levels of higher chlorinated SCCPs have risen in recent years. In addition, the degree of chlorination of SCCPs has strongly increased during the past 40 years, which may indicate its use as an additive for polymers, paints and coatings. CPs were also compared with polychlorinated biphenyls (PCBs) analyzed in these dated sediment slices. The peak level of CPs exceeded that of PCBs by about a factor of three. Comparison of both temporal trends showed an increase of CPs when PCB levels declined.

Generally, the total CP levels were considerably higher than the indicator PCB levels analyzed in all studies.



# 1 Introduction

## 1.1 Persistent Organic Pollutants

Persistent organic pollutants (POPs) are defined as chemical substances that possess certain toxic properties and resist degradation. Furthermore, POPs accumulate in living organisms as well as in terrestrial and aquatic ecosystems due to transport by air, water, and migratory species. They are transported over long distances even to remote regions far from their sources, where they have never been used or produced. Therefore, POPs are a cross-border problem on which international action is indispensable. This group of priority pollutants consists of pesticides (such as DDT), industrial chemicals (such as polychlorinated biphenyls, PCBs) and unintentionally produced by-products of industrial processes (such as polychlorinated dibenzo-p-dioxins and dibenzofurans).

International treaties have been declared to protect human health and the environment from POPs and to eliminate or reduce the release of POPs in the environment. In 2001, the Stockholm Convention was formally signed to control production, import, export, disposal and use of POPs. Due to similar properties, chlorinated paraffins are considered as a 'new' POP candidate. Especially short chain chlorinated paraffins are now under discussion to be included into the Stockholm Convention on POPs. They have been recently incorporated into the list of priority hazardous substances of the European Water Framework Directive (European Community, 2000). However, the application of medium chain chlorinated paraffins is currently increasing (WHO, 1996).

## 1.2 Chlorinated Paraffins

### 1.2.1 Production and Products

Chlorinated paraffins (CPs), also known as polychlorinated *n*-alkanes (PCAs) or chloroparaffins (see synonyms and common trade names in Table 1.1), are industrial chemicals introduced in the 1930s (Muir *et al.*, 2000). These complex mixtures with chlorine contents between 30 and 70% were formed by chlorination of *n*-alkanes applying UV irradiation and/or high temperature and pressure (Tomy *et al.*, 1998). The final product consists of several thousands of different homologues, diastereomers and enantiomers (Shojania, 1999).

**Table 1.1** Common trade names and synonyms of chlorinated paraffins (CPs).

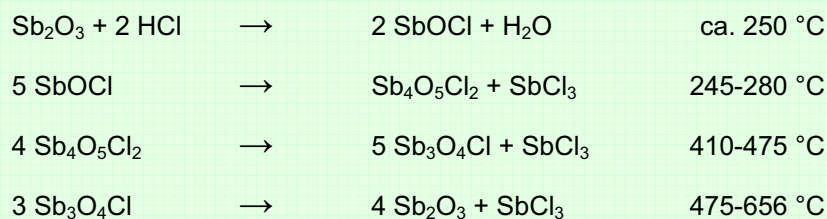
Chlorinated Paraffins			
A 70	Chlorocarbons	EDC-tar	Paraffin waxes chlorin.
Adekacizer E	Chlorofin	Electrofine	Paraffins, chloro
Arubren	Chloroflo	Enpara	Paroils, chlorin.
Cereclor	Chloroparaffin waxes	Hordaflam	Poliks
Chlorcosane	Chlorowax	Hordaflex	Polychlorin. alkanes (PCA)
Chlorez	Chlorparaffin	Hordalub	Polychloro alkanes
Chlorin. alkanes	Cloparin	Hulz	Tenekil
Chlorin. paraffin waxes	Cloparol	KhP	Toyoparax
Chlorinated waxes	Clorafin CW	Meflex	Unichlor
Chloroalkanes	Derminolfett / -öl	Monocizer	Witaclor

CPs of the general formula  $C_nH_{2n+2-z}Cl_z$  are subcategorized (see Table 1.3) into short chain (SCCPs,  $C_{10-13}$ ), medium chain (MCCPs,  $C_{14-17}$ ), and long chain compounds (LCCPs,  $C_{>17}$ ) according to the principal *n*-alkane resource derived from petroleum fractions (Tomy *et al.*, 1998). These fractions contain impurities, such as isoparaffins outside of the defined range, alkenes, branched alkanes, and aromatic compounds, which can also become chlorinated (POPRC, 2007).

### 1.2.2 Applications

Over 200 CP formulations (Serrone *et al.*, 1987) are in use for a wide range of industrial applications such as flame retardants and/or plasticizers in plastics, sealants, paints, textiles and coatings, as additives in metal working fluids, and as fat liquors for leather and furs (Campbell and McConnell, 1980; GDCh, 1992; Tomy *et al.*, 1998). Commercial products can contain between 1 and 20% of CPs, however, for special applications (e.g. metal working) it can be as much as 80% or more. The chlorine content of the applied technical SCCP mixtures ranges between 50 and 70%. The industrially produced MCCP mixtures usually contain between 40 and 60% of chlorine. CPs with high chlorine content were mainly used as flame retardants (WHO, 1996; Bayen *et al.*, 2006). They can act as flame retardants by releasing hydrochloric acid (HCl), which inhibits the flame. This vapor gas inhibition is strongly enhanced in presence of a Group V metal oxide such as antimony. Therefore, modern commercial CP products contain often antimony trioxide (see mechanism in Figure 1.1).

Further additives are epoxides and organotin compounds to inhibit the release of HCl at elevated temperatures (GDCH, 1992; WHO, 1996; European Commission, 2000).



**Figure 1.1** Mechanism of antimony trioxide as additive in CP flame retardant products. Antimony trioxide alone does not act as a flame retardant, but reaction with HCl lead to antimony trichloride ( $\text{SbCl}_3$ ), which is a radical scavenger and a vapor barrier to smother the flame.

Since their introduction in the 1930s (WHO, 1996), the world consumption of CPs has grown steadily as shown in Table 1.2. Global production estimates for 1993 were reported to be approx.  $300'000 \text{ t y}^{-1}$  (Tomy *et al.*, 1998). Based on the available information on recent and earlier production data (WHO, 1996; Tomy *et al.*, 1998) a total amount of more than  $7'000'000 \text{ t}$  of CPs has been produced since. Nevertheless, these estimations are based on production data from only North America and Europe, and nothing is known about the production amounts in industrial upcoming countries such as India and China.

**Table 1.2** Estimated worldwide consumption of CPs between 1930 and 1993.

Year	Estimated global consumption [ $\text{t y}^{-1}$ ]
1930s	Introduced
1964	38'000-50'000
1977	230'000
1993	300'000
Estimated total amount	$>7'000'000 \text{ t}$

Data from Tomy *et al.* (1998) and Iozza *et al.* (2008)

There had been a general decline in the amounts of SCCPs used within Europe, particularly for metal working and leather processing due to SCCP production restrictions in the last years. Between 1994 and 1997, the use of SCCPs within the European Union had been reduced from 13'000 to 4'000 t (European Commission, 2000). MCCPs are now substitutes for SCCPs in several applications. The consumption of MCCPs has already surpassed that of SCCPs (WHO, 1996). The MCCP production capacity in Europe is currently in the range of 45'000 to 160'000 t annually (European Commission, 2000). There was no known production of CPs in Switzerland. However, they are imported as both raw material or just processed products. The Swiss Federal Office for the Environment (BAFU) estimated SCCPs imports for 1994 to be about 70 t annually (Bolliger and Randegger-Vollrath, 2003).

### 1.2.3 Physico-chemical Properties

CPs are colorless or yellowish and thermally stable up to more than 200 °C (WHO, 1996). They are low to highly viscous or glassy to waxy solids depending on chain length and chlorine content (see Table 1.3) (GDCh, 1992).

**Table 1.3** General physico-chemical properties of CPs.

Category	Chain length	Physical state	Density at 20 °C [g cm <sup>-3</sup> ]
Short chain SCCP	C <sub>10-13</sub>	Cl <65%: liquid Cl >65% (<30 °C): glassy solid	1.18-1.59
Medium chain MCCP	C <sub>14-17</sub>	Liquid	1.095-1.345
Long chain LCCP	C <sub>&gt;17</sub>	Liquid and highly viscous to glassy Solid	1.055-1.300 0.89-ca. 1.63

Data from GDCh (1992)

### 1.2.3.1 Vapor Pressure, Water Solubility, Henry's Law Constant, and Octanol-Water Partition Coefficient

Due to the complexity of CP mixtures, environmentally important physico-chemical properties such as water solubility, vapor pressure, octanol-water partition coefficient ( $K_{OW}$ ), and Henry's law constant (HLC) vary within large ranges and are governed by two factors: the carbon chain length and the degree of chlorination. The specific physico-chemical properties of various CPs are summarized in Table 1.4.

The log  $K_{OW}$  values of CPs are in general above 4.4 and show that CPs are practically insoluble in water. The vapor pressures of SCCPs are in the range of other chlorinated organochlorines known to undergo long-range atmospheric transport such as PCBs and toxaphenes. They decrease with increasing chain length and chlorine content (Drouillard *et al.*, 1998b). HLCs for SCCPs are within 0.7-18 Pa m<sup>3</sup> mol<sup>-1</sup> and similar as for some organochlorine pesticides suggesting that SCCPs can remobilize from water to air or from moist soil to air (Drouillard *et al.*, 1998b). MCCPs with higher chlorine content have relatively low HLCs (<0.36 Pa m<sup>3</sup> mol<sup>-1</sup>). In general, HLCs decrease with increasing chlorine contents (Drouillard *et al.*, 1998b). However, HLC values for CPs do not show similar large differences between SCCPs, MCCPs and LCCPs as observed for vapor pressure and water solubility.

**Table 1.4** Environmentally relevant physical properties of CP mixtures and single congeners.

Compound	% Cl	$P_V^{a,b,c}$ [mPa]	HLC <sup>a,c</sup> [Pa m <sup>3</sup> mol <sup>-1</sup> ]	$S_W^{a,d,e}$ [ $\mu\text{g l}^{-1}$ ]	log $K_{OW}^{a,b,e,f}$
<i>SCCPs</i>					
C <sub>10-13</sub>	49	n.a.	n.a.	n.a.	4.39-6.93
C <sub>10-13</sub>	63	n.a.	n.a.	n.a.	5.47-7.30
C <sub>10-13</sub>	71	n.a.	n.a.	n.a.	5.37-8.69
C <sub>10</sub> H <sub>17</sub> Cl <sub>5</sub>	56	4.0-5.4 at 25 °C	2.62-4.92	692-975	n.a.
C <sub>10</sub> H <sub>13</sub> Cl <sub>9</sub>	71	0.24 at 20 °C	0.83	400	5.64
C <sub>11</sub> H <sub>19</sub> Cl <sub>5</sub>	48	1.3-2.0 at 25 °C	0.68-1.46	546-962	6.04-6.40
C <sub>12</sub> H <sub>19</sub> Cl <sub>7</sub>	59	n.a.	n.a.	n.a.	7.00
C <sub>13</sub> H <sub>23</sub> Cl <sub>5</sub>	49	0.32 at 20 °C	4.18	30	6.61
C <sub>13</sub> H <sub>16</sub> Cl <sub>12</sub>	70	2.8×10 <sup>-4</sup> at 20 °C	0.34	0.49	7.21
<i>MCCPs</i>					
C <sub>14-17</sub>	45	2.27 at 20 °C 160 at 80 °C	n.a.	n.a.	5.52-8.21
C <sub>14-17</sub>	52	0.13-0.27 at 20 °C 1.07 at 45 °C 6.0 at 60 °C 51 at 80 °C	10.9	n.a.	5.47-8.01
C <sub>14</sub> H <sub>26</sub> Cl <sub>4</sub>	42	0.25 at 20 °C	24.1	3.5	n.a.
C <sub>14</sub> H <sub>23</sub> Cl <sub>7</sub>	56	0.01 at 20 °C	0.36	14	n.a.
C <sub>17</sub> H <sub>32</sub> Cl <sub>4</sub>	37	4×10 <sup>-3</sup> at 20 °C	51.3	2.9×10 <sup>-2</sup>	n.a.
C <sub>17</sub> H <sub>27</sub> Cl <sub>9</sub>	58	1.7×10 <sup>-5</sup> at 20 °C	0.01	0.66	n.a.
<i>LCCPs</i>					
C <sub>18-26</sub>	34-54	n.a.	n.a.	n.a.	8.70-12.68
C <sub>18</sub> H <sub>34</sub> Cl <sub>4</sub>	36	7.9×10 <sup>-4</sup> at 20 °C	33	9.4×10 <sup>-3</sup>	n.a.
C <sub>18</sub> H <sub>30</sub> Cl <sub>8</sub>	54	1.1×10 <sup>-5</sup> at 20 °C	0.07	8.6×10 <sup>-2</sup>	n.a.
C <sub>20</sub> H <sub>33</sub> Cl <sub>9</sub>	54	1.9×10 <sup>-7</sup> at 20 °C	0.02	5.3×10 <sup>-3</sup>	n.a.
C <sub>26</sub> H <sub>44</sub> Cl <sub>10</sub>	50	6.3×10 <sup>-12</sup> at 20 °C	0.003	1.6×10 <sup>-6</sup>	n.a.

% Cl: chlorine content,  $P_V$ : vapor pressure, HLC: Henry's law constants,  $S_W$ : water solubility, log  $K_{OW}$ : octanol-water partition coefficient, n.a.: not available

References: a) Tomy et al. (1998), b) European Commission (2000), c) Drouillard et al. (1998b), d) Drouillard et al. (1998a), e) POPRC (2007), f) Sijm and Sinnige (1995)

### 1.2.3.2 Thermal Degradation

Excessive heating of CPs results in release of HCl, which is beneficial for the usage of CPs as flame retardants and metal cutting fluids (Muir *et al.*, 2000). Bergman *et al.* (1984) reported pyrolysis experiments which showed that the decomposition products formed were dependent on the CP chlorine content. The major decomposition products of a synthesized C<sub>12</sub> mixture containing 59% Cl were a large number of aromatic hydrocarbons as well as numerous polychlorinated aromatic compounds (benzenes, toluenes, naphthalenes and biphenyls). A C<sub>12</sub> mixture containing 70% Cl yielded higher quantities of chlorinated aromatics and formation of mono- and dichlorodibenzofurans. It was unclear if the latter were created directly from CPs or by degradation of also formed PCBs (Bergman *et al.*, 1984).

### 1.2.4 Toxicology

Although industrial exposures as well as secondary exposure via the food chain might be of special concern to human health, very little toxicological information is available from human studies (WHO, 1996). Herzberg (1947) reported about seven cases of chlorine acne after consumption of CPs as dripping for fried potatoes.

Available toxicity data indicate low acute toxicity of CPs (WHO, 1996). Severe negative effects were observed for aquatic biota after chronic exposures to SCCPs (Tomy *et al.*, 1998; European Commission, 2000; POPRC, 2007). Furthermore, some of the documented effects of SCCPs in rodents included liver, thyroid, and kidney carcinomas (WHO, 1996; European Commission, 2000; OSPAR Commission, 2001; POPRC, 2007).



The no observed adverse effect level (NOAEL) for general toxicity is 100 and 1000 mg kg<sup>-1</sup> day<sup>-1</sup> for rats and mice, respectively (POPRC, 2007). The International Agency for Research on Cancer (IARC) categorized SCCPs in group 2B as ‘possibly carcinogenic to humans’ (WHO, 1996).

### **1.2.5 Releases into the Environment**

There is no evidence of any significant natural source of CPs. Tomy *et al.* (1998) proposed that anthropogenic releases of CPs may occur during production, storage, transportation, industrial and consumer usage of CPs containing products, disposal and burning waste as well as land filling of products such as PVC, textiles, painted materials, and cutting oils. However, the major discharges into the environment are supposed to be from production and industrial usage. The possible sources of release to water from production sites include spills, facility wash-down and storm water run-off.

Furthermore, CPs in metal working fluids may be liberated into aquatic environments from drum disposal, carry-off and spent bath use (Environment Canada, 1993). Finally, these discharges end up in the environment via the effluents of wastewater treatment plants.

The major emission source of SCCPs in the European Union was from metal working applications (European Commission, 2000). A further significant source is from losses during the service life of products containing CPs such as PVC, other plastics, paints, and sealants (European Commission, 2000). These releases are supposed to end up foremost in urban or industrial soil and wastewater.

### **1.2.6 Environmental Fate**

Only few data are available about the environmental fate of CPs due to the complex nature of the mixtures and the difficulties in measuring low concentrations. Based on a comparison of the physical-chemical properties of CPs compared to other environmentally related substances, CPs are supposed to adsorb to soil, sediments and atmospheric particles (Environment Canada, 1993; WHO, 1996).

#### **1.2.6.1 Degradation in the Environment**

CPs are generally considered to be persistent, since photolysis, hydrolysis, and oxidation are insignificant routes of transformation at ambient temperatures. However, several government assessments and published reviews concluded that slow biodegradation in the environment may occur particularly in the presence of adapted micro-organisms (Environment Canada, 1993; WHO, 1996; European Commission, 2000).

Aerobic microorganisms are able to degrade a range of CPs. This biodegradation depends on the previous acclimatization of the microbes, the chain length, and the degree of chlorination of the CPs. The longer the carbon chain and the higher the chlorine content, the less the degradation (Environment Canada, 1993).

### 1.2.6.2 Transport and Mobility

Few data are available on transport and mobility of CPs from sites of industrial/manufacturing, use, or disposal. Calculated Henry's law constants of some CPs are similar to those of chlorinated pesticides such as toxaphene, chlordane and aldrin, which are known to be transported via the atmosphere (Environment Canada, 1993). A half-life of 0.81-10.5 days has been estimated for SCCPs in air. However, the high adsorption of CPs to atmospheric particles at low temperatures may limit the atmospheric degradation pathway (POPRC, 2007). Long-range atmospheric transport of CPs is documented by the occurrence of CPs in remote areas like the Arctic (Tomy *et al.*, 1999a; Borgen *et al.*, 2000; Reth *et al.*, 2006). Tomy *et al.* (1999a) showed a higher amount of the more volatile lower chlorinated SCCPs in samples from the Arctic compared to technical mixtures. Partial fractionation of the original technical composition may occur during atmospheric transport and phase transition.

### 1.2.6.3 Bioaccumulation

Despite a high bioaccumulation potential reflected in the physico-chemical data, only few studies of bioconcentration factors (BCFs) or biomagnification factors (BAFs) have been published (POPRC, 2007). Measurement of BCFs and BAFs is demanding due to the low water solubility of CPs and subsequent slow uptake rates. This requires long exposure periods to achieve a steady-state equilibrium (POPRC, 2007).

BCFs vary significantly between <1 to 138'000 depending on animal species and CP mixture (WHO, 1996). Fisk *et al.* (2000) suggested that MCCPs may be more easily bioaccumulated than SCCPs due to the reduced biotransformation resulting from the longer carbon chain lengths.

### **1.2.7 Environmental Levels**

The currently existing data show a ubiquitous presence of CPs in the environment. To date, they have been reported in abiota and biota (Hüttig and Oehme, 2005; Reth *et al.*, 2005a; Příbylová *et al.*, 2006; Brändli *et al.*, 2007) from industrial, urban, rural and remote areas (Tomy *et al.*, 1999a; Nicholls *et al.*, 2001; Štejnarová *et al.*, 2005; Stern *et al.*, 2005). Table 1.5 summarizes typical CP levels present in different environmental matrices.

**Table 1.5** Overview of reported environmental CP levels in different matrices.

Sample	Sampling location	Concentration	Reference
Air	Allert, Canada	<1-8.5 pg m <sup>-3</sup> SCCPs	(Stern and Tomy, 2000)
	Egbert, Canada	65-924 pg m <sup>-3</sup> SCCPs	(Stern and Tomy, 2000)
	Spitzbergen, Norway	9-57 pg m <sup>-3</sup> SCCPs	(Borgen <i>et al.</i> , 2000)
	Bear Island, Norway	1'800-10'600 pg m <sup>-3</sup> SCCPs	(Borgen <i>et al.</i> , 2002)
	Lancaster, United Kingdom	5-1'085 pg m <sup>-3</sup> SCCPs	(Peters <i>et al.</i> , 2000)
	Hazelrigg, United Kingdom	<185-3'430 pg m <sup>-3</sup> SCCPs	(Barber <i>et al.</i> , 2005)
		<811-14'500 pg m <sup>-3</sup> MCCPs	(Barber <i>et al.</i> , 2005)
Moss	Norway	3-100 ng g <sup>-1</sup> ww SCCPs	(Schlabach <i>et al.</i> , 2002)
Sewage sludge	Czech Republic	<0.002-0.40 µg g <sup>-1</sup> dw SCCPs	(Příbylová <i>et al.</i> , 2006)
		<0.002-2.3 µg g <sup>-1</sup> dw MCCPs	(Příbylová <i>et al.</i> , 2006)
	Switzerland	30 µg g <sup>-1</sup> dw MCCPs	(Schmid and Müller, 1985)
	United Kingdom	1.8-93.1 µg g <sup>-1</sup> dw SCCPs+MCCPs	(Nicholls <i>et al.</i> , 2001)
		6.9-200 µg g <sup>-1</sup> dw SCCPs	(Stevens <i>et al.</i> , 2003)
		30-9'700 µg g <sup>-1</sup> dw MCCPs	(Stevens <i>et al.</i> , 2003)
River Sediment	Czech Republic	<2-347 ng g <sup>-1</sup> dw SCCPs	(Příbylová <i>et al.</i> , 2006)
		<2-5'575 ng g <sup>-1</sup> dw MCCPs	(Příbylová <i>et al.</i> , 2006)
	Germany	47-75 ng g <sup>-1</sup> dw SCCPs	(Hüttig, 2006)
		75-153 ng g <sup>-1</sup> dw MCCPs	(Hüttig, 2006)
	France	28-51 ng g <sup>-1</sup> dw SCCPs	(Hüttig, 2006)
		24-85 ng g <sup>-1</sup> dw MCCPs	(Hüttig, 2006)
	Norway	21-66 ng g <sup>-1</sup> dw SCCPs	(Hüttig, 2006)
		63-137 ng g <sup>-1</sup> dw MCCPs	(Hüttig, 2006)
	Spain	250-3'040 ng g <sup>-1</sup> dw SCCPs	(Parera <i>et al.</i> , 2004)
	United Kingdom	<200-65'100 ng g <sup>-1</sup> dw MCCPs	(Nicholls <i>et al.</i> , 2001)

ww: wet weight; dw: dry weight

### **1.2.8 Regulations**

In 1995, the OSPAR Convention for the Protection of Marine Environment of the North-East Atlantic adopted a decision on SCCPs (PARCOM Decision 95/1, OSPAR Commission, 2001). It included a ban on the use of SCCPs in all fields of application. A phasing out of SCCPs was considered due to their presence in the aquatic environment of industrial and non-industrial areas as well as in aquatic and terrestrial organisms, their persistence, their toxicity to aquatic organisms, their bioaccumulation in certain species, their carcinogenicity in rats and mice and due to availability of less environmentally hazardous substitutes. Therefore, all sale and use of SCCPs should be prohibited by the end of 1999. Similar to OSPAR, the Baltic Marine Environment Protection Commission (HELCOM, Helsinki Commission) has included SCCPs on their list of harmful substances (HELCOM, 2002). SCCPs are listed as priority hazardous substances in the field of water policy within the Water Framework Directive of the EU (European Community, 2000) requiring an extensive monitoring of SCCPs in Europe from 2006 onwards. Use in metal working fluids as well as in leather fat liquors was restricted in the European Union (European Community, 2002). However, this directive did not cover SCCPs as polymer additives (another main application in Europe).

In 2005, the European Community proposed SCCPs to be added to the 'UNECE Convention on Long Range Transboundary Air Pollution, Protocol on Persistence Organic Pollutants', due to their consistency with the criteria of decision 1998/2 of the Executive Body for persistence, potential to cause adverse effects, bioaccumulation and potential for long range transport.

In December 2006, the Parties to the UNECE POPs Protocol agreed that SCCPs should be considered as a POP as defined under the Protocol (POPRC, 2007).

No regulations exist on MCCPs and LCCPs, though MCCPs and LCCPs are currently used in probably the same quantities as SCCPs before.

### **1.2.9 State of the Art of CP Analysis**

Technical CP mixtures contain thousands of different congeners (homologues and isomers) which cannot be resolved by any chromatographic and mass spectrometric technique. CP chromatograms show broad humps of unresolved CP isomers. Moreover, reference materials for calibrations as well as matrix-matched reference materials are lacking. Zencak and Oehme (2006) presented a review of current analytical methods employed in the years 2001-2006 and their applicability to different matrices. However, suitable analytical methods are needed, since SCCPs were included into the hazardous substance list of the European Water Framework Directive and environmental levels of CPs should be monitored from 2006 onwards (European Community, 2000).

Currently, the most applied analytical methods for CPs are based on gas chromatography coupled with mass spectrometry (GC/MS) combined with electron capture negative ionization (ECNI). However, also electron capture detection (ECD) is still applied for the determination of CPs (Randegger-Vollrath, 1998; Nilsson *et al.*, 2001; Friden *et al.*, 2004).

Recently, complementary techniques were reported such as using an alternative reagent gas mixture based on methane and dichloromethane for negative ion chemical ionization ( $\text{CH}_4/\text{CH}_2\text{Cl}_2\text{-NICI}$ ) MS (Zencak *et al.*, 2003), electron ionization tandem mass spectrometry (EI-MS/MS) (Zencak *et al.*, 2005) or carbon skeleton reaction gas chromatography (Koh *et al.*, 2002). Moreover, techniques have been proposed such as positive ion chemical ionization (PICI) MS (Castells *et al.*, 2004a), comprehensive two-dimensional GC combined with electron capture negative ion detection time-of-flight mass spectrometry (GC $\times$ GC/ECNI-TOF-MS) (Korytár *et al.*, 2005c), metastable atom bombardment (MAB) ionization (Moore *et al.*, 2004) or liquid chromatography combined with chloride-enhanced atmospheric pressure chemical ionization (LC-Cl<sup>-</sup>-APCI) (Zencak and Oehme, 2004).



## 2 Aim of the Work

The general objective of this work was to obtain information about the environmental distribution of CPs in the Alps and their surrounding areas. For this purpose, methods for the analysis of CPs in conifer needles and soil (humus) had to be developed. The aim of the method development was to combine new methodology with techniques developed in previous studies to a simple, reliable and versatile analytical approach for the determination of CPs in various matrices. Another major goal was the collection of environmental data for the evaluation of the spatial, altitudinal, and chronological distribution of CPs.

Specific goals were:

- To develop a method for the quantification of CPs in spruce needles providing evidence that they are a suitable passive sampling system for the monitoring of CPs distributed via the atmosphere (PAPER I).
- To apply the developed analytical methods to the determination of CPs in soil samples from the Swiss Soil Monitoring Network (NABO), in spruce needles and humus collected by the Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants (MONARPOP) (PAPER II). These data should allow examining the spatial exposure and a possible altitudinal variation of CP deposition in Switzerland and in the Alps.

- To investigate a dated sediment core from Lake Thun covering the past 120 years for the evaluation of the historical trend of the CP deposition. Comparison of the data with global production and polychlorinated biphenyl (PCB) deposition was a further goal (PAPER III).

## 3 General Discussion

### 3.1 Analytical Methodology

#### 3.1.1 State of the Art

Analysis of CPs is a demanding task due to the complex composition of CP products, the large number of CPs present and the lack of pure reference solutions as well as matrix-matched reference materials (Muir *et al.*, 2000; Zencak and Oehme, 2006). Therefore, only a limited number of methods exist for the analysis of CPs in environmental matrices and even fewer are suitable for routine analysis.

Most of the extraction and clean-up techniques used for the determination of persistent organochlorines can be transferred to the analysis of CPs, which is an advantage. Nevertheless, further considerable adaptations are needed. In particular, the clean-up has to be optimized to the applied detection technique minimizing interferences which are especially critical when low resolution mass spectrometric methods are employed (Reth *et al.*, 2005a; Zencak *et al.*, 2005). In the following, requirements and critical aspects of each step of the analysis of CPs will be discussed.

##### 3.1.1.1 Sample Extraction

CPs are usually isolated from environmental matrices with the same procedures applied for other organochlorines. The selection of the extraction method depends on the sample matrix. The most frequently used technique for solid matrices is Soxhlet extraction (Nicholls *et al.*, 2001; Hüttig and Oehme, 2005; Štejnarová *et al.*, 2005) due to its robustness and low costs despite the high solvent and time consumption.

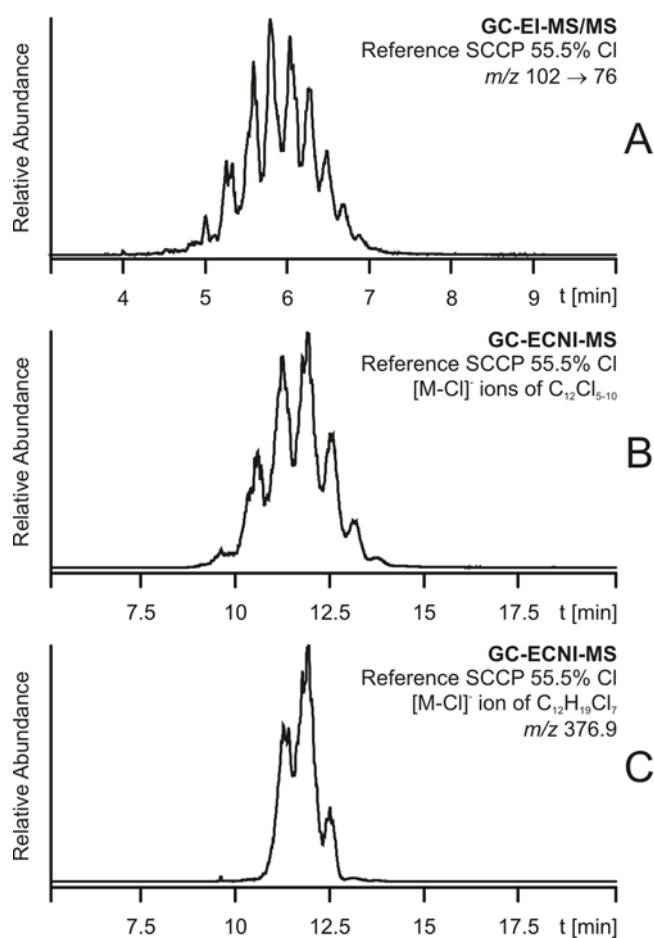
However, other techniques can also be applied such as pressurized liquid extraction (Tomy and Stern, 1999), microwave-assisted extraction (Parera *et al.*, 2004) and solid-phase extraction (Nicholls *et al.*, 2001; Castells *et al.*, 2004b). Non-polar to semi-polar organic solvents such as dichloromethane (DCM), *n*-hexane (nHex), a mixture of both (DCM/nHex) or toluene are used for the extraction of CPs. Matrices containing large amounts of elemental sulfur disturbing the GC analysis, are treated with activated copper for the elimination of sulfur during the extraction (Tomy and Stern, 1999; Hüttig and Oehme, 2005).

### **3.1.1.2 Sample Clean-up**

The sample clean-up is the most critical step since it has to remove other interfering organic compounds which extracted together with CPs (e.g. pesticides, PCBs, polybrominated diphenyl ethers PBDEs, toxaphenes, and chlordanes). It is one of the most challenging steps of CP analysis. Therefore, a wide variety of clean-up procedures has been published in the literature. Treatment by sulfuric acid (Coelhan, 1999; Nicholls *et al.*, 2001; Hüttig and Oehme, 2005; Reth *et al.*, 2005a; Štejnárová *et al.*, 2005) or gel permeation chromatography (Tomy *et al.*, 1997; Coelhan, 1999) is used to eliminate matrix components such as lipids and other organic materials. Adsorbents such as Florisil (Tomy *et al.*, 1997; Hüttig and Oehme, 2005; Reth *et al.*, 2005a), silica gel (Coelhan, 1999; Nicholls *et al.*, 2001; Štejnárová *et al.*, 2005), and aluminum oxide (Marvin *et al.*, 2003; Parera *et al.*, 2004) are frequently applied for fractionation.

### 3.1.1.3 Gas Chromatographic Separation

Currently, no gas chromatographic technique is able to separate partly or completely the extremely large number of different isomers ( $>10^4$ ) in CP mixtures into single congeners. The most commonly applied stationary phase is 5%-phenyl-methylpolysiloxane (e.g. DB5-MS, Ultra2), but others could also be used such as 100% methylpolysiloxane (Nilsson *et al.*, 2001) and 35%-phenyl-methylpolysiloxane (Zencak *et al.*, 2003). Whatever stationary phase is applied, the CP chromatograms are characterized by a few broad humps showing a large number of co-eluting peaks over a retention time of several minutes as shown in Figure 3.1. A short column technique was proposed by Coelhan (1999). His attempt was to simplify the GC analysis, because separation of the mixture cannot be achieved anyway. Therefore, the sample was introduced into the MS via a very short column and CPs elute all in one peak within few seconds. However, it may also contain other interferences not removed by the clean-up, which can lead to an overestimation of the CP quantity. Comprehensive two-dimensional gas-chromatography (GC $\times$ GC) coupled with  $\mu$ ECD, a fast scanning single quadrupole MS, or a time-of-flight MS improved considerably the separation of CPs (Korytár *et al.*, 2005a; 2005b; 2005c). However, this type of instrumentation is very expensive, needs expert knowledge and it is very time-consuming for data processing. Therefore, it is not suitable for routine analysis, but opens up interesting new possibilities of compound profile studies of CPs.



**Figure 3.1** Chromatograms of a reference SCCP mixture (55.5% Cl) detected by EI-MS/MS (A:  $m/z$  102  $\rightarrow$  67) and ECNI-MS (B: reconstructed ion current (RIC) for  $[M-Cl]^-$  ions of  $C_{12}Cl_{5-10}$ ; C:  $[M-Cl]^-$  ion of the congener group  $C_{12}H_{19}Cl_7$ ,  $m/z$  376.9).

#### 3.1.1.4 Detection

Mass spectrometry involving ECNI detection with methane as reagent gas is commonly used for CP determination due to its high selectivity and sensitivity when recording single ions of the  $[M-Cl]^-$  isotope clusters (Schmid and Müller, 1985; Tomy *et al.*, 1997; Castells *et al.*, 2004a; Zencak *et al.*, 2005). Moreover, ECNI with high resolution mass spectrometry (HRMS) was recommended as detection method, since it is a very selective method eliminating interferences from CP fragments with the same nominal  $m/z$  values or from other organochlorine compounds (Tomy *et al.*, 1997). Due to the high costs of HRMS instruments, this method is not available in many laboratories.

Nevertheless, low resolution MS (LRMS) methods based on ECNI or on electron ionization tandem mass spectrometry (EI-MS/MS) are well-suited for routine analysis despite some limitations (Castells *et al.*, 2004a; Reth and Oehme, 2004; Zencak *et al.*, 2005). However, a highly efficient clean up is mandatory to avoid interferences from both matrix and other POPs (Parera *et al.*, 2004; Reth and Oehme, 2004; Hüttig and Oehme, 2005). The major limitation of all ECNI methods is that errors of up to 300% are introduced, when reference standards are used with another CP composition than the samples (Tomy *et al.*, 1999b; Coelhan *et al.*, 2000; Zencak *et al.*, 2005). Low chlorinated CPs (<5 chlorine atoms) are not detected by ECNI-MS due to their low electron affinity. Furthermore, the evaluation of all congener and homologue groups by ECNI-MS is very time-consuming due to the large number of GC-MS runs and the corresponding data processing (Reth *et al.*, 2005b).

Zencak *et al.* (2003) showed that the use of an alternative reagent gas mixture (methane and dichloromethane) enhanced the formation of chloride adduct ions  $[M + Cl]^-$ . This technique reduced mass interferences between the CP congeners, suppressed the ionization of other organochlorines and resulted in similar response factors for CPs with different chlorine contents. Moreover, it could detect lower chlorinated CPs ( $Cl_{3-5}$ ). Unfortunately, this technique is not suitable for routine analysis, since the use of dichloromethane causes a quick loss of sensitivity due to deposition of carbon residues in the ion source.

#### 3.1.1.5 Identification and Quantification

Identification and quantification are the most demanding steps of CP analysis due to the high number of CP isomers present.

Reth and Oehme (2004) showed that ECNI detection at low resolution can lead to systematic errors due to gas chromatographic and mass spectrometric overlap between CP congeners ( $C_xH_yCl_z$  and  $C_{x+5}H_{y+12}Cl_{z-2}$ ;  $x = 10-12$ ; e.g. mass overlap between  $[M-Cl]^-$  ion of  $C_{10}H_{15}Cl_7$  and  $[M-Cl]^-$  ion of  $C_{15}H_{27}Cl_5$ ). Nevertheless, the quantification of major congener groups is not affected. However, a proper identification of the CP congeners ( $C_{10-17}Cl_{5-10}$ ) based on retention time, chromatographic signal shape and correct isotope ratio is essential.

The ECNI response factors of different technical CP mixtures and single compounds vary strongly (Zencak *et al.*, 2003). Congeners with higher chlorine content have higher response factors. Therefore, the selection of the CP reference standard has a significant



influence on the results and may lead to systematic errors up to several hundred percents if not properly carried out (Tomy *et al.*, 1999b; Zencak *et al.*, 2005).

Recently, a novel quantification procedure was described by Reth *et al.* (2005b) which enabled a reliable quantification even if the chlorine content of sample and reference standards is different. These authors found a linear correlation between the response factor of CPs in a technical mixture and the degree of chlorination. This approach allowed the compensation of response factor differences between sample and applied reference standard. Therefore, it is mandatory to use the available reference CP mixtures (e.g. from Ehrenstorfer: SCCP 51%, 55%, and 63% Cl; MCCP 52% and 57% Cl) with different chlorine content to compensate such effects.

### **3.1.2 Before Starting Analyzing CPs**

Contamination and blank problems are severely limiting factors. They are caused by the ubiquitous use of CPs e.g. as sealants (Randegger-Vollrath, 1998) and paints (Zencak and Oehme, 2004) as well as due to the high desorptivity of CPs on glass surfaces. Therefore, it is fundamental to check blanks during method development and throughout analyses.

In particular, it is important to clean the glassware thoroughly. Cross contamination via glassware could be minimized by the following procedure. First, all glassware is washed in a dishwasher, then immersed into a detergent solution (5% RBS<sup>®</sup>35 concentrate, Fluka) for 12 hours and finally rinsed with high purity solvents (e.g. DCM and nHex). After this cleaning procedure, it is mandatory to heat all glassware to 450 °C

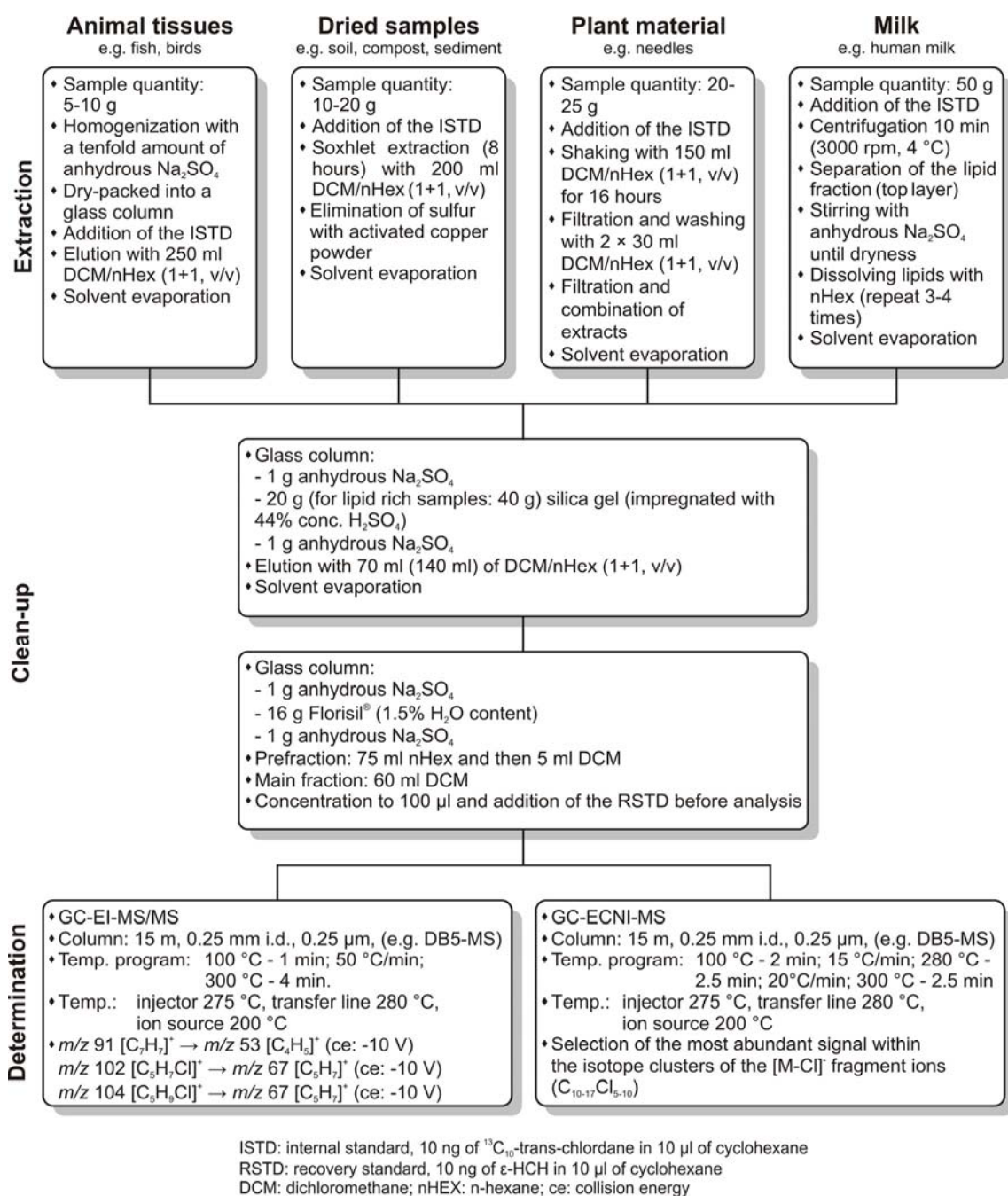
for at least two hours and to rinse them again with the same solvents prior to use. It is recommended to start with new glassware.

Glass wool and glass fiber filters should be heated to 450 °C, as well for two hours. Chemicals used for sample clean-up such as Florisil<sup>®</sup>, anhydrous sodium sulfate and silica gel can be used after heating them overnight at 220 °C. Teflon stopcocks can cause a problem as well. For this reason, they should be cleaned with solvents.

### 3.1.3 Concept of an Analytical Scheme

What is necessary to perform routine CP analysis in e.g. a service laboratory? An analytical pathway is presented in Figure 3.2, which is suitable and applicable in any kind of laboratory as a routine standard method. The presented extraction procedures and standardized clean-up are applicable to all kind of sample extracts. It allows the determination of CPs in various matrices (animal tissues, sediments, human milk, soil/humus, compost, and spruce needles). The whole concept is based on a simple, cost-efficient, and modular system which avoids expensive techniques such as pressurized liquid extraction, microwave-assisted extraction, and high resolution MS. Extraction is matrix specific (see Figure 3.2) followed by a standardized clean-up applicable to all kind of samples (Hüttig and Oehme, 2005; Reth *et al.*, 2005a; Reth *et al.*, 2006).

However, also the extraction procedures have some parameters in common. Except for milk samples, all matrices were extracted with DCM/nHex (1+1, v/v). Soxhlet extraction was preferred for dried samples. Liquid extraction provided optimal results for biota after drying by homogenization with sodium sulfate. A simple solvent extraction over night was sufficient to achieve high recoveries of CPs for plant material. The extraction of human milk samples is more complex due to the separation of the lipid fraction.

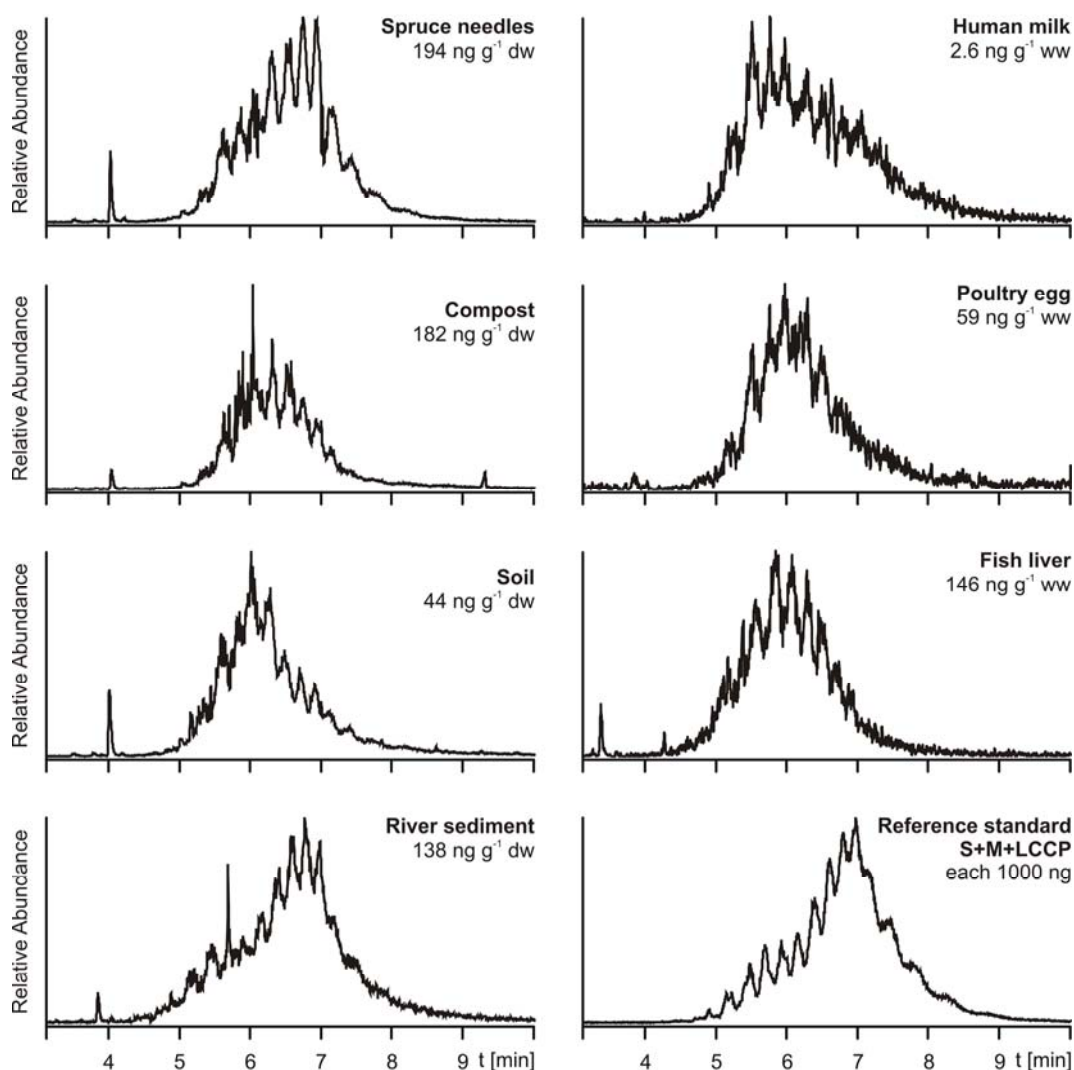


**Figure 3.2** Scheme of analytical procedures for the determination of chlorinated paraffins in different materials.

The clean-up procedure was the same for all samples. It consisted of a silica gel column impregnated with sulfuric acid. Hereby, interfering compounds degradable by sulfuric acid were removed such as waxes and lipids. If the extract is not colorless and/or clear this part has to be repeated. Finally, a deactivated Florisil<sup>®</sup> column was applied to separate CPs from other organochlorines such as toxaphenes and PCBs.

It is recommended to perform quantification by a triple quadrupole in the EI-MS/MS mode (Zencak *et al.*, 2004) for routine analysis. It has an huge advantage compared with other quantification methods, which are either highly complex and time consuming (e.g. ECNI) or too expensive (e.g. HRMS). This method allows determining the sum of short, medium, and long chain paraffins within 10 minutes (Zencak and Oehme, 2006).

For the first time spruce needle, compost, humus, and soil samples were included in this analytical approach. Soil (see chapter 3.2.2), humus (see PAPER II), and compost (see chapter 3.2.3 and (Brändli *et al.*, 2007)) samples were extracted in the same way as sediment samples. A new extraction was developed for spruce needles (see PAPER I). The combination of the described extraction and clean-up methodologies resulted in chromatograms with a low background showing the typical CP profile without interferences (see EI-MS/MS chromatograms in Figure 3.3).



**Figure 3.3** EI-MS/MS chromatograms ( $m/z$  102  $[C_5H_7Cl]^+ \rightarrow m/z$  67  $[C_5H_7]^+$ ) of CPs in different sample matrices and of a standard mixture of short (55% Cl), medium (57% Cl) and long chain (49% Cl) chlorinated paraffins (1+1+1). Poultry egg samples were analyzed with extraction procedure for animal tissue. Chromatograms of river sediment, human milk, poultry egg, and fish liver provided by courtesy of J. Hüttig (2006) and M. Reth (2006).

## 3.2 Evaluation of CP Levels in the Alps and in Switzerland

### 3.2.1 Alps as a Trap for POPs

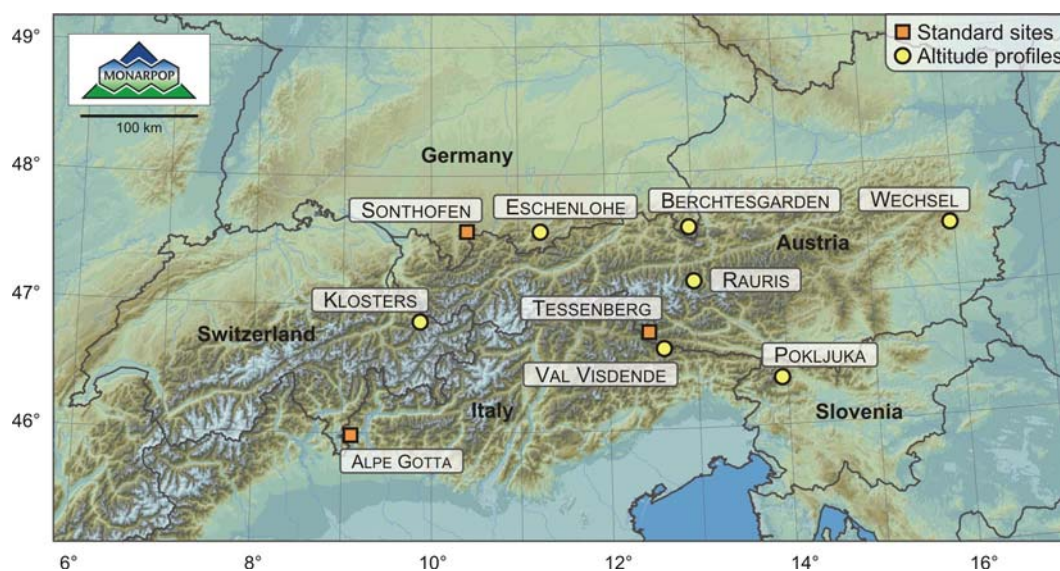
Mountains are a topographical and meteorological trap for atmospheric pollutants including semivolatile organic compounds (SOCs). Reasons are barrier effects, high precipitation rates, and low ambient temperatures (cold condensation) (McLachlan and Horstmann, 1998; Daly and Wania, 2005).

Furthermore, the canopy of forests is acting as an efficient trap due to the high organic content amplifying the transfer of SOC from the atmosphere to soil via leaves and needles. Therefore, forest ecosystems are reservoirs for organochlorines due to the litter fall (McLachlan and Horstmann, 1998; Schmid *et al.*, 2005).

The Alps are an important geographical division in Central Europe representing a barrier for atmospheric circulation. Moreover, they are surrounded by industry regions with a dense population. Transport, fate and effect of POPs are influenced by meteorological processes. POP contamination of various biota and abiotic media has occasionally been reported even from remote spots in the Alps (Weiss *et al.*, 2003; Schmid *et al.*, 2005; Nizzetto *et al.*, 2006; Tremolada *et al.*, 2008). However, the geographic distribution of POPs across the Alps was not investigated in detail. Moreover, CP levels from the Alps have never been reported.

The Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants (MONARPOP) project included a cross-alpine survey of POPs in mountainous forest ecosystems to reveal geographical and altitudinal patterns on a transnational scale and to understand the relevance of high mountains in the global atmospheric transport of POPs (Moche *et al.*, 2005).

This study presents CP levels in humus layers and spruce needles collected within the MONARPOP project from various regions of the European Alps (Switzerland, Austria, Germany, Slovenia, and Italy) to obtain a first overview about the environmental fate (see Figure 3.4). Furthermore, this study presents the first data for humus and spruce needles.



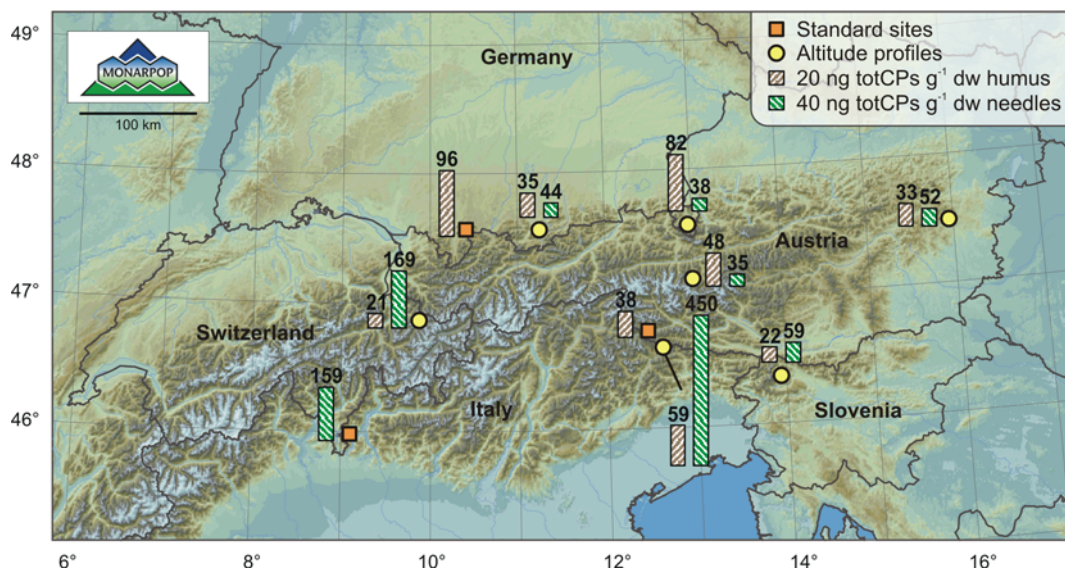
**Figure 3.4** Sampling locations of the Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants (MONARPOP) selected for the analysis of CPs.



Sampling sites were selected with special attention to remoteness and species homogeneity (>80% Norway spruce) of adult stands. Spruce needles (six months old) were collected due to their epicuticular wax layer, which has been shown to trap and accumulate lipophilic compounds (Buckley, 1982; Gaggi et al., 1985). Humus was selected because of its property as a natural sink for POPs. The high organic carbon content favors the accumulation of POPs.

### 3.2.1.1 Spatial Distribution of CPs in the Alpine Ecosystem - MONARPOP

First data about CP levels in the European Alps are presented in PAPER I and PAPER II. Figure 3.5 summarizes the CP concentrations in humus and spruce needles from selected locations at a standard altitude ( $1400 \pm 150$  m) in the Alps in autumn 2004. The analyses were performed by GC-EI-MS/MS determining the sum of SCCP, MCCP and LCCP levels within one run. Therefore, results are presented as total CPs (totCPs).



**Figure 3.5** Overview of the spatial distribution of totCPs in humus and spruce needles from the Alps taken within the MONARPOP project.

TotCP levels were between 21 and 96 ng g<sup>-1</sup> dw (mean 48 ng g<sup>-1</sup> dw) in humus and between 35 and 450 ng g<sup>-1</sup> dw (mean 126 ng g<sup>-1</sup> dw) in spruce needles. These results show that CPs are widely distributed in the Alps and reached regions with little or no industrialization.

Two hypotheses of origin are possible:

- The main CP load to the Alps originates outside the Alps.
- The alpine range is a barrier for long-range atmospheric CP transport.

Both imply that the lowest concentrations should be expected at the center and the highest at the border of the Alps. The two highest CP levels in humus were located in the northern part of the Alps, whereas two of the three highest CP levels in spruce needles were located in the south. Although concentrations varied between the two matrices, highest concentrations occurred only at the fringe of the alpine region. This was also observed for other pollutants within the MONARPOP project, e.g. PBDEs (Knoth *et al.*, 2008), dioxin and dioxinlike PCBs (Offenthaler *et al.*, 2007). Nevertheless, further studies are needed to make an accurate assessment.

### 3.2.1.2 Altitudinal Distribution of CPs in the Alps - MONARPOP

In the framework of the MONARPOP project, seven altitude profiles were sampled in order to investigate the vertical distribution of organic pollutants in different regions of the Alps. Each altitude profile consisted of four to five subplots between 700 and 1900 m in spruce forests reaching from valley ground to upper tree limit and with avoidance of known local sources in the vicinity. Locations of the seven profiles are shown in Figure 3.4.

TotCP concentrations in humus and spruce needles from these altitude profiles are discussed in PAPER I. TotCPs were found in all samples from valley to upper tree limit. As shown in Table 3.1 the concentrations varied between 7 and 199 ng g<sup>-1</sup> dw in humus and between 26 and 450 ng g<sup>-1</sup> dw in spruce needles.

**Table 3.1** Summary of totCP concentrations in alpine humus layers (n = 31) and in spruce needles (n = 27) obtained by GC-EI-MS/MS.

Sample matrix	TotCP concentration [ng g <sup>-1</sup> dw]						
	n	min	max	mean	SD	median	MDL
Humus	31	7	199	39	37	28	2.5 (n = 6)
Spruce needles	27	26	450	84	82	56	1.8 (n = 5)

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

Most of the humus (n = 25; 10-50 ng g<sup>-1</sup> dw) and spruce needle (n = 22; 20-100 ng g<sup>-1</sup> dw) samples showed a background concentration (see Figure 2 in PAPER II). Furthermore, mean needle concentrations (mean 84 ng g<sup>-1</sup> dw) were about two-fold higher compared to humus (mean 39 ng g<sup>-1</sup> dw). This could not be observed for the

other POPs studied by the MONARPOP project. There, concentrations in humus were always higher than in needles. One explanation could be that CPs have a higher affinity to the spruce needles.

CPs were found in higher located and remote sampling stations indicating a long-range transport of CPs. This observation is consistent with studies in the arctic (Tomy *et al.*, 1997; Tomy *et al.*, 1999a; Borgen *et al.*, 2000; Reth *et al.*, 2006), where the presence of CPs was demonstrated in this remote region.

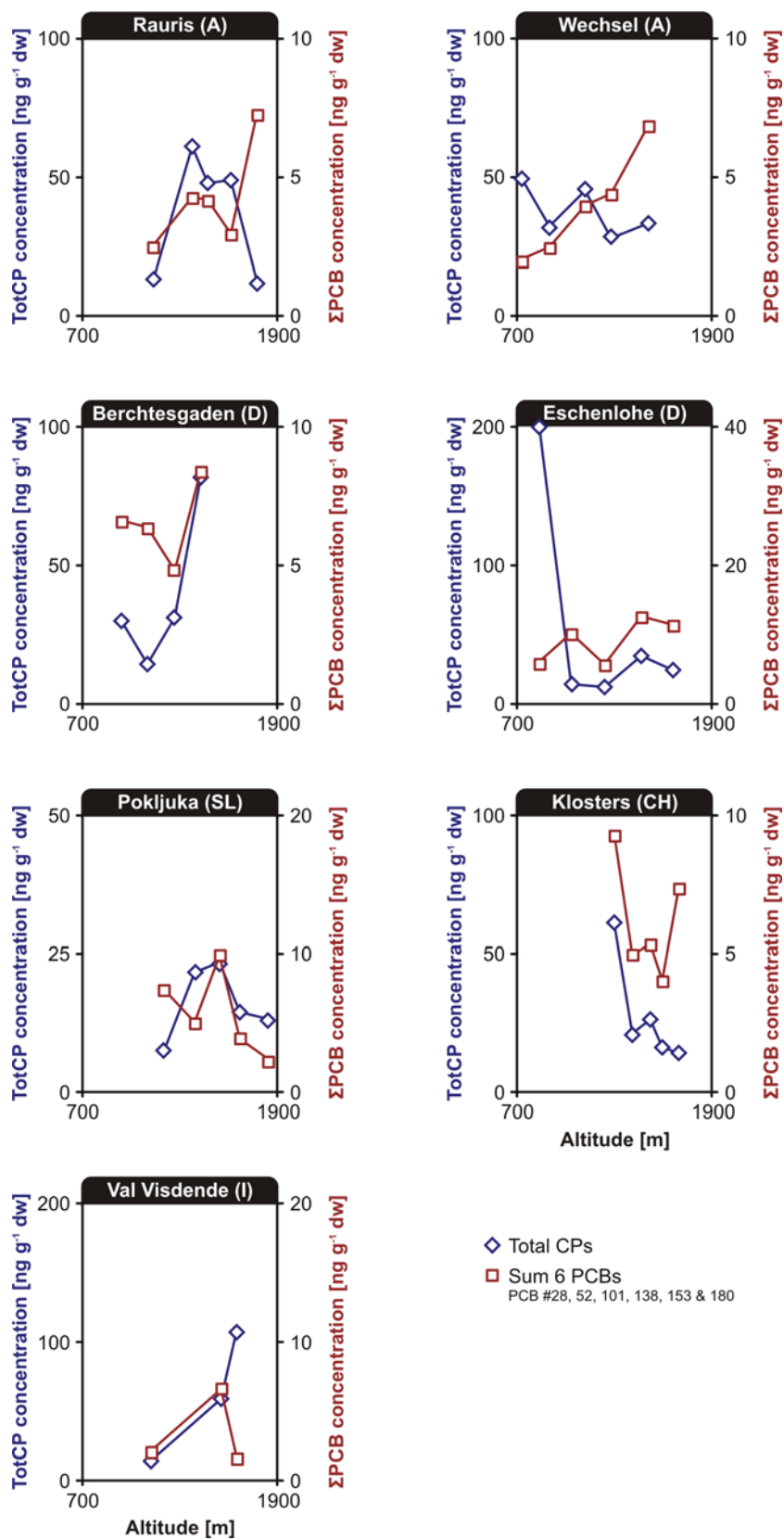
Altitude profiles of totCPs in humus and spruce needle samples are shown in Figure 3 of PAPER II. No coherent trend could be observed for the different locations. This could be due to different parameters influencing the respective sampling location such as meteorological aspects, local influence and the position of each plot. In some sampling stations, CP levels were higher at the lowest altitude, which might be due to the vicinity to densely populated valleys.

As mentioned, meteorology influences the input of CPs into the Alps. A higher precipitation rate, more fog or more inversion layer events can lead to an increased input. Studies of these parameters indicated such influences for other POPs (Ribes *et al.*, 2002; Tremolada *et al.*, 2008). For humus, a slight correlation was observed between CP levels and altitude (see Figure 5 in PAPER II).

Besides higher CP concentrations at low altitudes (700-900 m), a second maximum was present around 1400 m, which could be due to a higher occurrence of fog, more precipitation or inversion layers. Since levels in spruce needles were quite scattered, future research should include a more detailed study of meteorological parameters on CP accumulation.

Generally, totCP levels in humus and needles were highest compared to other POPs present in the same samples from the MONARPOP network (see Table 2 in PAPER II). This was also reported by a study of POP concentrations in the U.K. atmosphere (Barber *et al.*, 2005).

A comparison of CP altitude profiles in humus with those for PCBs and PBDEs (see Figure 3.6 and Figure 3.7), revealed the same concentration variability for some locations (Klosters, Berchtesgarden, Eschenlohe). This indicated a similar origin.



**Figure 3.6** Comparison of CP and PCB altitude profiles in humus from the Alps.

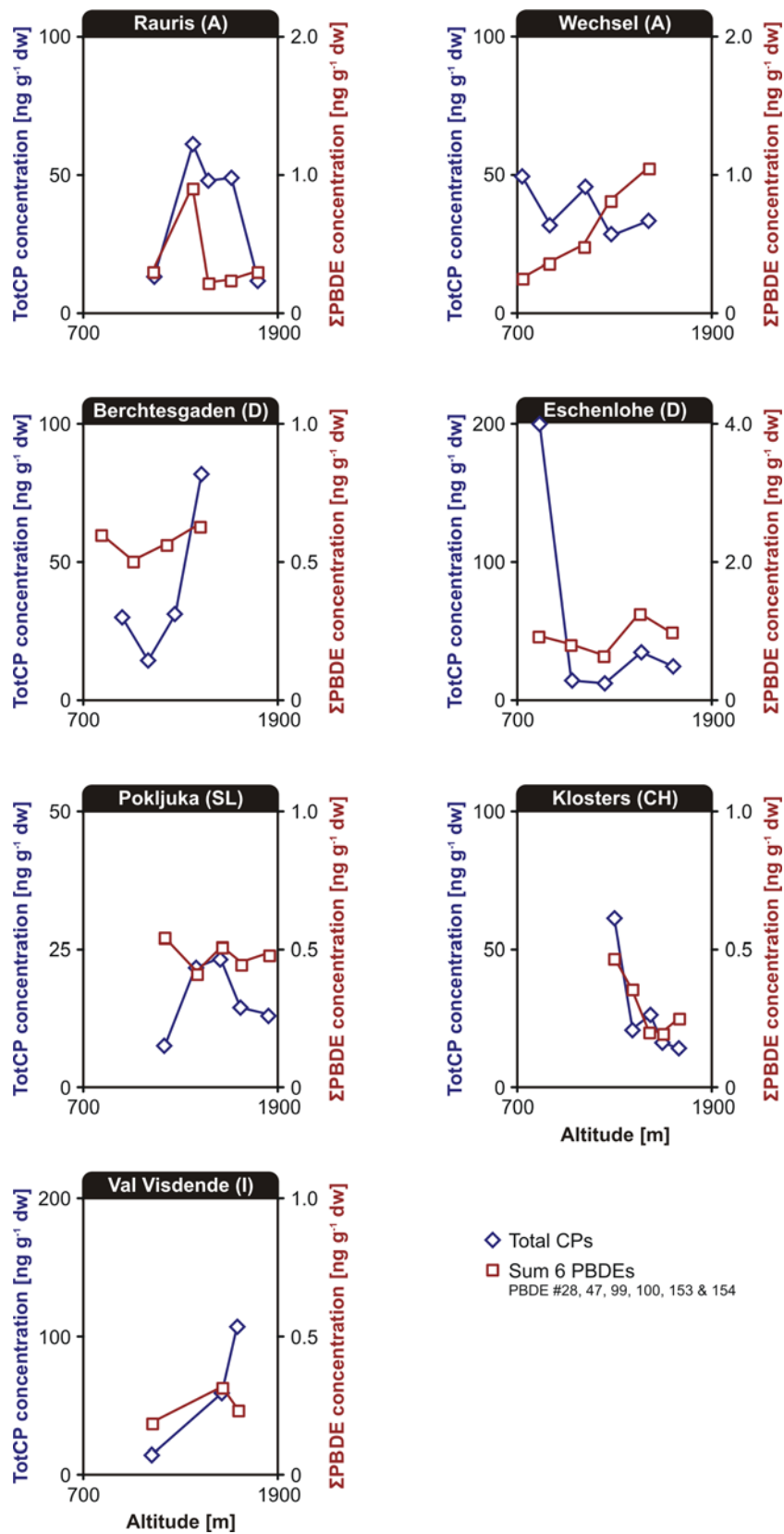


Figure 3.7 Comparison of CP and PBDE altitude profiles in humus from the Alps.

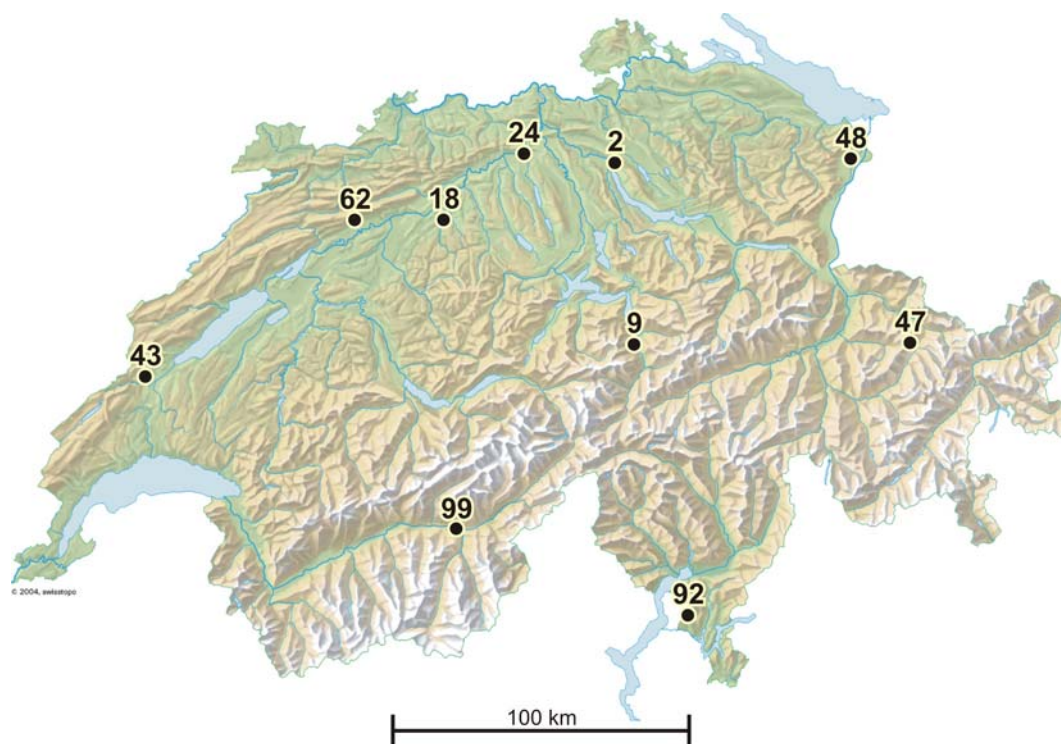
### 3.2.2 CP Levels in Soil from Switzerland - NABO

In 1986, the Swiss ordinance relating to impacts on the soil (OIS) initiated the operation of a reference national soil monitoring network (NABO). The main objective of this network is the monitoring of anthropogenic contaminants in the environment. The NABO program includes 105 reference sites (Desaules and Dahinden, 2000). The sites are distributed throughout Switzerland including rural/remote areas as well as urban, urban fringe and industrial regions (Desaules and Studer, 1993). For selected soil samples, Schmid *et al.* (2005) presented PCDD/F and PCB concentrations. Bucheli *et al.* (2004) elucidated polycyclic aromatic hydrocarbons (PAH) and biogeochemical parameters such as total organic carbon (TOC) and black carbon (BC). No data on CP concentrations in samples from the NABO network were available so far and to the best of the authors' knowledge, there is only one publication, in which CPs were determined in soil (Nicholls *et al.*, 2001). Unfortunately, all concentrations in this study were below the limit of detection (Nicholls *et al.*, 2001).

Only a few data about CP levels in the Swiss environment were available so far. In 1985, Schmid and Müller reported  $5 \text{ ng g}^{-1}$  ww of MCCPs in sediment from Lake Zürich,  $200 \text{ ng g}^{-1}$  ww in human adipose tissue, and  $30\,000 \text{ ng g}^{-1}$  in sewage sludge from an industrialized region (Schmid and Müller, 1985). Reth (2006) detected between  $19$  to  $42 \text{ ng g}^{-1}$  ww of total CP concentration in brown trout samples from the rivers Liechtensteiner Binnenkanal ( $n = 3$ ) and Necker ( $n = 3$ ) as well as  $25 \text{ ng g}^{-1}$  ww in lake trout sample from the alpine lake "Lei da Diavolezza".



The aim of this present work was to achieve the load of CPs in Switzerland. Ten soil samples (0–10 cm, including the top humus layer) were collected at reference sites by the Swiss national soil monitoring network (NABO) between March and July 2002. Locations and ancillary data on the sample sites are presented in Figure 3.8 and in Table 3.2. Further information about these soil samples are also published (Bucheli *et al.*, 2004; Schmid *et al.*, 2005).



**Figure 3.8** Sampling locations of the Swiss Soil Monitoring Network (NABO) selected for the analysis of CPs.

EI-MS/MS was used for a fast determination of the total CP amount. Total CP concentrations were between 34 and 151 ng g<sup>-1</sup> dw (see Table 3.2).

**Table 3.2** Total CP concentrations ( $\text{ng g}^{-1}$  dw) obtained by EI-MS/MS in Swiss soil monitoring network (NABO) samples.

sample site no.	location	altitude [m]	characteristic	total CPs [ $\text{ng g}^{-1}$ dw]	TOC * [ $\text{mg g}^{-1}$ dw]	CPs in TOC [ $\text{ng g}^{-1}$ ]	BC * [ $\text{mg g}^{-1}$ dw]	CPs in BC [ $\mu\text{g g}^{-1}$ ]	sum 7 PCBs ** [ $\text{ng g}^{-1}$ ]
2	Zürich	668	forest	46	35.77	1291	0.72	64	9.0
18	Langenthal	525	forest	48	113.80	421	1.07	45	12.0
24	Niederlenz	387	forest	36	28.51	1279	0.92	40	5.6
43	Orbe	622	forest	44	47.16	928	0.56	78	3.1
47	Davos	1655	forest	72	227.29	316	1.71	42	3.7
48	<i>Oberriet</i>	409	<i>arable land</i>	<i>13-1463</i>	<i>146.05</i>	<i>89-10019</i>	<i>3.73</i>	<i>3-392</i>	<i>2.6</i>
62	Bettlach	1065	forest	39	57.15	687	1.29	31	3.2
92	Novaggio	1080	forest	44	129.62	343	1.83	24	7.8
98	Erstfeld	455	grassland intensive	34	70.41	483	1.11	31	8.4
99	Visp	830	forest	151	66.31	2283	1.62	94	3.3

dw: dry weight; TOC: total organic carbon; BC: black carbon; \* see Bucheli et al. (2004); \*\* see Schmid et al. (2005); *italic*: sample site no. 48 were excluded in the discussion, since the high level ( $1463 \text{ ng g}^{-1}$  dw) could not be confirmed in follow-up measurements (see chapter 3.2.2.1)

The high level at sample site no. 48 could not be confirmed by follow-up measurements (see following chapter 3.2.2.1). Therefore, this site was excluded in the following discussion. Total CP levels in soil were compared with concentrations in humus samples from the Alps (see chapter 3.2.1.1 and 3.2.1.2). Soil levels (34-151 ng g<sup>-1</sup> dw; mean: 57 ng g<sup>-1</sup> dw) were in the same range as humus levels (21-96 ng g<sup>-1</sup> dw; mean: 48 ng g<sup>-1</sup> dw). It seems that the background levels are similar for both Switzerland and the whole alpine region.

Hüttig and Oehme (2005) reported between 5 and 499 ng g<sup>-1</sup> dw of totCPs in sediments from the North and Baltic Sea for samples from 2001 to 2003. This is higher than the concentrations found in this study. TotCP concentrations were between 19 to 42 ng g<sup>-1</sup> ww in six brown trout samples from the Swiss rivers Liechtensteiner Binnenkanal and Necker, and 25 ng g<sup>-1</sup> ww in one lake trout sample from the Swiss alpine lake Lei da Diavolezza (Reth, 2006).

Total CP levels are considerably higher than the sum of the indicator PCB concentrations (sum of PCB #28, 52, 101, 118, 138, 153, and 180) in these samples (Schmid *et al.*, 2005). The same relationship was observed for the samples of the MONARPOP network (see chapter 3.2.1.2).

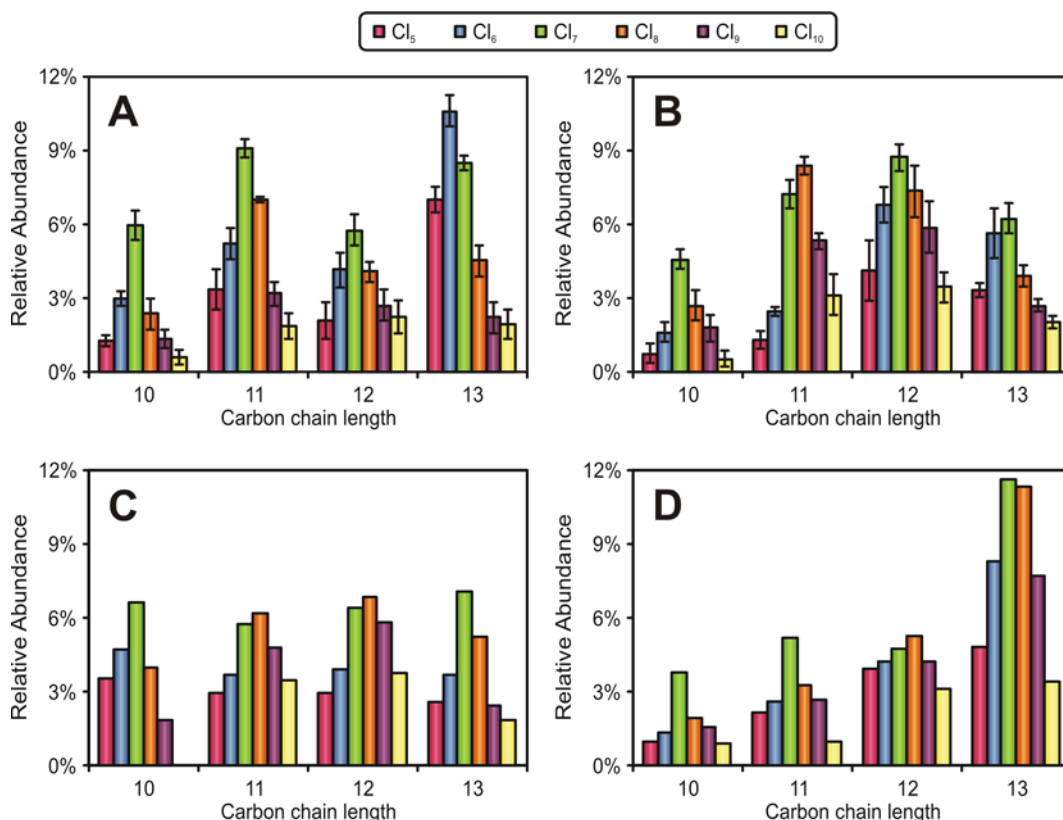
Furthermore, ECNI-LRMS was applied for the determination of SCCP and MCCP concentrations (see Table 3.3) and for elucidation of congener group patterns (see Figure 3.9 and Figure 3.10).

**Table 3.3** SCCP and MCCP concentrations and chlorine contents determined by ECNI-LRMS in samples of the Swiss soil monitoring network (NABO).

Sample site no.	SCCPs [ng g <sup>-1</sup> dw]	Cl content [%]	MCCPs [ng g <sup>-1</sup> dw]	Cl content [%]	S+MCCPs [ng g <sup>-1</sup> dw]
2	21	62.0	20	54.2	42
18	2	61.8	30	54.9	32
24	11	61.6	20	54.7	31
43	5	62.1	37	55.4	42
47	13	62.5	35	55.8	48
48	73	<i>61.0</i>	<i>749</i>	52.5	821
62	16	60.8	21	53.9	37
92	15	60.5	15	54.2	30
98	14	60.8	20	54.2	34
99	51	60.1	85	54.3	136

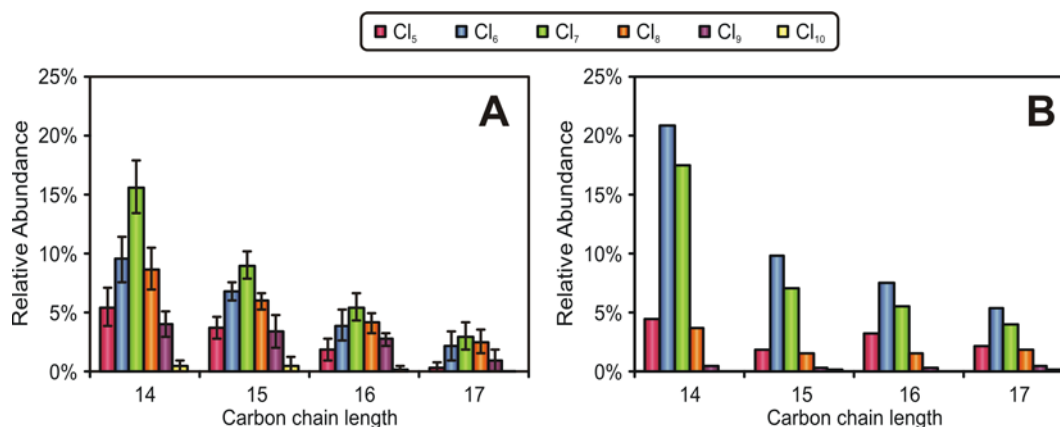
dw: dry weight; *italic*: samples from site no. 48 are excluded in the discussion (see chapter 3.2.2.1)

MCCP concentrations (15-85 ng g<sup>-1</sup> dw) were similar or higher than for SCCPs (2-51 ng g<sup>-1</sup> dw). The chlorine content of SCCPs was between 60.5 and 62.5%, whereas that of MCCPs varied between 53.9 and 55.4%. The results obtained by ECNI-LRMS and EI-MS/MS were generally in good agreement within a factor of two. Difference could be traced back to the detection of congeners with 1-4 chlorine atoms as well as to the presence of long-chain CPs (C<sub>>17</sub>) both only detectable with the EI-MS/MS method.



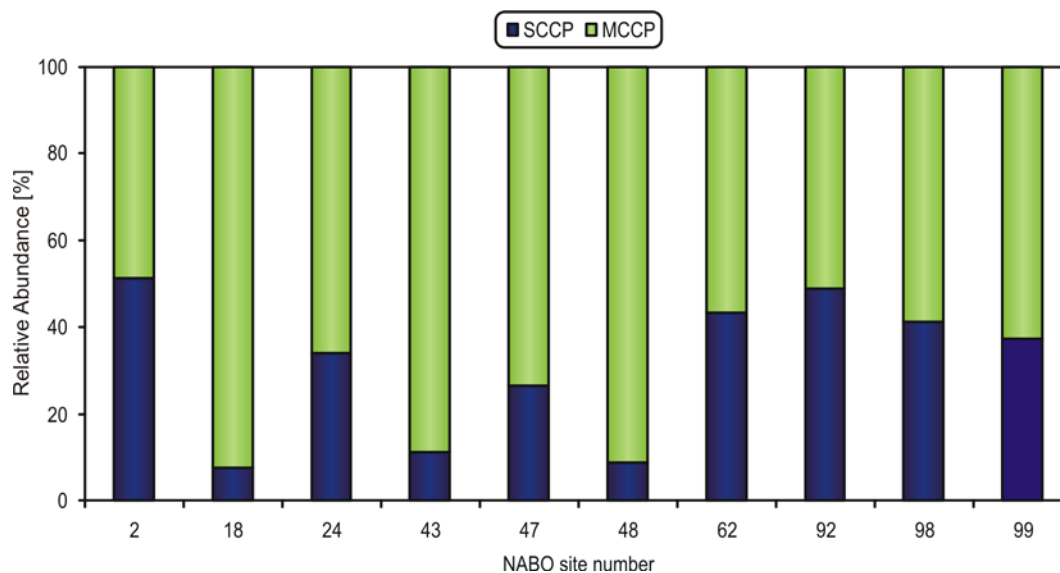
**Figure 3.9** A and B show the average SCCP congener group patterns of the following NABO samples: A 62, 92, 98, 99; B 2, 18, 24, 47. Standard deviations are assigned. C and D show the SCCP congener group pattern of NABO samples 43 and 48 (highest level), respectively.

Four different pattern types were observed. Congeners with eleven and thirteen carbon atoms were most abundant among SCCPs in the average pattern of samples 62, 92, 98 and 99, whereas eleven and twelve carbon atom congeners dominated in samples 2, 18, 24 and 47. Two further samples (43 and 48: highest level) did not fit with these average patterns. In addition, sample 48 (highest level) is the only sample that differs from the other samples in the MCCP pattern (see Figure 3.10). MCCPs with seven chlorine atoms were predominant in most of the samples, whereas six chlorine atoms prevailed in sample 48.



**Figure 3.10** MCCP congener group patterns of the following NABO samples: A all samples excluding sample 48 (standard deviations are assigned); B only sample 48 (highest level).

Figure 3.11 shows the relative amounts of SCCPs and MCCPs in the samples. Samples 18, 43, 47 and 48 (highest level) have considerably higher MCCP than SCCP concentrations.



**Figure 3.11** Proportion of SCCP and MCCP in NABO samples.

### 3.2.2.1 Sample 48 – Oberriet

The high concentration value and the atypical CP congener pattern of site 48 compared to the other sites in the first analysis campaign initiated more investigations to confirm this result. Table 3.4 shows a compilation of the results.

**Table 3.4** Total CP concentrations in soils from sampling site 48 from four sampling campaigns (PCDD/PCDF 2002, regular 1997, 2002 and 2007).

Analysis	Sample	Campaign	Sampling Year	TotCP conc. [ng g <sup>-1</sup> dw]	Comments
1	48	PCDD/PCDF	2002	1463	Sampling depth 0-10 cm; dried at room temperature, ground with a vibrating cup mill, filled in a glass jar stored in the dark at room temperature
2	48	PCDD/PCDF	2002	13	
3	48	PCDD/PCDF	2002	18	
4	48	PCDD/PCDF	2002	97	
5	48 1.3	Regular	1997	19	Sampling depth 0-20 cm; dried at 40 °C, ground with a jaw crusher, sieved <2 mm, filled in honey jars and stored in the dark at cellar temperature
6	48 1.4	Regular	2002	9	
7	48 1.5	Regular	2007	69	
8	48 1.5	Regular	2007	79	

dw: dry weight

The high value (1463 ng g<sup>-1</sup> dw) could not be confirmed. Further analysis of site 48 using samples from the PCDD/PCDF campaign revealed total CP levels between 13 and 97 ng g<sup>-1</sup> dw. Furthermore, four samples were analyzed from the regular campaigns, which differed in sampling depth (0-20 cm instead of 0-10 cm) and sample preparation (e.g. drying temperature). Total CP concentrations were 19 ng g<sup>-1</sup> dw for the sample taken in 1997, 9 ng g<sup>-1</sup> dw for year 2002 and 69 and 79 ng g<sup>-1</sup> dw for the two analyzed samples from year 2007. The first high value could not be confirmed by any regular campaign.

### 3.2.3 CPs in Compost

Compost is an important recycling fertilizer having nutritional effects on soil. However, it can contain significant amounts of pollutants that enter compost via atmospheric deposition and by the input material.

Three Swiss compost samples were analyzed in collaboration with the Swiss Federal Institute of Aquatic Science and Technology (EAWAG, Dübendorf, Switzerland) and Agroscope Reckenholz-Tänikon Research Station (ART, Zürich, Switzerland). An efficient clean-up method is required due to the specific properties of compost. It is described in chapter 3.1.3.

The concentrations summarized in Table 3.5 were between 57–140 ng g<sup>-1</sup> dw for SCCPs, 29–245 ng g<sup>-1</sup> dw for MCCPs (both determined with ECNI-LRMS) and 182–614 ng g<sup>-1</sup> dw for total CPs (obtained with EI-MS/MS).

**Table 3.5** Overview of the SCCP, MCCP, total CP levels in three compost samples.

Sample No.	SCCP conc. [ng g <sup>-1</sup> dw]	CI [%]	MCCP conc. [ng g <sup>-1</sup> dw]	CI [%]	SCCP+MCCP [ng g <sup>-1</sup> dw]	totCP conc. [ng g <sup>-1</sup> dw]
1	117	62.5	29	58.5	146	182
10	140	63.3	245	59.2	384	614
16	57	61.0	138	57.9	194	268

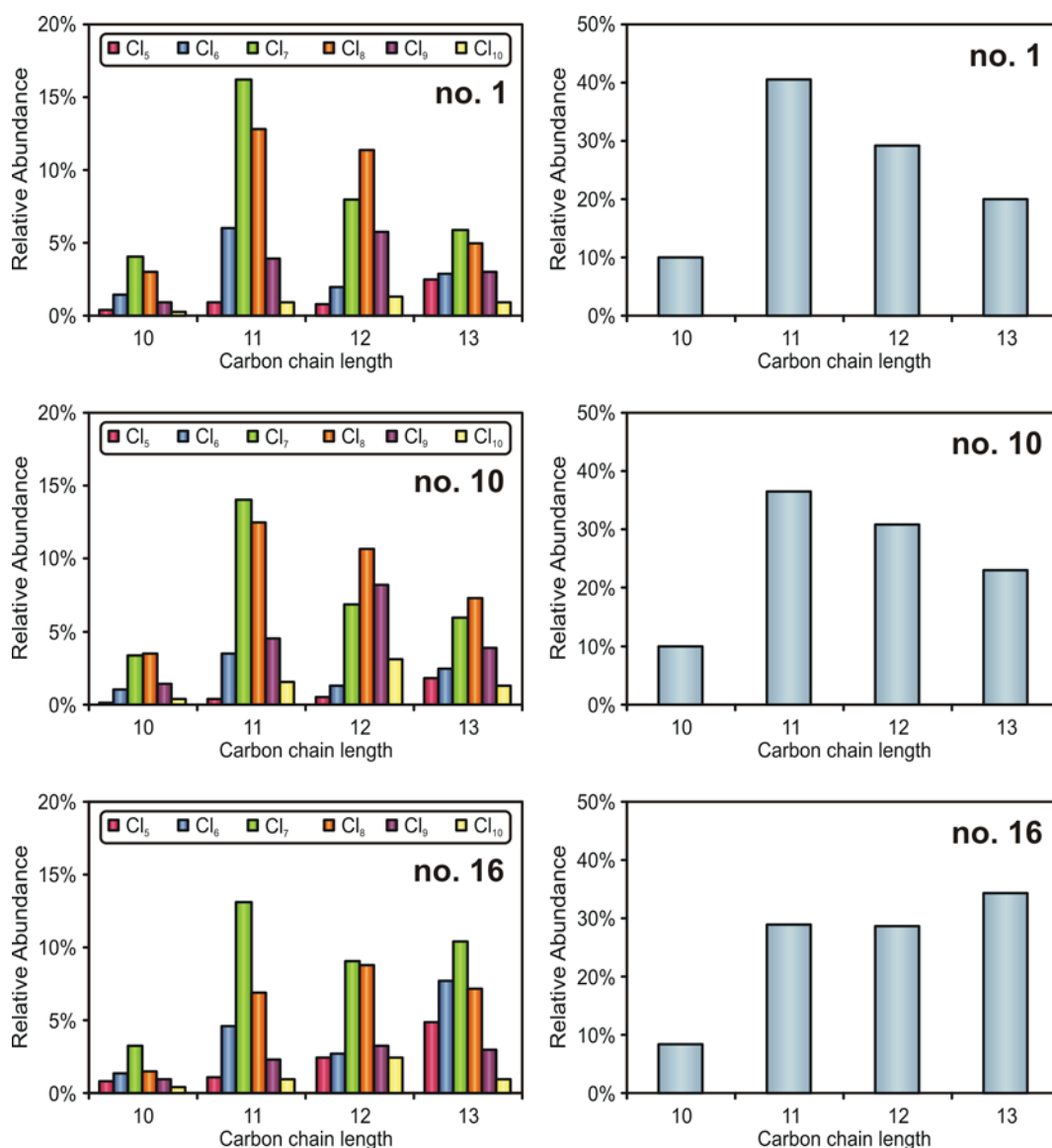
dw: dry weight



The results obtained by EI-MS/MS and ECNI-LRMS were generally in good agreement. The total CP concentration determined by EI-MS/MS was 20-37% higher than the respective sum of SCCPs and MCCPs.

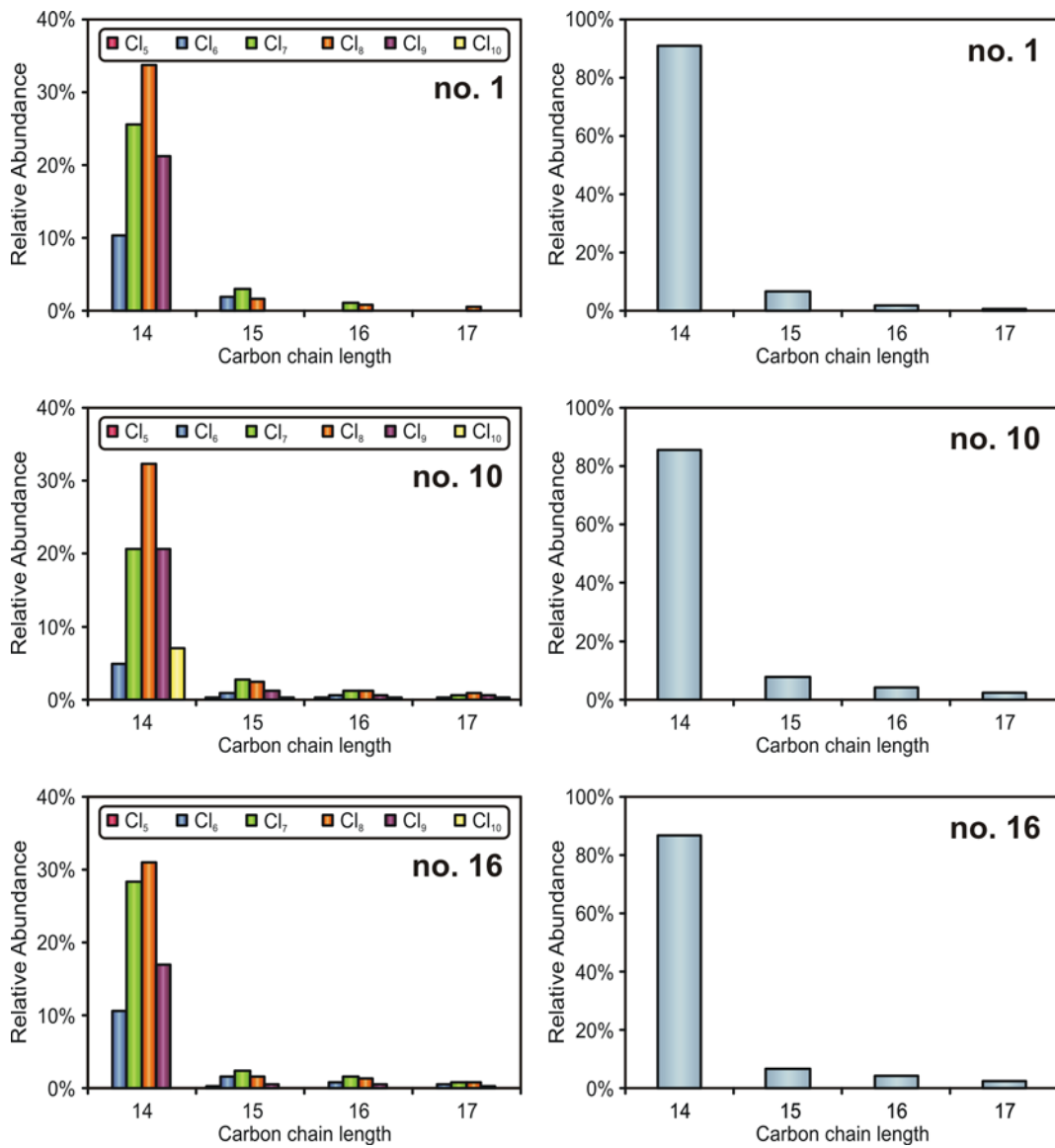
These concentrations were lower than the values in sewage sludge (Nicholls *et al.*, 2001; Stevens *et al.*, 2003), but generally higher than those of Swiss soils (see chapter 3.2.2) and alpine humus (see chapter 3.2.1). It is not surprising that CPs were found in compost, since they belong to high production chemicals and are incorporated into a various number of products for daily use that end up in organic waste.

CP levels were also highest in compost compared to other POPs present in these samples such as PCBs and PBDEs (Brändli *et al.*, 2007). Figure 3.12 shows the SCCP congener and homologue group patterns determined by ECNI-LRMS in three compost samples. CPs with eleven carbon atoms were most abundant in sample no. 1 and no. 10 which is typical for technical SCCP mixtures. CPs with thirteen carbon atoms were highest in sample no. 16. SCCPs with seven and eight chlorine atoms were dominant.



**Figure 3.12** SCCP congener and homologue group patterns in compost samples determined by GC-ECNI-LRMS.

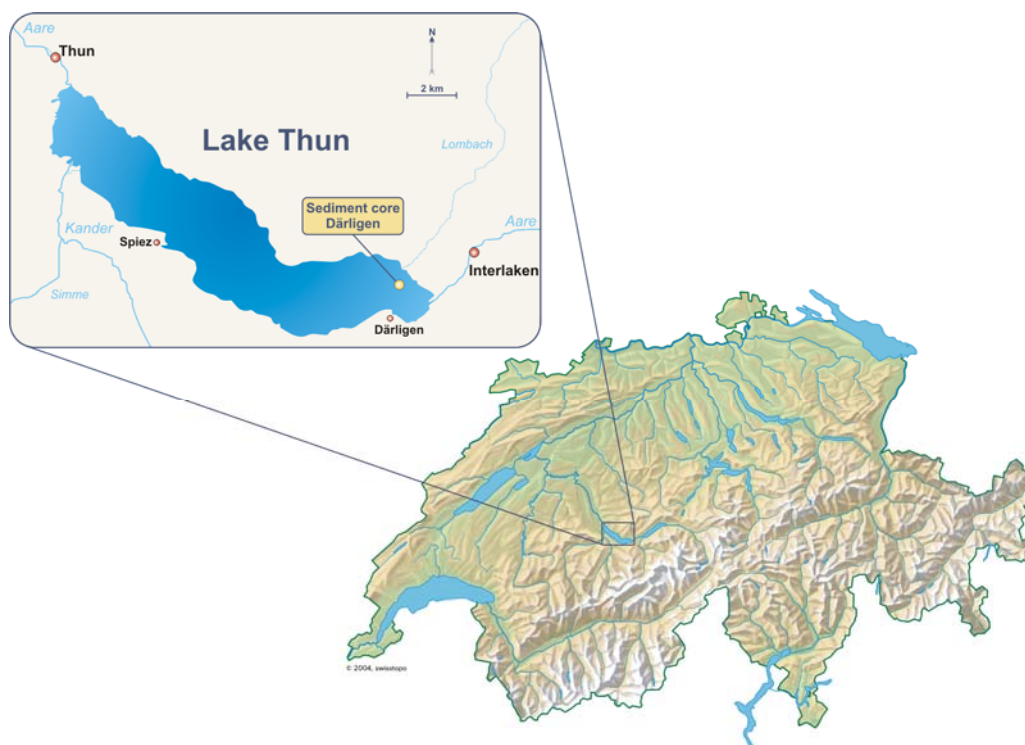
The MCCP congener and homologue group patterns determined by ECNI-LRMS are shown in Figure 3.13. Among MCCPs, C<sub>14</sub> chain length was predominant in all samples. The most abundant congeners were MCCPs with seven and eight chlorine atoms. Both the congener and homologue patterns are similar to technical MCCP mixtures.



**Figure 3.13** MCCP congener and homologue group patterns in compost samples determined by GC-ECNI-LRMS.

### 3.2.4 Chronological Evaluation of CPs in a Lake Sediment Core

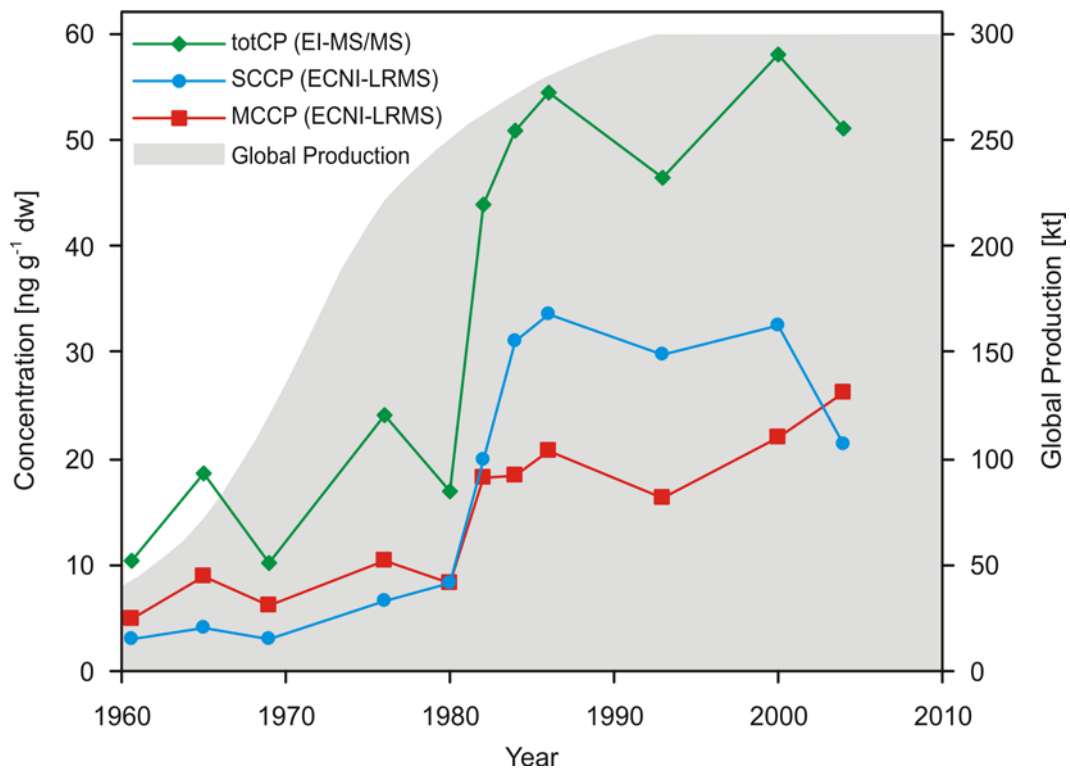
Studies of dated layers of sediment cores are an excellent way to investigate concentration trends over time. PAPER III gives an overview of the temporal trend of CP concentrations in a dated sediment core covering the past 120 years. This sediment core was taken from Lake Thun near the mouth of the river Aare and the village Därliigen (see Figure 3.14).



**Figure 3.14** Sampling location of the analyzed sediment core from Lake Thun (Switzerland).

Lake Thun is located in the alpine region of the Canton Bern in the centre of Switzerland and has a surface area of 47.69 km<sup>2</sup>, a mean depth of 136 m, and a volume of 6.42 km<sup>3</sup>. Lake Thun is situated in a rural, densely populated catchment area without known point sources such as e.g. metal and polymer industry.

PAPER III shows that total CP levels increased by 500% within two decades (1970s and 1980s) and leveled off thereafter (see Figure 1 in PAPER III and in Figure 3.15). Moreover, the concentration-versus-time profile is in good agreement with the available information on global production data.



**Figure 3.15** Historical time trends of total CP (green line), SCCP (blue line), and MCCP (red line) concentrations in a sediment core from Lake Thun. The global CP production (grey background) is also given. Analysis was performed by GC-EI-MS/MS and GC-ECNI-LRMS.

Based on the calculated flux profile of this core (see Figure 6B in PAPER III), the input of total CPs is still rising and has its maximum in the surface layer (2004,  $164 \mu\text{g m}^{-2} \text{y}^{-1}$ ). The evaluation of the ECNI-LRMS measurements revealed an increase of higher chlorinated SCCPs in recent years (see Figure 2A and 3 in PAPER III), which may indicate the ongoing use of CPs as an additive for plastics, paints and coatings. However, a shift of the relative inputs from SCCPs to MCCPs was observed after year 2000 in the surface layer (see Figure 3 and 4A in PAPER III and in Figure 3.15). It is not yet clear, if this change of the CP composition can be attributed to effectiveness of the regulations of the EU Water Framework Directive and the preceding discussions about a general ban of SCCPs, but it may open up an important topic for future researches. For example, the ban of PCBs has had a substantial effect on the input to the environment (Zennegg *et al.*, 2007; Bogdal *et al.*, 2008). Therefore, PCBs were analyzed in this dated sediment core from Lake Thun as well (see Figure 6A in PAPER III). Figure 6A illustrated also how fast the ban of use of PCB for open systems in Switzerland in 1972 influenced the environmental release. The temporal trends of PCB (sum of the six indicator congeners) and total CP levels showed an increase of CPs when PCB levels declined (see Figure 6A in PAPER III). This is in line with a partial replacement of PCBs by CPs. Furthermore, the peak level of CPs exceeded that of PCBs by a factor of three.

## 4 Conclusion and Outlook

In the last decades, the volume of CP production increased and, consequently, the input into the environment. Therefore, there is an urgent need for information on environmental CP concentrations. However, the number of publications concerning CPs rapidly decreased in the recent years, although numerous unclear aspects still require further research. This could be due to the demanding and tedious analytical methods. Although several methods have been published for the analysis of CPs, their application is generally not convenient. Therefore, it is still very important to improve currently available methods and to develop more simple, rugged and versatile techniques.

The developed analytical scheme consists of module-based extraction and clean-up methods, which allows the determination of CPs in different matrices. In this way, it was possible to determine CPs in spruce needles, soils (humus) and compost samples with a similar sample preparation for the first time. It could be shown that CPs were ubiquitously present in the environment and could even be transported to remote regions of the Alps as shown in this work.

The time-dependence of SCCP and MCCP input into the environment is very interesting. SCCPs are now partially banned or regulated by several environmental agencies. The dated sediment core from Lake Thun revealed already a shift of the relative levels from SCCPs to MCCPs. Obviously, the CP producing industry replaced SCCPs with MCCPs. This may be an important topic for future research.

A further aspect is the newest development of mixed-halogenated analogues of CPs, which is promoted by the CP industry. These products would pose even a bigger challenge for the analyst. Therefore, it should be addressed as quickly as possible.

Moreover, it would be interesting to analyze dust and indoor air samples from work and home places since CPs may be applied in carbonless toner for printers and as flame retardants for miscellaneous electronic equipments such as computers and television. Indoor air has been identified as an important source of chemical exposure, and house dust has been demonstrated to be an important exposure pathway for children. Furthermore, studies of brominated flame retardants showed high levels in dust. These analyses could also help to answer the question, if the increasing CP levels in the environment might also have toxicological consequences for humans.



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P A P E R I

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DEVELOPMENT OF A COMPREHENSIVE ANALYTICAL METHOD  
FOR THE DETERMINATION OF CHLORINATED PARAFFINS IN SPRUCE NEEDLES  
APPLIED IN PASSIVE AIR SAMPLING

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## Development of a comprehensive analytical method for the determination of chlorinated paraffins in spruce needles applied in passive air sampling

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*A developed method for chlorinated paraffins (CPs) provided evidence that spruce needles are a suitable passive sampling system for the monitoring of atmospheric CPs.*

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### ABSTRACT

Conifer needles are used for the monitoring of atmospheric persistent organic pollutants. The objective of the present study was to develop a method for the detection of airborne chlorinated paraffins (CPs) using spruce needles as a passive sampler. The method is based on liquid extraction of the cuticular wax layer followed by chromatographic fractionation and detection of CPs using two different GCMS techniques. Total CP concentrations (sum of short (SCCP), medium (MCCP) and long chain CPs (LCCP)) were determined by EI-MS/MS. SCCP and MCCP levels as well as congener group patterns (*n*-alkane chain length, chlorine content) could be evaluated using ECNI-LRMS. For the first time, data on environmental airborne CPs on spruce needles taken within the Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants (MONARPOP) are presented providing evidence that spruce needles are a suitable passive sampling system for the monitoring of atmospheric CPs.

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### 1. Introduction

Conifer needles are suitable as passive sampler for air pollutants. A number of publications described the accumulation of airborne organic compounds in the cuticular wax layer of conifer needles such as PCBs, PCNs, DDTs, HCHs, and dioxins (Buckley, 1982; Gaggi et al., 1985; Eriksson et al., 1989; Jensen et al., 1992; Kylin et al., 1994; Strachan et al., 1994; Levy et al., 2007; Wyrzykowska et al., 2007). Air pollutants in the vapor phase are trapped in the waxy surface, while particle-associated compounds are deposited on the needle surface (Kylin et al., 1994; Strachan et al., 1994). Particularly, conifer needles are well-suited as passive samplers exhibiting a high interception capacity for rain, fog and snow (Umlauf and McLachlan, 1994). Moreover, conifers do not lose their canopy in autumn and, therefore, sampling is possible at all seasons. The amount of accumulated air pollutants generally increases with needle age (Hellström et al., 2004; Romanic and Krauthacker, 2004). Furthermore, the high prevalence of spruce forests in temperate areas allows comparisons of geographical, seasonal, and temporal variations of levels of air pollutants (Eriksson et al., 1989;

Jensen et al., 1992; Levy et al., 2007; Romanic and Krauthacker, 2007; Wyrzykowska et al., 2007).

Chlorinated paraffins (CPs), also known as polychlorinated *n*-alkanes (PCAs), were introduced in the 1930s. CPs are produced by the reaction of specific *n*-alkane fractions from petroleum distillation with chlorine. They are differentiated into three main categories according to their carbon chain length: short chain CPs (SCCPs, C<sub>10–13</sub>), medium chain CPs (MCCPs, C<sub>14–17</sub>) and long chain CPs (LCCPs, C<sub>>17</sub>) (Muir et al., 2000). The chlorination degree of CPs can vary between 30 and 70% (Muir et al., 2000). CPs are in use for a wide range of industrial applications such as flame retardants and plasticizers in sealants, paints and coatings, and as additives in metal working fluids (Campbell and McConnell, 1980; Tomy et al., 1998).

CPs are persistent chemicals and their physical properties (log K<sub>OW</sub> 4.4–8, depending on the chlorination degree) imply a high potential of bioaccumulation as well as of global long-range atmospheric transport (Muir et al., 2000). Their presence was detected in the Canadian (Tomy et al., 1999, 2000) and European Arctic (Reth et al., 2006). Moreover, CP levels in the environment increased in the last decades. In a sediment core from Lake Thun, Switzerland, Iozza et al. observed a substantial rise of CP levels in the 1980s (Iozza et al., 2008).

The acute toxicity of CPs is low (World Health Organization, 1996). Nevertheless, SCCPs showed chronic toxicity in aquatic organisms and are carcinogenic in rats and mice (OSPAR Commission, 2001).

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Therefore, SCCPs were categorized in group 2B as 'possibly carcinogenic to humans' by the International Agency for Research on Cancer (IARC) (World Health Organization, 1996). Due to their higher tendency of bioaccumulation (World Health Organization, 1996) and higher toxicity of SCCPs than MCCPs and LCCPs they have also been included in the list of priority hazardous substances of the European Water Framework Directive (European Community, 2000). For the same reasons, SCCPs are now under discussion to be included in the Stockholm Convention on POPs (Persistent Organic Pollutants Review Committee (POPRC) 2004). Consequently, environmental CP levels should be monitored more comprehensively.

Technical CP mixtures contain thousands of different congeners (homologues and isomers) which cannot be resolved into single congeners by any chromatographic and mass spectrometric technique. Currently, three analytical methods for CPs are used based on gas chromatography coupled with mass spectrometry (GCMS). All methods fully exploit the specificity of mass spectrometry:

- Tandem mass spectrometry (EI-MS/MS) is based on fragment ions with low mass-to-charge ratios, which are common to all CPs. The response factors of different CP mixtures are independent from their chlorine content (Zencak et al., 2004, 2005).
- Electron capture negative ionization with low resolution mass spectrometry (ECNI-LRMS) records single ions of the  $[M-Cl]^-$  isotope clusters ions (Schmid and Müller, 1985; Castells et al., 2004; Zencak et al., 2005).
- Electron capture negative ionization with high resolution mass spectrometry (ECNI-HRMS) is a very selective method eliminating interferences from CP fragments with the same nominal  $m/z$  values or from other organochlorine compounds (Tomy et al., 1997) not removed by preceding clean-up procedures. Due to the high costs of HR instruments, this method is not available at many laboratories.

LRMS methods based on ECNI or on EI-MS/MS are well-suited for routine analysis (Castells et al., 2004; Zencak et al., 2005). However, a highly efficient clean-up is mandatory to avoid interferences from both matrix and other POPs (Parera et al., 2004; Reth and Oehme, 2004; Hüttig and Oehme, 2005).

Only a few more analytical methods are described in the literature enabling quantitative routine analysis of CPs (Pellizzato et al., 2007). Moreover, only few laboratories analyze CPs worldwide (UNECE ad hoc Expert Group on POPs, 2003), although they are ubiquitously present in the environment including remote areas. Therefore, limited information is available about environmental levels, metabolic pathways and toxicokinetics of CPs compared to other polychlorinated environmental pollutants such as polychlorinated biphenyls (PCBs), dioxins, and organochlorine pesticides (Muir et al., 2000; Pellizzato et al., 2007).

The aim of the present work was to develop an integral analytical method for the determination of CPs in conifer needles. This required the development of a sample clean-up procedure handling the waxy matrix. The properties of the wax differ from lipids present in fish or mammals. Moreover, separation and quantification had to be optimized to minimize interferences from the remaining sample matrix. Besides a detailed method description, first data about CP environmental levels in spruce needles from the Alps taken within the MONARPOP project are presented including recommendations concerning the appropriate handling of spruce needles as passive sampling material.

With support from the European Union the project MONARPOP (Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants) was set up in 2003 by Austria, Germany, Italy, Switzerland, and Slovenia to investigate input, pathways and fate of

atmospheric anthropogenic contaminants such as POPs in the Alps (Moche et al., 2005). The monitoring of anthropogenic contaminants including CPs and using spruce needles as passive sampling material is one of the objectives within this project.

## 2. Experimental

### 2.1. Chemicals and solvents

Cyclohexane, dichloromethane (DCM) and *n*-hexane (*n*Hex) for residue analysis were obtained from Biosolve (Vallenswaard, Netherlands). The internal standard  $^{13}C_{10}$ -*trans*-chlordane (100 ng  $\mu l^{-1}$ , solution in *n*-nonane, purity 99%) was purchased by Cambridge Isotope Laboratories (Andover, USA). Reference SCCP ( $C_{10-13}$ , chlorine contents of 51.5, 55.5 and 63.0%) and reference MCCP mixtures ( $C_{14-17}$ , chlorine contents of 52.0 and 57.0%) with concentrations of 100 ng  $\mu l^{-1}$  in cyclohexane as well as  $\epsilon$ -hexachlorocyclohexane ( $\epsilon$ -HCH, solution in cyclohexane, 10 ng  $\mu l^{-1}$ ) were supplied from Ehrenstorfer GmbH (Augsburg, Germany). Florisil® PR (60–100 mesh) and anhydrous sodium sulfate (Pestanal®) were obtained from Fluka (Buchs, Switzerland). Silica gel for column chromatography (230–400 mesh, 0.045–0.063 mm) and sulfuric acid (98%) were purchased from Merck KGaA (Darmstadt, Germany).

### 2.2. Spruce needle samples

Spruce needle samples from eight selected sampling sites distributed in the Alps were taken in five countries (Austria, Germany, Italy, Slovenia, and Switzerland) in autumn 2004 (see Table 1). All sampling sites were located in alpine remote forests of Norway spruce (>80% specific purity) being 30 or more years old and of at least 0.5 ha surface. 3–5 spruce needle branches were cut from the 7th whirl (from top) of two dominant adult trees in October 2004. Six months old twigs were collected, transported on dry ice and stored at  $-20^{\circ}C$  until further processing. After immersion into liquid nitrogen needles were separated from twigs, immediately transferred to pre-cleaned brown glass containers and stored at  $-20^{\circ}C$ . Ancillary information about the spruce needle samples will be published by Offenthaler et al. (2009).

### 2.3. Needle extraction

In a 250 ml Duran glass bottle (Schott®), 20–25 g of fresh needles were spiked with the internal standard (10 ng of  $^{13}C_{10}$ -*trans*-chlordane) and extracted by shaking at room temperature (ca.  $22^{\circ}C$ ) with 150 ml of dichloromethane/*n*-hexane 1 + 1 (DCM/*n*Hex, v/v) for 16 h. The extract was filtered through a glass funnel of 115 mm diameter filled with glass wool (Riedel-de Haën, Seelze, Germany) directly into a Turbo Vap vessel (Zymark, Hutchinson, USA) of 200 ml. A second portion of 30 ml DCM/*n*Hex was added to the needles and the procedure repeated. The combined extracts were concentrated to 1 ml using a Turbo Vap 500 (Zymark, Hutchinson, USA).

### 2.4. Extract clean-up

A 20 mm i.d. glass column was filled from bottom to top with 1 g of anhydrous sodium sulfate, 20 g of silica gel impregnated with concentrated sulfuric acid (44%) and 1 g of anhydrous sodium sulfate. It was rinsed with 20 ml of DCM/*n*Hex 1 + 1 (v/v). The sample extract was transferred to the column, and CPs were eluted with 70 ml of DCM/*n*Hex 1 + 1 (v/v). The eluate was evaporated to 0.5 ml with a Turbo Vap 500. After dilution with 10 ml of *n*Hex the extract was reduced to 0.5 ml and the latter procedure was repeated.

A further clean-up step was carried out on a chromatographic column containing 16 g of Florisil® deactivated with 1.5% water and conditioned with 20 ml of *n*Hex. After passing the extract to the column, the first fraction obtained with 75 ml of *n*Hex and 5 ml of DCM was discarded. CPs were collected in a second fraction of 60 ml of DCM, which was concentrated to 0.5 ml. 10 ml of cyclohexane were added, the volume was reduced to 100  $\mu l$  with a Turbo Vap 500 and this step was repeated. Then, 10 ng of  $\epsilon$ -HCH in 10  $\mu l$  of cyclohexane were added as recovery standard.

### 2.5. Instrumentation

Quantification was performed on a gas chromatograph CP-3800 coupled to a 1200L triple quadrupole mass spectrometer (Varian, Walnut Creek, USA). The gas chromatograph was equipped with a fused silica capillary column (15 m length, 0.25 mm i.d.) coated with 0.25  $\mu m$  of crosslinked 5% phenyl-methylpolysiloxane (DB5-MS, J&W Scientific, Folsom, USA). Helium (99.996%, Sauerstoffwerk Lenzburg, Lenzburg, Switzerland) at a constant flow of 2 ml  $min^{-1}$  was used as carrier gas. The temperature of the split/splitless injector was set to  $275^{\circ}C$ . Splitless injections (3.0 min) of 2.5  $\mu l$  were carried out with a Combi Pal autosampler (CTC Analytics, Zwingen, Switzerland). The following temperature program was used:  $100^{\circ}C$  (3 min), then with  $50^{\circ}C min^{-1}$  to  $300^{\circ}C$  (isothermal for 3 min). The temperatures of

**Table 1**  
CP concentrations in conifer needles from the Alps determined by GC-ECNI-LRMS (SCCPs and MCCPs) and by GC-EI-MS/MS (total CPs). Samples 8.1 and 8.2 are replicates. Sample 8.3 + SCCP 55.5 and sample 8.4 + MCCP 52.0 are samples spiked with 100 ng of reference SCCPs or MCCPs before analysis.

Sample number	Sampling location	Altitude [m]	Date	ECNI-LRMS				Calculated SCCP + MCCP [ng g <sup>-1</sup> fw]	EI-MS/MS Total CP conc. [ng g <sup>-1</sup> fw]	Recovery IST [%]	Recovery CPs [%]
				SCCP conc. [ng g <sup>-1</sup> fw]	Chlorine content [%]	MCCP conc. [ng g <sup>-1</sup> fw]	Chlorine content [%]				
Sample 1	Val Visdende (IT)	1325	05.10.2004	43	61.6	95	57.8	138	194	63	
Sample 2	Klosters (CH)	1410	27.10.2004	31	62.0	27	56.4	58	83	60	
Sample 3	Eschenlohe (DE)	1450	11.10.2004	9	63.4	10	56.4	19	21	56	
Sample 4	Pokljuka (SL)	1397	08.10.2004	7	63.6	20	56.4	27	24	57	
Sample 5	Wechsel (AT)	1510	07.10.2004	19	61.8	6	55.7	25	22	65	
Sample 6	Alpe Gotta (IT)	1451	18.10.2004	44	64.0	29	55.8	73	69	52	
Sample 7	Rauris (AT)	1470	28.09.2004	5	62.7	10	55.8	16	16	81	
Sample 8.1	Berchtesgarden (DE)	1420	07.10.2004	12	63.1	5	55.7	17	16	65	
Sample 8.2	Berchtesgarden (DE)	1420	07.10.2004	13	62.6	5	55.8	18	17	59	
Sample 8.3 + SCCP 55.5	Berchtesgarden (DE)	1420	07.10.2004	17	61.3	7	56.0	24	22	72	78
Sample 8.4 + MCCP 52.0	Berchtesgarden (DE)	1420	07.10.2004	13	62.7	11	56.5	24	23	70	89

fw: fresh weight; IST: internal standard; IT: Italy; CH: Switzerland; DE: Germany; SL: Slovenia; AT: Austria.

the transfer line and of the ion source were 280 °C and 200 °C, respectively. The detailed GC-EI-MS/MS parameters are published elsewhere and hence only briefly described (Zencak et al., 2004). Mass spectrometry measurements were carried out by both EI-MS/MS and ECNI-MS. EI mass spectra were recorded at 70 eV electron energy with a filament emission current of 150 µA and a scan cycle time of 0.25 s. Argon (99.5%, Sauerstoffwerk Lenzburg) at a pressure of 0.13 Pa was employed as collision gas. The mass spectrometer was regularly tuned to optimal performance using perfluorotributylamine fragment masses at  $m/z$  69, 219, and 502. The selection of the fragment masses as described by Zencak et al. (2004) was slightly modified for the determination of the total CP amount:  $m/z$  91 →  $m/z$  53 (collision energy: -10 eV),  $m/z$  102 →  $m/z$  67 (-10 eV) and  $m/z$  104 →  $m/z$  67 (-10 eV). The precursor ion at  $m/z$  383 [M - Cl]<sup>+</sup> and the product ion at  $m/z$  276 [M-4Cl]<sup>+</sup> were selected for the detection of the internal standard <sup>13</sup>C<sub>10</sub>-*trans*-chlordane (-28 eV).

GC-ECNI-LRMS parameters for the determination of SCCP and MCCP levels as well as homologue profiles and degrees of chlorination are described elsewhere (Reth et al., 2005a; Hüttig and Oehme, 2006). The temperature program was as follows: 100 °C (2 min), with 15 °C min<sup>-1</sup> to 280 °C (2.5 min), with 20 °C min<sup>-1</sup> to 300 °C (2.5 min). Methane (99.995%, Carbagas, Rümlang, Switzerland) was employed as reagent gas at an ion source pressure of 730 Pa. The ion source was tuned to optimum performance using perfluorotributylamine fragment masses at  $m/z$  283, 452 and 633. The most abundant signal within the isotope clusters of the [M-Cl]<sup>-</sup> fragment ion (CPs with 5–10 chlorine atoms and of ε-HCH recovery standard) and of the molecular ion of <sup>13</sup>C<sub>10</sub>-*trans*-chlordane were selected for the detection in the selected ion monitoring (SIM) mode (total dwell time 0.250 s per cycle).

### 2.6. Pre-treatment of glassware and chemicals

Cross contamination via glassware was minimized by the following measures. All glassware was washed in a glassware washer, then immersed into a detergent solution (5% RBS<sup>®</sup>35 concentrate, Fluka) for 12 h and rinsed with DCM and nHex. This was followed by heating to 450 °C overnight and rinsing with the same solvents prior to use. Chemicals used for sample clean-up such as Florisil<sup>®</sup>, anhydrous sodium sulfate, and silica gel were heated overnight at 220 °C. Glass wool was heated to 450 °C overnight.

## 3. Results and discussion

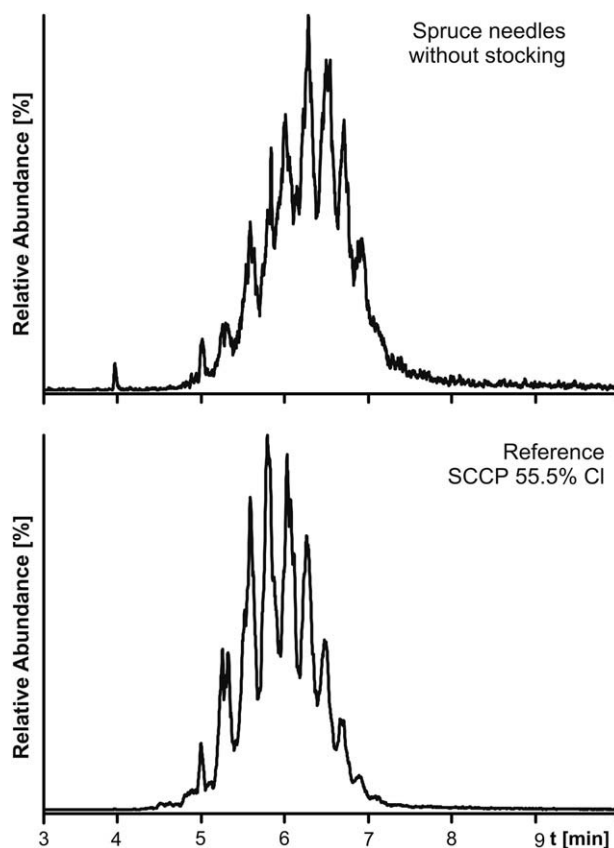
### 3.1. Evaluation of a suitable extraction and clean-up procedure

Extraction at room temperature of the fresh, intact needles with a mixture of DCM and nHex was chosen to solve the waxy layer and to exclude as far as possible undesirable interfering substances from the needle body such as chlorophyll and essential oils. Gel permeation chromatography is not able to separate CPs from such compounds. However, column chromatography with silica gel impregnated with sulfuric acid is suitable to remove interfering compounds from the needle matrix. It changes the dark green opaque raw extract of the needles to a colorless and clear solution. Finally, chromatography on Florisil allows separating CPs from other organochlorines such as chlordanes, PCBs and toxaphenes.

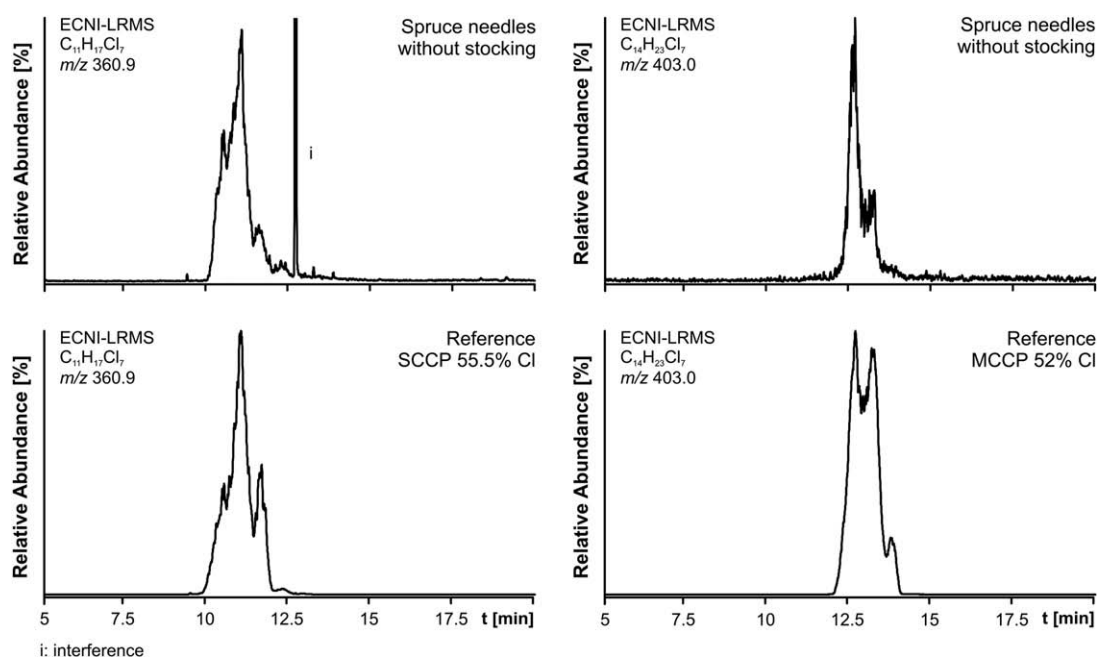
This is essential since other organochlorines with similar mass-to-charge ratios and retention times can interfere the detection of CPs by LRMS methods (Reth et al., 2005a).

### 3.2. Detection, identification and quantification

Detection, speciation and quantification of CPs were accomplished at two levels using two different GCMS procedures: (i) Total CPs (totCPs) were determined by a recently developed mass spectrometric technique based on EI-MS/MS (Zencak et al., 2004) which enables the simultaneous detection of SCCPs, MCCPs, and LCCPs;



**Fig. 1.** GC-EI-MS/MS chromatograms ( $m/z$  102 → 65) of a spruce needle sample from the Alps and an SCCP reference standard with 55.5% Cl.



**Fig. 2.** GC-ECNI-LRMS chromatograms of  $C_{11}H_{17}Cl_7$  ( $m/z$  360.9) and of  $C_{14}H_{23}Cl_7$  ( $m/z$  403.0) of an alpine spruce needle sample and an SCCP reference standard with 55.5% Cl, respectively (i: unknown interference).

(ii) More detailed data regarding the chlorine content as well as the congener and the homologue patterns of CPs were obtained by an ECNI-LRMS detection method (Reth et al., 2005a; Hüttig and Oehme, 2006). Reth and Oehme (2004) showed that ECNI measurements at low resolution can lead to systematic errors due to gas chromatographic and mass spectrometric overlap between CP congeners. Therefore, a proper identification of the CP congeners ( $C_{10-17}Cl_{5-10}$ ) of retention time, chromatographic signal shape and correct isotope ratio is essential. Furthermore, the quantification procedure described by Reth et al. (2005b) was applied to enable a reliable quantification even at differences between chlorine content of sample and reference standards. Three SCCP (51%, 55%, and 63% Cl) and two MCCP references (52% and 57% Cl) with different chlorine content were applied to compensate for such effects.

### 3.3. Quality control

Limits of detection (LOD) at a signal-to-noise ratio of 3:1 (detection of the most abundant congener groups) were between 0.1 and 0.5  $ng\ \mu l^{-1}$  for a reference SCCP mixture (55.5% chlorine content) and between 0.2 and 0.7  $ng\ \mu l^{-1}$  for a reference MCCP mixture (52% chlorine content) determined by ECNI-LRMS. The detection limits for EI-MS/MS were 0.09, 0.16 and 0.23  $ng\ \mu l^{-1}$  respectively for  $m/z$  102  $\rightarrow$   $m/z$  67,  $m/z$  91  $\rightarrow$   $m/z$  53 and  $m/z$  104  $\rightarrow$   $m/z$  67 applying a reference SCCP mixture (55.5% chlorine content).

Method blanks included extraction and clean-up. Blank concentrations were  $1.3 \pm 0.2\ ng\ g^{-1}$  fresh weight (fw) totCPs assuming a mean sample weight of 18.2 g ( $n = 5$ ).

In order to test the reproducibility of the analytical method each two aliquots (sample aliquot 8.1 and 8.2) of the same sample (sample 8) were processed separately. The deviation between these two samples was 10% for totCPs, 10% for the sum of SCCPs and 6% for the sum of MCCPs. The calculated chlorine contents of the two aliquots were 62.6% and 63.1% for SCCPs and 55.7% and 55.8% for MCCPs. Two further aliquots (sample aliquot 8.3 and 8.4) were processed separately after spiking with 100 ng of reference SCCPs

(55% chlorine content) and with 100 ng of reference MCCPs (52% chlorine content), respectively. Deviations from expected values obtained by ECNI-MS were 22% for SCCPs and 11% for MCCPs. Recoveries of the internal standard were between 52 and 81% (mean 64%) for all analyzed samples.

The efficiency of this clean-up and detection method is clearly demonstrated by the ECNI and EI-MS/MS chromatograms of an extract without stocking showing the typical CP profile essentially free of interferences (see Figs. 1 and 2) and by the reproducibility and recovery of the reference and internal standards.

### 3.4. CP levels in needle samples

CPs were determined in eight alpine spruce needle samples from the MONARPOP project with both EI-MS/MS and ECNI-LRMS. Results are summarized in Table 1. Total CP concentrations were between 16 and 194  $ng\ g^{-1}$  fw. SCCP levels quantified by ECNI-LRMS according to Reth et al. (2005b) varied between 5.4 and 44  $ng\ g^{-1}$  fw and MCCP concentrations between 5.2 and 95  $ng\ g^{-1}$  fw. The chlorine content of SCCPs and MCCPs obtained by ECNI was within 61.6–64.0% and 55.7–57.8%, respectively.

### 3.5. Homologue and congener patterns of CPs in spruce needles

Fig. 3 shows the homologue patterns and SCCP/MCCP ratios of the needle samples. The ratio between SCCPs and MCCPs covered a wide range (0.3–3.2). Moreover, the samples can be arranged in two groups according to their SCCPs homologue patterns.  $C_{11}$  is the major homologue group for samples no. 1, 2, 3, and 8 and  $C_{10}$  for samples no. 4, 5, 6, and 7.  $C_{14}$  is the dominant MCCPs chain length for all samples, which showed similar MCCP patterns. The corresponding congener group patterns are shown in Fig. 4. Congeners with 7–8 chlorines were most frequent for SCCPs and MCCPs. Samples 4–7 contained shorter chained SCCPs compared to current technical SCCP mixtures (Reth et al., 2006). Tomy et al. (1998) observed in air samples an enrichment of lower chlorinated lower chain length congeners, as well. They related their observation with

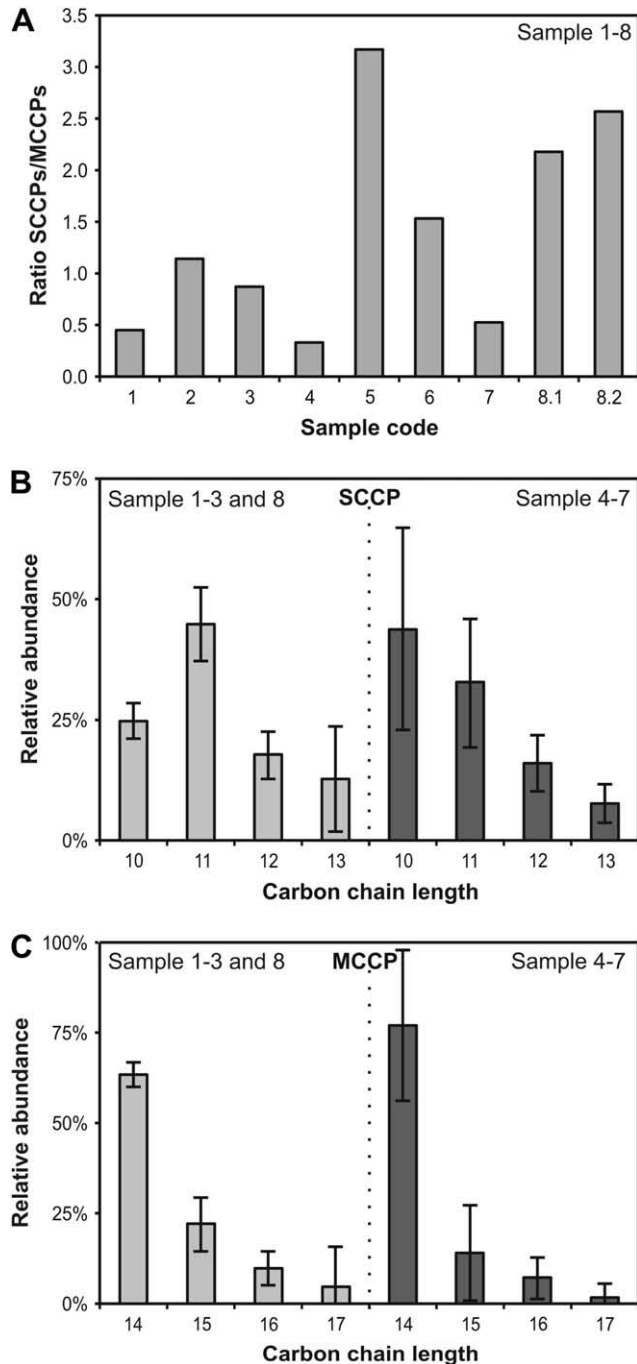
the findings of Drouillard et al. (1998), who remarked that shorter chained and lower chlorinated congeners are the most volatile components of technical CP mixtures due to their higher Henry's Law Constant.

### 3.6. Comparison with other airborne pollutants in conifer needles

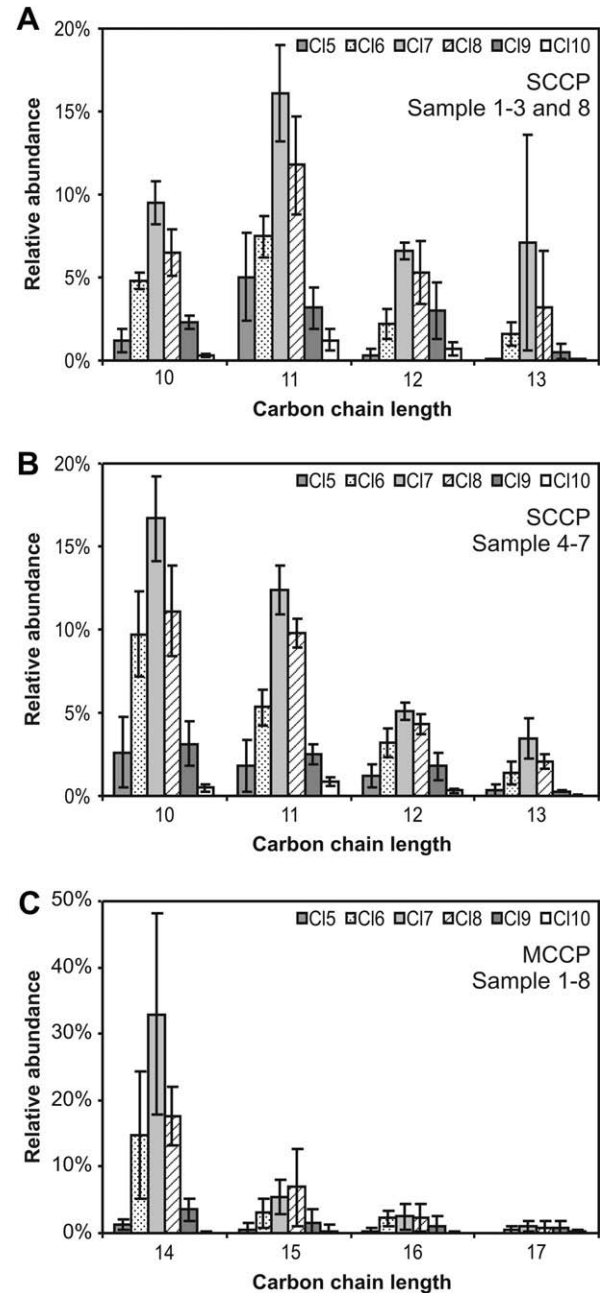
Since Kylin and Sjödin (2003) observed a higher accumulation rate during summer compared to the remaining seasons for

hexachlorocyclohexanes (HCHs) in conifer needles, spruce needles were collected in the early autumn period within the MONARPOP project to ensure a highest possible accumulation.

The CP levels in conifer needles determined in this first study were compared with levels published for other POPs in Table 2. As can be seen, totCP levels are highest. This is consistent with a study of POP levels in ambient air of the U.K. by Barber et al. (2005). Concentrations were highest for SCCPs and MCCPs compared to other POPs such as PCBs. However, due to the unknown accumulation characteristics of conifer needles for CPs, a direct comparison of levels in needles with concentrations in air is not possible at the moment.



**Fig. 3.** Ratios of SCCPs and MCCPs (A), SCCP homologue group pattern (B: mean of samples 1–3 and 8 and mean of samples 4–7), and MCCP homologue group pattern (C: mean of samples 1–3 and 8 and mean of samples 4–7) in analyzed needle samples from the Alps obtained by GC-ECNI-LRMS. Samples 8.1 and 8.2 are replicates. Standard deviations are assigned.



**Fig. 4.** Average SCCP congener group patterns of needle samples 1–3 and 8 (A) as well as of samples 4–7 (B) and average MCCP congener group pattern of the needle samples 1–8 determined by GC-ECNI-LRMS. Standard deviations are assigned.

**Table 2**

Comparison of CP concentrations with POP levels from the literature in conifer needles.

Substance	Kind of needles	Sampling location <sup>a</sup>	Exposure time	Concentration	Ref.
HCB	Spruce	Slovenia and Austria	6 months	0.5–0.9 ng g <sup>-1</sup> dw	(I)
	Pine	Croatia	12 months	0.24–1.38 ng g <sup>-1</sup> dw	(II)
	Pine	Croatia	24 months	0.14–2.81 ng g <sup>-1</sup> dw	(II)
	Pine	Germany, Denmark and Sweden	12 months	0.05–0.43 ng g <sup>-1</sup> fw	(III)
	Pine	Germany, Denmark and Sweden	24 months	0.2–1.03 ng g <sup>-1</sup> fw	(III)
	Pine	Germany, Denmark and Sweden	36 months	0.12–1.40 ng g <sup>-1</sup> fw	(III)
	Pine	Germany, Denmark and Sweden	48 months	0.29–2.40 ng g <sup>-1</sup> fw	(III)
PCB <sup>b</sup>	Spruce	Slovenia and Austria	6 months	0.2–2.0 ng g <sup>-1</sup> dw	(I)
	Pine	Germany	12 months	6.14–43.11 ng g <sup>-1</sup> dw	(IV)
	Pine	Sweden	12 months	2.24–5.71 ng g <sup>-1</sup> dw	(IV)
	Pine	Croatia	12 months	1.45–18.89 ng g <sup>-1</sup> dw	(II)
	Pine	Croatia	24 months	3.20–30.07 ng g <sup>-1</sup> dw	(II)
PCB <sup>c</sup>	Pine	Poland	12 months	2.7–50 ng g <sup>-1</sup> fw	(V)
PCDD/F	Spruce	Slovenia and Austria	6 months	2.8–16.9 pg g <sup>-1</sup> dw	(I)
PCN	Pine	Poland	12 months	170–920 pg g <sup>-1</sup> fw	(V)
PCP	Spruce	Slovenia and Austria	6 months	<0.4–0.5 ng g <sup>-1</sup> dw	(I)
	Pine	Germany, Denmark and Sweden	12 months	1.7–5.6 ng g <sup>-1</sup> fw	(III)
	Pine	Germany, Denmark and Sweden	24 months	1.4–5.6 ng g <sup>-1</sup> fw	(III)
	Pine	Germany, Denmark and Sweden	36 months	1.5–5.6 ng g <sup>-1</sup> fw	(III)
	Pine	Germany, Denmark and Sweden	48 months	2.2–7.3 ng g <sup>-1</sup> fw	(III)

dw: dry weight, fw: fresh weight, HCB: hexachlorobenzene, PCB: polychlorinated biphenyls, PCDD/F: polychlorinated dibenzodioxins and -furans, PCN: polychlorinated naphthalenes, PCP: pentachlorophenol (I) Weiss et al., 2003, (II) Romanic and Krauthacker, 2007, (III) Strachan et al., 1994, (IV) Kylin et al., 1994, (V) Wyrzykowska et al., 2007.

<sup>a</sup> From different locations within the stated countries.

<sup>b</sup> Sum of the six indicator PCBs no. 28, 52, 101, 138, 153 and 180.

<sup>c</sup> Total PCBs.

### 3.7. Comparison with other passive samplers

Compared to synthetic passive sampler materials such as polyurethane foams (PUFs) and semi-permeable membrane devices (SPMDs) conifer needles exhibit several benefits: (i) Conifer needles are an inexpensive sampling material requiring no installations or maintenance such as protection against climatic conditions (sunlight or wind) (Zhu et al., 2007); (ii) Conifers are widespread in temperate areas; (iii) The same tree can be used over a sampling period of several years. Moreover, retrospective studies on temporal trends of airborne pollutants are possible due to the long lifetime of the needles. However, collection of conifer needles in the forest and defined age determination requires much experience. Furthermore, the analysis of the needle matrix is highly demanding compared to synthetic passive samplers.

Levy et al. (2007) compared accumulation of PCDD/F in spruce needles and SPMDs. They concluded that needles can take up compounds from both particles and the gas phase and thus cover the whole range of PCDD/F homologues. In contrast, SPMDs preferentially accumulate compounds from the gas phase such as lower chlorinated PCDD/Fs. Due to the physical properties of CPs the World Health Organization estimates an atmospheric transportation preferentially adsorbed to particles (World Health Organization, 1996) which makes SPMDs less suitable for passive sampling.

## 4. Conclusions

An analytical method was developed which enables the use of spruce or other conifer needles as a passive sampler material for the determination of airborne CPs. For the first time, CP concentrations in spruce needles are presented. This study affords also comparisons with other studies in the future, since conifer forests, especial spruce forests, are widespread present. Spruce needles provide a suitable matrix system for evaluating CP concentrations. Thereby, spruce needles can be used to determine the regional exposures

from a single-year-class, as well as, the time trend between year-classes. The results from this preliminary study were used for a further extended investigation (Iozza et al., 2009), in which the here described analytical method was used to evaluate the concentrations of airborne CPs determined in spruce needles and in humus in a program (MONARPOP) aimed at mapping the distribution of CPs and other organic pollutants in the European Alps.

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P A P E R I I

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ALTITUDE PROFILES OF TOTAL CHLORINATED PARAFFINS IN HUMUS  
AND SPRUCE NEEDLES FROM THE ALPS (MONARPOP)

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## Altitude profiles of total chlorinated paraffins in humus and spruce needles from the Alps (MONARPOP)

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For the first time, CP levels of humus and spruce needle samples from the Alps (MONARPOP) were presented including the evaluation of altitude profiles.

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### ABSTRACT

Chlorinated paraffins (CPs) are toxic, bioaccumulative, persistent, and ubiquitously present in the environment. CPs were analyzed in humus and needle samples, which were taken within the Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants (MONARPOP) at sampling sites of 7 different altitude profiles in the Alps. Gas chromatography combined with electron ionization tandem mass spectrometry (EI-MS/MS) was used for the determination of total CPs (sum of short, medium and long chain CPs). CPs were found in all samples; the concentrations varied between 7 and 199 ng g<sup>-1</sup> dry weight (dw) and within 26 and 460 ng g<sup>-1</sup> dw in humus and needle samples, respectively. A clear vertical tendency within the individual altitude profiles could not be ascertained. Within all altitude profiles, elevated concentrations were observed in humus samples taken between 700 and 900 m and between 1300 and 1500 m. In the needle samples no similar correlation could be observed due to higher variation of the data.

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### 1. Introduction

Chlorinated paraffins (CPs) are highly complex mixtures of polychlorinated *n*-alkanes containing thousands of homologues and stereoisomers. They are produced by the reaction of chlorine with selected *n*-alkane fractions from petroleum distillation. According to their carbon chain length CPs are divided into three main categories: short chain CPs (SCCPs, C<sub>10–13</sub>), medium chain CPs (MCCPs, C<sub>14–17</sub>) and long chain CPs (LCCPs, C<sub>>17</sub>). Furthermore, the chlorination degree of CPs can vary between 30 and 70% depending on the field of application (Muir et al., 2000). Over 200 CP

formulations are in use for a wide range of industrial applications, such as flame retardants and plasticizers, and as additives in metal working fluids, in sealants, paints and coatings (Campbell and McConnell, 1980; Alcock et al., 1999). Since their introduction in the 1930s, the global production of CPs has increased steadily. Reported estimated world consumption was 38–50 kt yr<sup>-1</sup> in 1964 and 230 kt yr<sup>-1</sup> in 1977. From 1993 to the present time the global production seems to have leveled off at 300 kt yr<sup>-1</sup> (Muir et al., 2000). Nevertheless, these estimations are based on production data only from North America and Europe and nothing is known about the production amounts in industrial upcoming countries such as India and China.

The physical properties of CPs imply a high potential for bioaccumulation as well as for global long-range atmospheric transport (Muir et al., 2000). Among the different CP mixtures, SCCPs have been classified as toxic to aquatic organisms, and carcinogenic

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to rats and mice (OSPAR Commission, 2001). Moreover, the International Agency for Research on Cancer (IARC) categorized SCCP in group 2B as 'possibly carcinogenic to humans' (World Health Organization, 1996). Because of the greater bioaccumulation (World Health Organization, 1996) and toxicity of SCCPs than MCCPs and LCCPs, production and use have been banned in the European Community. It is assumed that the quantity of imported SCCPs is still huge, although the production of SCCPs has been voluntarily reduced from 13,000 tons in 1994 to 4000 tons in 1998 by the European industry (OSPAR Commission, 2001). In the meantime, SCCPs are included in the list of priority hazardous substances of the European Water Framework Directive (European Community, 2000) and the 'Persistent Organic Pollutants Review Committee' (POPRC, 2004) is evaluating to include SCCPs in the Stockholm Convention on Persistent Organic Pollutants (POPs).

The release into the environment can occur through different pathways such as emission during production, transport, and industrial use, as well as leaching from plastics, paints, and sealants (Tomy et al., 1998). Up to now, limited information is available about environmental CP concentrations compared to other persistent organochlorine compounds like PCBs, DDT, or toxaphenes (Muir et al., 2000). However, a permanent monitoring of CPs has become more and more important due to their ubiquitous presence in the environment in a variety of matrices (Tomy et al., 2000; Barber et al., 2005; Hüttig and Oehme, 2005; Reth et al., 2005, 2006; Thomas et al., 2006; Brändli et al., 2007). In addition, the levels in the environment increased with the production amount in the last decades (Iozza et al., 2008).

Mountains are a geographical and meteorological trap for atmospheric pollutants including semivolatile organic compounds because of barrier effects, high precipitation rates, and low ambient temperatures (cold condensation) (McLachlan and Horstmann, 1998; Daly and Wania, 2005). Particularly, the Alps are surrounded by regions of significant industrial production with a dense population. Several investigations on the behavior of POPs in the Alps were conducted in various matrices (e.g. in fish: (Grimalt et al., 2001; Vives et al., 2004; Schmid et al., 2007), in deposition: (Carrera et al., 2002; Nizzetto et al., 2006a); in snow: (Herbert et al., 2004; Finizio et al., 2006); in ice cores: (Villa et al., 2003; Maggi et al., 2006), in sediments: (Grimalt et al., 2001), in soils: (Schmid et al., 2005; Tremolada et al., 2008); in needles: (Weiss et al., 2003; Nizzetto et al., 2006b), and in air: (Jaward et al., 2005; Finizio et al., 2006)). In contrast to these local studies, MONARPOP (Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants) is intended to a more transboundary assessment of the POP input in the Alps. Five states within the region of the Alps (Austria, Germany, Italy, Switzerland, and Slovenia) have launched this project with support from the European Union (Moche et al., 2005). The major aim of this network is to monitor anthropogenic contaminants within this environment.

Conifer needles are covered by an epicuticular wax layer, which has been shown to trap and accumulate lipophilic compounds (Buckley, 1982; Gaggi et al., 1985). Air pollutants in the vapor phase can diffuse into the waxy surface, while particle-associated compounds are deposited on the needle surface (Kylín et al., 1994; Strachan et al., 1994). Since conifers do not shed their canopy in autumn, the amount of accumulated air pollutants generally increases over years with needle age (Hellström et al., 2004; Romanic and Krauthacker, 2004). Therefore, needles have been used for monitoring to investigate both the local and the regional distribution of lipophilic air pollutants (Eriksson et al., 1989; Jensen et al., 1992; Weiss et al., 2003; Hellström et al., 2004).

Humus is a natural sink for POPs. The high organic carbon content favors the accumulation of POPs. Beside the direct absorption from the atmosphere by trapping compounds from the

vapor phase and by deposition of particle-bound pollutants, the input of POPs to the humus increases by litter fall (McLachlan and Horstmann, 1998).

This study presents altitude profiles of CP levels in humus layers and spruce needles collected within the MONARPOP project. Instrumental analysis was performed using electron ionization tandem mass spectrometry (EI-MS/MS) to determine the total CP concentration (totCPs; sum of SCCPs, MCCPs, and LCCPs) (Zencak et al., 2004).

## 2. Experimental

### 2.1. Chemicals and solvents

Cyclohexane, dichloromethane (DCM), and *n*-hexane (nHex) for residue analysis were obtained from Biosolve (Vallenswaard, Netherlands). Reference SCCP (chlorine content of 55.5%) and MCCP mixtures (chlorine content of 52.0%) with concentrations of 100 ng  $\mu\text{l}^{-1}$  in cyclohexane as well as  $\epsilon$ -hexachlorocyclohexane ( $\epsilon$ -HCH, solution in cyclohexane, 10 ng  $\mu\text{l}^{-1}$ ) were purchased from Ehrenstorfer GmbH (Augsburg, Germany).  $^{13}\text{C}_{10}$ -*trans*-chlordane (100 ng  $\mu\text{l}^{-1}$ , solution in *n*-nonane, purity 99%) was supplied by Cambridge Isotope Laboratories (Andover, USA). Silica gel for column chromatography (230–400 mesh, 0.045–0.063 mm), sulfuric acid (98%), and copper powder (63  $\mu\text{m}$ ) were purchased from Merck KGaA (Darmstadt, Germany). Florisil<sup>®</sup> PR (60–100 mesh) and anhydrous sodium sulfate (Pestanal<sup>®</sup>) were obtained by Fluka (Buchs, Switzerland). Sodium sulfate, Florisil<sup>®</sup>, and silica gel (230–400 mesh, 0.045–0.063 mm; Merck KGaA, Darmstadt, Germany) were dried at 220 °C overnight.

### 2.2. Site selection

Humus and spruce needle samples from seven selected locations representing altitude profiles in the Alps were taken in five countries (Austria, Germany, Italy, Slovenia, and Switzerland) in autumn 2004 (see Fig. 1). Sampling sites were selected with a special attention to remoteness and specific homogeneity (>80% Norway spruce) of adult stands. Every altitude profile consisted of four to five subplots reaching from valley ground to upper tree limit between 700 and 1900 m above sea level (a.s.l.) to examine the vertical CP distribution. Beside these altitude profile locations, all sampling sites of the MONARPOP network are situated at an altitude of 1400  $\pm$  150 m. Therefore, this height can be regarded as a standard altitude. Ancillary information about the site selection will be published by Offenthaler et al. (2009).

### 2.3. Spruce needles samples

3–5 Branches were cut from the top 7th whirl of two dominant adult spruce trees in October 2004. Six months old twigs were collected, pooled, and transferred at  $-50$  °C (dry ice) to airtight glass jars to the analyzing lab and then stored at  $-20$  °C until further processing. Needles were separated from twigs after immersion into liquid nitrogen, immediately filled into airtight and light-protected glassware, and stored at  $-20$  °C.

### 2.4. Humus samples

The humus layer was taken within a 30  $\times$  30 cm area. Sampling depth corresponded to the variable thickness of the humus layer (mean depths: 0.8–23.8 cm). The material from seven to ten pits along a 5  $\times$  30 m rectangular grid was pooled for one sample. This yielded up to 60 l of humus per sampling plot. Humus samples were lyophilized, ground to particle diameter <0.5 mm and filled into airtight and light-protected glass containers.

### 2.5. Extraction and clean-up

Details of the applied extraction and clean-up procedures are given elsewhere (Hüttig and Oehme, 2005; Iozza et al., 2009) and, hence, are only briefly described. For all analysis 10 ng of  $^{13}\text{C}_{10}$ -*trans*-chlordane in 10  $\mu\text{l}$  of cyclohexane were used as internal standard (ISTD).

#### 2.5.1. Humus

20 g of dried and homogenized samples were spiked with ISTD and then Soxhlet extracted with 200 ml of dichloromethane and *n*-hexane (DCM/nHex, 1 + 1, v/v) for 8 h. Activated copper powder was added to eliminate sulfur.

#### 2.5.2. Spruce needles

20 g of fresh spruce needle samples were spiked with ISTD and cold extracted under shaking with 150 ml of dichloromethane and *n*-hexane (DCM/nHex, 1 + 1, v/v) for 16 h. After decanting, the needles were washed twice with additional 30 ml of

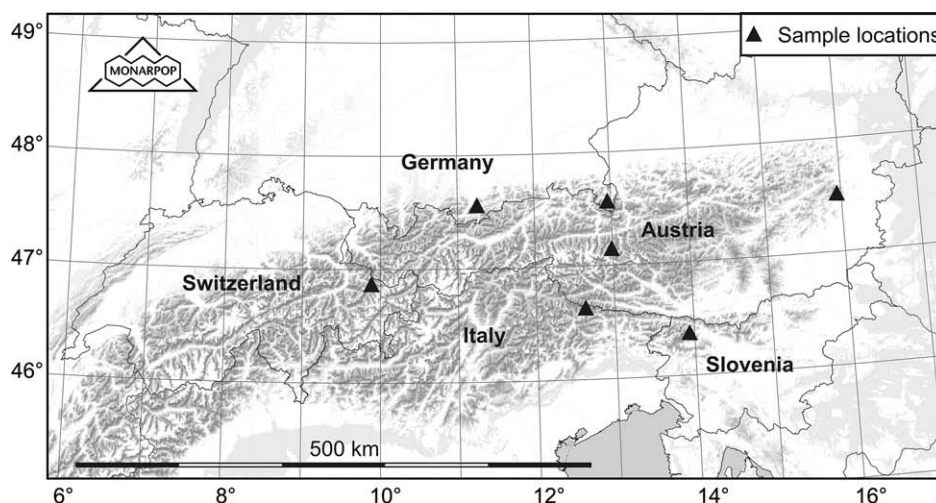


Fig. 1. Map of the seven sampling sites in the European Alps.

DCM/nHex (1 + 1, v/v). Subsequently, combined extracts were concentrated to 1 ml with a Turbo Vap 500 (Zymark, Hutchinson, USA).

The following clean-up method was applied to both sample extracts, humus and spruce needles. After solvent evaporation, the extract was further treated by column chromatography on 20 g of silica gel impregnated with concentrated sulfuric acid (44%). CPs were eluted with 70 ml of DCM/nHex (1 + 1, v/v). Further fractionation was carried out on 16 g of Florisil® (1.5% water content) eluted with 75 ml of nHex and 5 ml of DCM (prefraction) and 60 ml of DCM (main 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  $\epsilon$ -HCH in 10 µl of cyclohexane were added as recovery standard.

All spruce needle and humus CP concentrations refer to dry mass, which was determined by oven-drying at 105 °C.

## 2.6. Instrumentation

Parameters of the GC-EI-MS/MS analysis are published in detail elsewhere (Zencak et al., 2004) and, hence, are only briefly described. 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 length  $\times$  0.25 mm i.d.) coated with 0.25 µm of crosslinked methyl-phenylpolysiloxane (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<sup>-1</sup>. The injector temperature was set to 275 °C. Splitless injections 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<sup>-1</sup> to 300 °C, then isothermal for 4 min. The transfer line temperature was set to 280 °C and the ion source temperature to 200 °C. The EI mass spectra were recorded at 70 eV electron energy with a filament emission current of 150 µA and a scan time of 0.25 s per cycle. Argon (99.5%, Sauerstoffwerk Lenzburg) was employed as collision gas at a pressure of 0.13 Pa. The mass spectrometer was tuned to optimal performance using perfluorotributylamine masses at  $m/z$  69, 219, 502. The following fragmentations and collision energies were used for the determination of the total CP amount:  $m/z$  91  $\rightarrow$   $m/z$  53 (collision energy: -10 eV),  $m/z$  102  $\rightarrow$   $m/z$  67 (-10 eV) and  $m/z$  104  $\rightarrow$   $m/z$  67 (-10 eV). The precursor ion  $m/z$  383 and the product ion  $m/z$  276 were selected for the detection of the internal standard <sup>13</sup>C<sub>10</sub>-trans-chlordane (-28 eV).

## 2.7. Quality assurance

Background and cross contaminations were kept at minimum by a special treatment of the glassware used. Further details were published elsewhere (Iozza et al., 2008).

Method blanks were analyzed with the above described extraction and clean-up procedure. The method detection limit (MDL) was determined as the sum of the mean concentration and three times the standard deviation of six (humus) and five (spruce needles) blank measurements. Hereby, blank concentrations were calculated on an assumed mean sample weight of 20.3 g of lyophilized humus and 19.7 g of fresh needles. MDLs were 2.7 and 4.1 ng g<sup>-1</sup> dry weight (dw) for humus and spruce needles, respectively. Recoveries of the internal standard ranged between 58 and 110% (mean 75%) for humus samples and between 52 and 107%

(mean 67%) for spruce needle samples. More details are available elsewhere (Iozza et al., 2009).

## 3. Results and discussion

### 3.1. Analytical approach

Spruce needle and humus samples were analyzed to obtain an overview of the load of CPs in the Alps. Humus samples were processed in the same way as sediment samples as described elsewhere (Hüttig and Oehme, 2005; Iozza et al., 2008) whereas a new method was developed for spruce needle (Iozza et al., 2009). The CP determination was carried out with the recently developed EI-MS/MS method described by Zencak et al. (2004). This technique allows the determination of total CP concentration (totCPs; sum of SCCPs, MCCPs, and LCCPs) within one fast measurement. The analysis with EI-MS/MS revealed several benefits compared to ECNI-MS methods such as the independence of the response factor of the reference standard from chlorine content and a short analysis run time (10 min). The evaluation of the data is not demanding and, consequently, the data processing time is short. These benefits contribute to an overall cost-efficient routine analysis of total CP levels including the recently regulated SCCPs and the now more frequently applied MCCPs.

### 3.2. TotCP levels in spruce needles and in humus

CPs were detected in all spruce needle and humus samples. The totCP levels summarized in Table 1 ranged between 7 and 199 ng g<sup>-1</sup> dw in humus and between 26 and 450 ng g<sup>-1</sup> dw in spruce needles. Overall, mean needle concentrations (mean 66 ng g<sup>-1</sup> dw) were by a factor of 1.5 higher compared to humus (mean 40 ng g<sup>-1</sup> dw) at a standard altitude (1400  $\pm$  150 m; without Val Viscende). The levels in humus and in spruce needles were approx 10 and 40 times higher compared to total PCB concentrations (sum of PCB 28, 52, 101, 138, 153 and 180; mean 4.5 µg kg<sup>-1</sup> dw humus and 1.2 µg kg<sup>-1</sup> dw ½-year old spruce needles) in this region (Weiss et al., 2003).

A frequency histogram of totCP levels in humus and spruce needles is shown in Fig. 2. Most of the humus samples ( $n = 25$ ) exhibited a concentration between 10 and 50 ng g<sup>-1</sup> dw (50th percentile: 28 ng g<sup>-1</sup> dw). A similar frequency was also observed for dried needle samples (20–100 ng g<sup>-1</sup> dw,  $n = 22$ , 50th percentile: 56 ng g<sup>-1</sup> dw), which is considered as a general

**Table 1**

TotCP concentrations in alpine humus layers ( $n = 31$ ) and in spruce needles ( $n = 27$ ) obtained by GC-EI-MS/MS. Results in bold are from samples taken at a “standard” altitude ( $1400 \pm 150$  m) typical for all MONARPOP sampling sites.

Location	Country	Altitude [m]	TotCP concentration [ $\text{ng g}^{-1}$ dw]	
			Humus	Needles
Rauris	Austria	1134	14	
		1381	61	26
		<b>1470</b>	<b>48</b>	<b>35</b>
		1614	49	70
		1779	12	45
Wechsel	Austria	732	49	33
		898	32	31
		1117	45	53
		1282	28	52
		<b>1510</b>	<b>33</b>	<b>52</b>
Klosters	Switzerland	1300	61	
		<b>1410</b>	<b>21</b>	<b>169</b>
		1520	26	49
		1600	16	60
		1700	14	98
Eschenlohe	Germany	830	199	86
		1030	15	70
		1230	13	56
		<b>1450</b>	<b>35</b>	<b>44</b>
		1650	25	47
Berchtesgaden	Germany	805	31	113
		1005	15	125
		1210	32	96
		<b>1420</b>	<b>82</b>	<b>38</b>
Val Visdende	Italy	1123	15	
		<b>1325</b>		<b>450</b>
		<b>1553</b>	<b>59</b>	
		1656	108	
Pokljuka	Slovenia	1200	7	41
		<b>1397</b>	<b>22</b>	<b>59</b>
		1551	23	80
		1671	14	193
Minimum			7	26
Maximum			199	450
<b>Mean<sup>a</sup></b>			<b>40</b>	<b>66</b>
<b>Standard deviation<sup>a</sup></b>			<b>21</b>	<b>47</b>
Method detection limit (MDL)			2.5 ( $n = 6$ )	1.8 ( $n = 5$ )

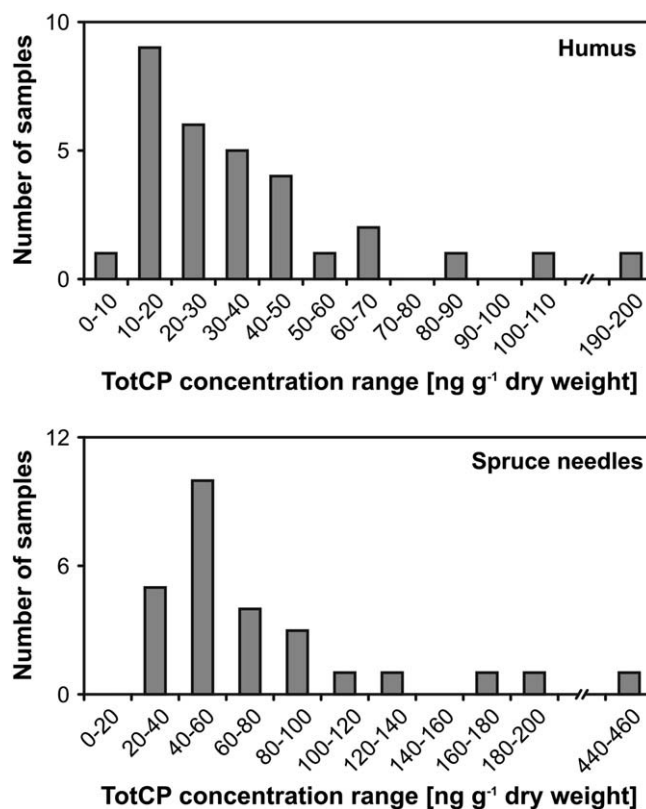
dw: dry weight; **bold**: standard altitude sites ( $1400 \pm 150$  m).

<sup>a</sup> Mean and standard deviation is calculated with the results from the standard altitude sites without the site from Val Visdende since the humus and needle samples were not from the same altitude.

background. As shown for both matrices in Fig. 2, some values distinctly protrude above the determined background levels. The highest levels were  $199 \text{ ng g}^{-1}$  dw (humus) and  $450 \text{ ng g}^{-1}$  dw (spruce needles) (see Table 1).

### 3.3. Altitude profiles of totCP levels in humus

Altitude profiles of totCPs in humus are shown in Fig. 3. No general trend could be observed for the different locations. The gradients from Val Visdende (Italy) and Berchtesgaden (Germany) showed a concentration increase with altitude. Levels at Eschenlohe (Germany) and Klosters (Switzerland) were generally higher at the lowest altitude, which might be due to the vicinity of densely populated valleys. Moreover, the highest concentration in humus was found at Eschenlohe ( $199 \text{ ng g}^{-1}$  dw at  $830 \text{ m a.s.l.}$ ). No change by altitude was observed for the sampling sites Wechsel (Austria) and Pokljuka (Slovenia). A maximum was found between the lowest and the highest altitude in Rauris (Austria).



**Fig. 2.** Frequency histogram of total CP levels in spruce needles and in humus layers from the Alps obtained by GC-EI-MS/MS.

### 3.4. Altitude profiles of totCP levels in spruce needles

Also here, the altitude profiles of totCP levels did not show any coherent trend for all sites (Fig. 3). CP levels increased with altitude at some places (Pokljuka, Slovenia and Rauris, Austria). The altitudinal gradient from Wechsel (Austria) shows similar CP levels ( $33$  and  $31 \text{ ng g}^{-1}$  dw) at the two lowest altitude stations and a leap of  $60\%$  for the three highest stations ( $53$ ,  $52$ , and  $52 \text{ ng g}^{-1}$  dw). In Germany, a decrease with height was found for both sampling sites (Berchtesgaden:  $113$ – $38 \text{ ng g}^{-1}$  dw; Eschenlohe:  $86$ – $47 \text{ ng g}^{-1}$  dw). In Klosters (Switzerland), the highest CP level was observed at the lowest altitude. After a steep decrease, the CP concentrations increased with the altitude. The highest CP concentration in spruce needles of all locations was found in Val Visdende ( $450 \text{ ng g}^{-1}$  dw at  $1325 \text{ m a.s.l.}$ ). No straight forward explication was found.

### 3.5. Comparison between humus and spruce needle data

A correlation between humus and spruce needle altitude profiles is hardly possible since these two matrices act differently in the environment. Spruce needles have a large surface area covered with a waxy layer trapping pollutants from the atmosphere. The humus layer consists of much organic matter and accumulates organochlorine pollutants both from direct atmospheric deposition and from litter fall such as needles (Weiss, 2002). Humus accumulates organochlorine pollutants over a long period (3–5 years) whereas spruce needles taken in the sampling for this study represents an accumulation time of a half year.

Three altitude profiles (Rauris, Wechsel, both Austria, and Eschenlohe, Germany) revealed a comparable mean concentration in spruce needles and humus. At Berchtesgaden (Germany), Pokljuka (Slovenia) and Klosters (Switzerland) levels were higher in



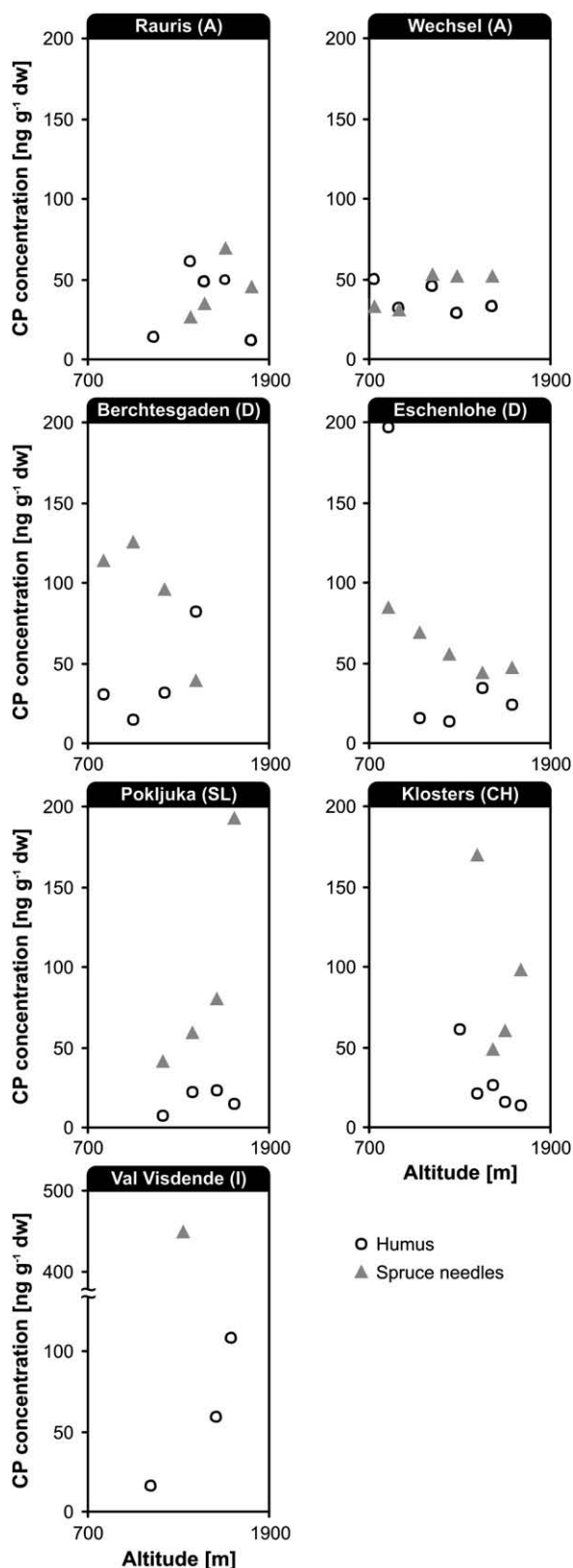


Fig. 3. Altitude profiles of CPs in humus and spruce needles from the Alps.

spruce needles than in humus (see Fig. 4). The opposite was not observed.

The trends of CP accumulation in humus and in spruce needles for each location in Eschenlohe, in Rauris and in Wechsel show

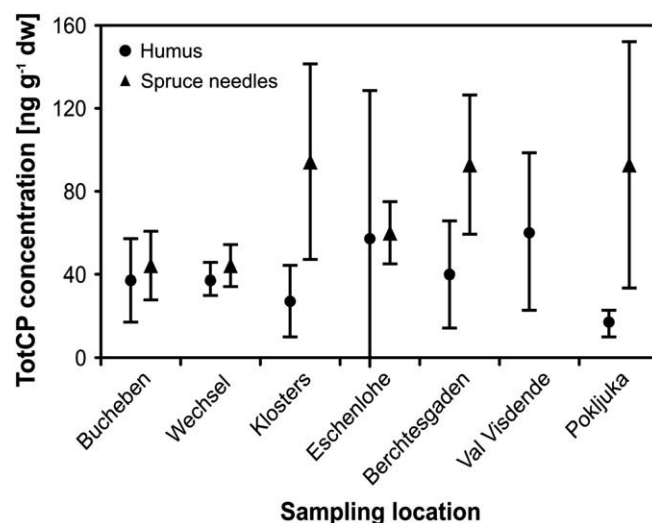


Fig. 4. Average CP concentrations in humus and spruce needles from sites selected for altitude profiles. Standard deviations are assigned.

a correlation (Fig. 3). A crossing trend is observable in Berchtesgaden (Germany). The altitudinal gradient analyzed in spruce needles show a decreasing trend whereas the CP concentration measured in humus increased. Each altitude profiles from Pokljuka (Slovenia) and Klosters (Switzerland) show different trends.

### 3.6. Influence of meteorological parameters

Several parameters can lead to an increased input of CPs into the Alps such as a higher precipitation rate, more fog, or more inversion layer events. Ribes et al. (2002) showed the influence of the latter for mountain soils from Teide (Tenerife island, Spain). Concentrations were highest in the inversion layer section for industrial related compounds such as pentachlorobenzene and polychlorinated biphenyls (PCBs) as well as for agriculture related compounds such as DDTs, hexachlorobenzene HCB and hexachlorocyclohexanes (HCHs) except  $\gamma$ -HCH. Tremolada et al. (2008) observed a correlation between precipitation rate and levels of persistent organic pollutants.

Fig. 5 correlates CP levels with altitude. Generally, CP concentrations were highest at low altitudes (700–900 m a.s.l.). A second maximum was observed between 1300 and 1500 m a.s.l. for the range 900–1900 m. This could be due to higher occurrence of fog, more precipitation or inversion layers around 1400 m. Details of the site meteorology are discussed by Kirchner et al. (2009). However, levels in needle samples were scattered possibly due to the rather short accumulation period (6 months) compared to humus built-up (3–5 years). Future research should include a possible relationship between meteorological parameters and CP accumulation.

### 3.7. Comparison of CP levels with other matrices

Total CP levels in humus were also compared with sediment concentrations determined by EI-MS/MS due to lack of soil data. Hüttig and Oehme (2005) reported between 5 and 499  $\text{ng g}^{-1}$  dw of totCPs in sediments from the North and Baltic Sea samples from 2001 to 2003 which is much higher than the concentrations found in this study. The analysis of a sediment core in Lake Thun, Switzerland, revealed a totCP concentration of 51  $\text{ng g}^{-1}$  dw at the surface slice in the year 2004 (Iozza et al., 2008), which is consistent with the background concentration reported here.

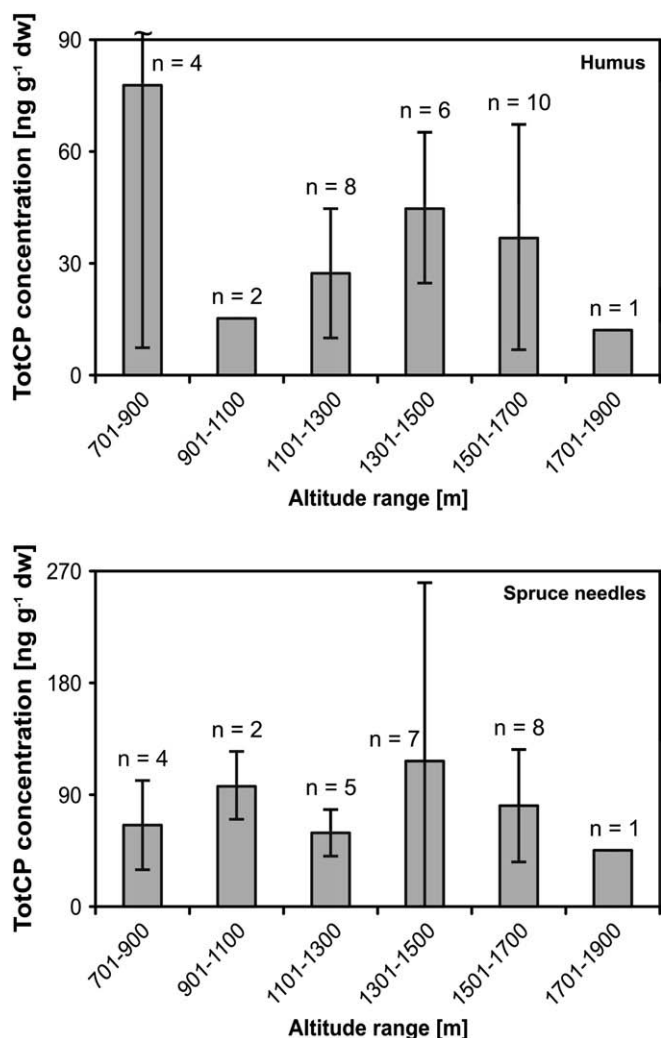


Fig. 5. Altitude related histogram of total CP levels in humus layers (top) and spruce needles (bottom) from the Alps. Error bars indicate standard deviations.

### 3.8. Comparison of CP levels with other airborne persistent pollutants

Table 2 compares totCP concentrations with those of other pollutants determined in humus at the height profiles Klosters, Berchtesgaden, and Wechsel during the project MONARPOP. TotCP

**Table 2**  
Levels of various pollutants in humus (14 samples) from Norway spruce stands at the height profiles Klosters, Berchtesgaden and Wechsel.

Compounds	Median [ng kg <sup>-1</sup> dw]	90th percentile [ng kg <sup>-1</sup> dw]	Maximum [ng kg <sup>-1</sup> dw]
TotCPs	31145	57417	81981
Sum 6 PCBs	5155	8081	9280
Sum 8 PFTs	4985	7523	8280
Sum HCH isomers	3918	7032	8638
HCB	1944	2556	2900
Sum 6 BDEs	475	760	1048
BDE 209	1459	6776	28505
BDE 183	139	363	916

dw: dry weight; sum 6 PCBs: sum of six PCB congeners 28, 52, 101, 138, 153, 180; sum 8 PFTs: sum of eight perfluorotensides (PF-hexa-, hepta-, octa-, nona-, deca-, undeca-, dodecaonic acid, and PF-octanilsulfate); HCHs: sum of hexachlorocyclohexane isomers; HCB: hexachlorobenzene; sum 6 BDEs: sum of 6 brominated diphenylethers 28, 47, 99, 100, 153, 154, BDE 209: decabrominated diphenylether; BDE 183: heptabrominated diphenylether.

levels were generally higher compared to polychlorinated biphenyls (PCBs) and polybrominated diphenylethers, as well as hexachlorocyclohexanes.

Schmid et al. (2005) determined PCBs in Swiss soils. They found PCB levels (sum of 7 PCBs no. 28, 52, 101, 118, 138, 153, and 180) between 1.7 and 3.2 ng g<sup>-1</sup> dw in the Jura mountains (n = 3; 622–1215 m a.s.l.) and between 0.86 and 8.4 ng g<sup>-1</sup> dw in the Alps (n = 7; 455–2120 m a.s.l.). HCB levels between <0.02 and 0.93 ng g<sup>-1</sup> dw and total PCB levels between 0.61 and 8.9 ng g<sup>-1</sup> dw was observed in the Italian Alps (Tremolada et al., 2008). Again, totCP levels were higher than the PCB and HCB concentrations reported above.

There are only a few studies of POP levels in conifer needles from the Alps. PCB (sum of the six indicator PCBs no. 28, 52, 101, 138, 153, and 180) and HCB levels of six months old spruce needles were between 0.2 and 2.0 ng g<sup>-1</sup> dw and between 0.5 and 0.9 ng g<sup>-1</sup> dw, respectively in the Slovenian and Austrian Alps in 2000 (Weiss et al., 2003). Six month old spruce needle samples from the Italian Alps at two different altitudes were investigated by Nizzetto et al. (2006b). HCB levels were 0.44 ng g<sup>-1</sup> dw at 1400 m as well as 0.48 ng g<sup>-1</sup> dw at 1800 m and PCB levels were 1.51 ng g<sup>-1</sup> dw at 1400 m as well as 1.59 ng g<sup>-1</sup> dw at 1800 m. Also here, totCP levels were higher.

## 4. Conclusion

Analyses of humus and spruce needles revealed that CPs are widely distributed in the Alps. CPs were found in higher located and remote sampling stations consolidating the ability of CPs for long-range transport. Generally, totCP levels in humus and needles are higher than for other POPs. This observation is consistent with a study of POP concentrations in the UK atmosphere by Barber et al. (2005), where also CP levels were highest.

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P A P E R   I I I

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HISTORICAL PROFILES OF CHLORINATED PARAFFINS AND  
POLYCHLORINATED BIPHENYLS IN A DATED SEDIMENT CORE  
FROM LAKE THUN (SWITZERLAND)

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# Historical Profiles of Chlorinated Paraffins and Polychlorinated Biphenyls in a Dated Sediment Core from Lake Thun (Switzerland)

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A dated sediment core from Lake Thun covering the last 120 years was analyzed to get an overview of the historical trend of the chlorinated paraffin (CP) and polychlorinated biphenyl (PCB) deposition, because CPs and PCBs have/had similar applications as plasticizers and flame retardants. Total CP concentrations (sum of short chain (SCCP), medium chain (MCCP), and long chain CPs (LCCP)) showed a steep increase in the 1980s and a more-or-less stable level of 50 ng g<sup>-1</sup> dry weight (dw) since then. The concentration-time profile is in good agreement with the available information on global production data. The quantification of higher chlorinated SCCPs using electron capture negative ionization low resolution mass spectrometry (ECNI-LRMS) revealed an increase in recent years. In addition, the degree of chlorination of SCCPs has strongly increased during the past 40 years, which may indicate its use as an additive for plastics, paints, and coatings. Furthermore, PCBs were analyzed in dated sediment slices. The PCB concentrations (sum of the six indicator congeners) peaked around 1969 (18 ng g<sup>-1</sup> dw) and decreased to 1.3 ng g<sup>-1</sup> dw in the surface layer corresponding to 2004. The peak level of CPs exceeded those of PCBs by about a factor of 3.

## Introduction

Chlorinated paraffins (CPs), also known as polychlorinated *n*-alkanes (PCAs) or chloroparaffins, are industrial chemicals introduced in the 1930s (1). Their actual global annual production is estimated to approximately 300 000 tons (1). Based on the most recently available information on production data (2) a total amount of more than 7 000 000 tons of CPs has been produced since their introduction. They are mainly used as additives in metal working fluids, as flame retardants, and as plasticizers (3). CPs are subdivided into short chain (SCCPs, C<sub>10–13</sub>), medium chain (MCCPs, C<sub>14–17</sub>), and long chain compounds (LCCPs, C<sub>>17</sub>) with chlorine contents between 30 and 70% (1). CPs with high chlorine content (>65%) are mainly used as flame retardants (2).

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Because of their persistence, CPs are ubiquitous in the environment, and they have a high potential for bioaccumulation (log *K*<sub>OW</sub> = 4.4–8, depending on the chlorination degree) (1). Whereas the acute toxicity of CPs is generally low, chronic toxicity in aquatic organisms has been observed for SCCPs (2). Furthermore, SCCPs are carcinogenic in rats and mice (4) and were categorized in group 2B as “possibly carcinogenic to humans” by the International Agency for Research on Cancer (IARC) (2). They have been included in the list of priority hazardous substances of the European Water Framework Directive (5). In addition, SCCPs are now under discussion to be included in the Stockholm Convention on persistent organic pollutants (POPs) (6).

Currently, information on environmental levels is scarce as compared to other POPs such as polychlorinated biphenyls (PCBs), dioxins, and organochlorine pesticides. The main reason is the demanding analysis of CPs in environmental matrices due to their complex composition. So far, worldwide, only a few data on CP levels in lakes (7–10) as well as in the Swiss environment are available (11–13). A review of current analytical methods employed in the past five years and their applicability to different matrices was presented by Zencak and Oehme (14).

PCBs were used for similar applications as CPs, such as additives in cutting oils, paints, coatings, sealings, and as plasticizers. Although the toxicity of PCBs is higher than of CPs (2, 15), the environmental behavior of both contaminants is similar. Industrial production of PCBs started in the 1930s and ceased in the 1970s. About 1 300 000 tons of PCBs were produced during this period (16). The use of PCBs was prohibited for open systems such as printing inks, sealants, and cutting oils in Switzerland in 1972 (17). In 2004, the Stockholm Convention on POPs issued a ban of PCBs in 128 countries (6).

The aim of this work was to get an overview of the temporal trends of CP and PCB concentrations in a dated sediment core from Lake Thun covering the past 120 years. Studies of dated sediment cores are an excellent way to investigate concentration trends over decades. Time-related profiles of CPs and PCBs were discussed and were compared with other studies. Moreover, evidence of a partial substitution of PCBs by CPs was evaluated. Furthermore, similarities and differences in the observed congener group patterns were studied.

Two analytical techniques were applied for the in-depth characterization of CPs. First, screening of CP levels in 15 sediment slices was performed using a recently developed technique (18) based on gas chromatography (GC) combined with electron ionization tandem mass spectrometry (EI-MS/MS). This method enables the determination of total SCCPs, MCCPs, and LCCPs (total CPs, totCPs). Electron capture negative ionization low resolution mass spectrometry (ECNI-LRMS) supplied additional information for the characterization of CPs regarding the degree of chlorination as well as the congener and the homologue patterns in all slices from the past 40 years (19, 20). This is a demanding task because gas chromatographic and mass spectrometric overlap of SCCPs and MCCPs can lead to corruption of quantitation results. To minimize such effects, possible interferences have to be identified and eliminated (21). Therefore, the method of Reth et al. was employed to allow a minimization of such interferences (22).

## Materials and Methods

**Sampling.** A sediment core from Lake Thun was taken on May 18, 2005 near the mouth of the river Aare (46°39'53" N, 7°48'54" E, near the village Därligen) at a depth of 60 m using

a gravity corer. Lake Thun is located in the alpine region of the Canton Bern in the center of Switzerland and has a surface area of 47.69 km<sup>2</sup>, a mean depth of 136 m, and a volume of 6.42 km<sup>3</sup>. Lake Thun is situated in a rural, densely populated catchment area without known point sources such as, for example, metal and polymer industries. The core was 1.1 m in length and 56 mm in diameter. It was cut into 1 cm slices that were lyophilized, weighed, homogenized, and stored in glass jars in the dark before dating and analysis.

**Sediment Core Dating and Flux Calculations.** Dating of the sediment core by <sup>137</sup>Cs and <sup>210</sup>Pb (23) analysis as a function of depth revealed an average sedimentation rate of 0.45 cm per year (see Supporting Information Figure S1). Thus, the 1 cm thick surface layer corresponds to the deposition of year 2004.

Fluxes ( $\mu\text{g m}^{-2} \text{y}^{-1}$ ) were calculated for each sediment slice:

$$\text{Flux} = \frac{c_{\text{totCP}} \times r_{\text{sed}} \times \text{wt}_s}{v_s} \quad (1)$$

where  $c_{\text{totCP}}$  is the total CP concentration in each slice obtained by EI-MS/MS ( $\mu\text{g g}^{-1}$  dry weight),  $r_{\text{sed}}$  is the sedimentation rate in each slice ( $\text{m y}^{-1}$ ),  $\text{wt}_s$  is the total dry weight (dw) of the sediment slice (g) and  $v_s$  is the volume of the slice ( $\text{m}^3$ ).

**Chemicals.** Cyclohexane, dichloromethane (DCM), *n*-hexane (*n*Hex) and toluene for residue analysis were obtained from Biosolve (Vallenswaard, Netherlands). Reference SCCP (chlorine contents of 51.5, 55.5, and 63.0%) and MCCP mixtures (chlorine contents of 52.0 and 57.0%) with concentrations of 100 ng  $\mu\text{L}^{-1}$  in cyclohexane as well as  $\epsilon$ -hexachlorocyclohexane ( $\epsilon$ -HCH, solution in cyclohexane, 10 ng  $\mu\text{L}^{-1}$ ) were purchased from Ehrenstorfer GmbH (Augsburg, Germany). <sup>13</sup>C<sub>10</sub>-*trans*-chlordane (100 ng  $\mu\text{L}^{-1}$ , solution in *n*-nonane, purity 99%) and <sup>13</sup>C<sub>12</sub>-PCBs standard mixture containing the congeners 28, 52, 101, 138, 153, 180 were supplied by Cambridge Isotope Laboratories (Andover, USA). <sup>15</sup>N<sub>3</sub>-musk xylene (1-*tert*-butyl-3,5-dimethyl-2,4,6-trinitrobenzene, <sup>15</sup>N<sub>3</sub>-MX) was synthesized in our laboratories (24). Copper powder (63  $\mu\text{m}$ ), silica gel for column chromatography (230–400 mesh, 0.045–0.063 mm), and sulfuric acid (98%) were obtained from Merck KGaA (Darmstadt, Germany). Florisil PR (60–100 mesh) and anhydrous sodium sulfate (Pestanal) were purchased from Fluka (Buchs, Switzerland). Florisil, sodium sulfate, and silica gel were dried overnight at 220 °C.

**Extraction and Clean-up.** Details of the applied cleanup procedure are given elsewhere (25, 26) and, hence, are only briefly described. A 5–10 g portion of dried and homogenized sediment was spiked with the corresponding internal standards (CP analysis: 10 ng of <sup>13</sup>C<sub>10</sub>-*trans*-chlordane; PCB analysis: 8 ng of a <sup>13</sup>C<sub>12</sub>-PCB-mixture) and then Soxhlet extracted with 200 mL of DCM and *n*Hex (DCM/*n*Hex, 1:1, v/v) for 8 h. Sulfur was eliminated by the addition of activated copper powder. After solvent evaporation, sample matrix not persistent to sulfuric acid was removed by column chromatography on 20 g of silica gel impregnated with concentrated sulfuric acid (44%). PCBs and CPs were eluted with 70 mL of DCM/*n*Hex (1:1, v/v). Further fractionation was carried out on a glass column packed with 16 g of Florisil (1.5% water content) that was eluted with 75 mL of *n*Hex and 5 mL of DCM (first fraction) followed by 60 mL of DCM (second fraction). The first fraction containing PCBs was concentrated to 0.5 mL, and the solvent was changed to toluene. The remaining solvent was concentrated to about 100  $\mu\text{L}$ , which was transferred to a GC vial containing the recovery standard (9.84 ng of <sup>15</sup>N<sub>3</sub>-MX). The second fraction containing all CPs was concentrated to 0.5 mL, and the solvent was changed to cyclohexane. Finally, the extract was reduced to 100  $\mu\text{L}$ , and 10 ng of  $\epsilon$ -HCH in 10  $\mu\text{L}$  of cyclohexane were added as recovery standard.

**Quality Assurance.** Extreme care was taken to keep background and cross contamination at a minimum. All glassware was washed in a glassware washer and immersed in a detergent bath (5% RBS35 concentrate, Fluka) for 12 h. Then, glassware and glass fiber thimbles (30 × 100 mm, 603G, Wathman, Schleicher & Schuell, Meidsone, England) were rinsed with DCM and *n*Hex and heated to 450 °C overnight. Prior to use, glassware was rinsed with the same solvents.

Method blanks were analyzed using the above-mentioned extraction and cleanup procedure. Blank concentrations calculated assuming a mean sample weight of 8.5 g dw were 3.3 ng g<sup>-1</sup> dw and 0.1 ng g<sup>-1</sup> dw for totCPs and  $\Sigma$ PCBs, respectively.

A “prechlorine industry” sediment slice (1899) was analyzed to detect possible cross-contamination during sampling. Whereas CP concentrations were similar to method blank levels (approximately 200% of method blank) concentrations of PCBs were slightly higher than the respective method blank levels (approximately 400% of method blank). In addition, the same sample was spiked with 30 ng of reference SCCPs (55% chlorine content) and 8 ng of a PCB mixture (congener 28, 52, 101, 138, 153, 180). The recoveries were 82 and 102%, respectively.

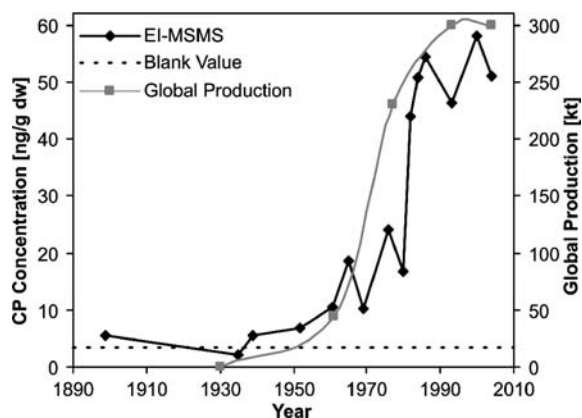
Reproducibility of the analytical method was tested by separate processing of the two halves of the same sediment slice (1993). The difference of these two samples was 14% for totCPs, 3% for the sum SCCPs, 8% for the sum of MCCPs, and 11, 2.8, 7.5, 23, 58, and 39% for the PCB congeners 28, 52, 101, 138, 153, and 180, respectively. The calculated chlorine contents of the two halves were 67.8 and 68.2% for SCCPs and 55.9 and 56.2% for MCCPs.

**Instrumental Analysis of CPs.** Instrumental analysis was performed on a gas chromatograph CP-3800 coupled to a 1200L triple quadrupole mass spectrometer (Varian, Walnut Creek, USA) using EI-MS/MS and ECNI-LRMS. The gas chromatograph was equipped with a split/splitless injector and a fused silica capillary column (15 m × 0.25 mm) coated with 0.25  $\mu\text{m}$  of cross-linked methylphenylpolysiloxane (DB5-MS, J&W Scientific, Folsom, USA). The injector temperature was set to 275 °C. The transfer line temperature was 280 °C, and the ion source temperature was 200 °C. Splitless injections (3.0 min) of 2.5  $\mu\text{L}$  volume were carried out with a Combi Pal autosampler (CTC Analytics, Zwingen, Switzerland).

**GC-EI-MS/MS.** Instrumental parameters are published elsewhere in detail and, hence, are only briefly described (18). The temperature program for the GC-EI-MS/MS analysis was as follows: 3 min isothermal at 100 °C, increased at 50 °C min<sup>-1</sup> to 300 °C, then isothermal for 3 min. Helium (99.996%, Sauerstoffwerk Lenzburg, Lenzburg, Switzerland) was employed as carrier gas at a constant flow of 2 mL min<sup>-1</sup>. The EI mass spectra were acquired at 70 eV electron energy with a filament emission current of 150  $\mu\text{A}$  and a scan time of 0.25 s scan<sup>-1</sup>. Collision-induced dissociation (CID) gas pressure (argon, 99.5%, Sauerstoffwerk Lenzburg) was set to 0.13 Pa. The mass spectrometer was regularly tuned to optimal performance using perfluorotributylamine for both quadrupoles at *m/z* 69, 219, and 502. The fragmentation masses were slightly modified for the determination of the total CP amount: *m/z* 91 → *m/z* 53 (collision energy: -10 eV), *m/z* 102 → *m/z* 67 (-10 eV), and *m/z* 104 → *m/z* 67 (-10 eV). The precursor ion *m/z* 383 [M - Cl]<sup>+</sup> and the product ion *m/z* 276 [M - 4Cl]<sup>+</sup> were selected for the detection of the internal standard <sup>13</sup>C<sub>10</sub>-*trans*-chlordane (-28 eV).

**GC-ECNI-LRMS.** Parameters for the determination of homologue profiles and degrees of chlorination by ECNI-LRMS are described elsewhere (19, 20). The temperature program for the GC-ECNI-LRMS analysis was as follows: isothermal at 100 °C for 2 min, increase at 15 °C min<sup>-1</sup> to 280 °C and isothermal for 4 min, then increase at 50 °C min<sup>-1</sup>





**FIGURE 1.** Historical time trend of total CP concentration (black line) in a sediment core from Lake Thun. Blank levels (dotted line) and global CP production (grey line) are also given. Analysis was performed by GC-EI-MS/MS.

to 300 °C and isothermal for 1.6 min. The mass spectrometer was employed in the ECNI mode with methane (99.995%, Carbagas, Rümliang, Switzerland) as reagent gas at an ion source pressure of 730 Pa. The transfer line temperature was set to 280 °C, and the ion source temperature was set to 200 °C. The ion source was tuned to optimum performance using perfluorotributylamine at  $m/z$  283, 452, and 633. The most abundant isotopes of the  $[M - Cl]^-$  ions of CPs with 5–13 chlorine atoms and of the  $[M]^-$  ion ( $m/z$  419.8) of  $^{13}C_{10}$ -*trans*-chlordane were recorded in the selected ion monitoring (SIM) mode (0.250 s dwell time per cycle). The most abundant isotope of the  $[M - Cl]^-$  ion ( $m/z$  254.9) was selected for the recovery standard  $\epsilon$ -HCH.

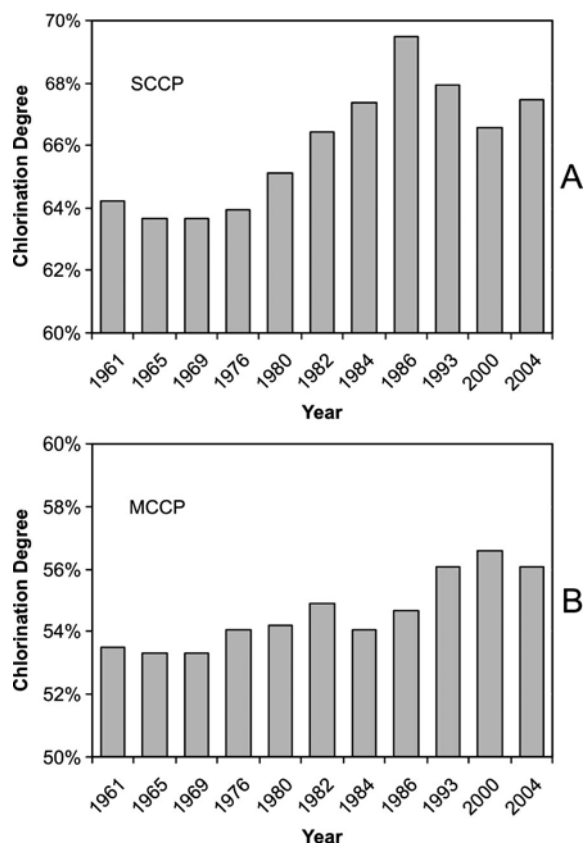
**ECNI-LRMS Identification and Quantification.** Identification of the CP congener groups was performed by comparison of retention time, signal shape, and correct isotope ratio according to Reth and Oehme (21). The applied quantification procedure was described by Reth et al. (22). Using this method, a reliable quantification can be achieved even if the degree of chlorination of the samples and of the reference standards are different. For this purpose, three SCCP (51, 55, and 63% Cl) and two MCCP references (52 and 57% Cl) from Ehrenstorfer were used as described in ref 21.

**PCB Analysis by GC-EI-HRMS.** PCBs were determined using GC EI high resolution (HR) MS according to Schmid et al. (27).

## Results and Discussion

**Screening of Total CP Levels by GC-EI-MS/MS.** The historical time trend of totCP concentrations in Lake Thun between 1899 and 2004 is shown in Figure 1. Each data point represents the average age of the respective sediment sample. Levels start at 5 ng g<sup>-1</sup> dw for the deeper, preindustrial sediment slice, which is in the range of the blank concentrations, and rise slowly from the 1950s to the 1970s. Then, the totCP level increased more rapidly in the 1980s and became more or less stable in the 1990s to present. The maximum concentration of 58 ng g<sup>-1</sup> dw was observed in 2000. The totCP concentration in the surface slice (2004) was slightly lower than the maximum level (51 ng g<sup>-1</sup> dw). This trend is consistent with the few data available on global production (2), also shown in Figure 1.

Because totCP data determined by EI-MS/MS from other lake sediments are missing, the obtained data were compared with levels in other environmental matrices. Reth reported between 19 and 42 ng g<sup>-1</sup> wet weight (ww) of totCPs in six brown trout samples from the Swiss rivers Liechtensteiner Binnenkanal and Necker and 25 ng g<sup>-1</sup> ww in one lake trout sample from the Swiss alpine lake Lei da Diavolezza (12);



**FIGURE 2.** Degree of chlorination of the SCCP (A) and MCCP (B) congeners in a dated sediment core from Lake Thun obtained by GC-ECNI-LRMS.

totCP concentrations were between 5 and 499 ng g<sup>-1</sup> dw in sediments from the North and Baltic Sea sampled from 2001 to 2003 (26).

**CP Characterization by GC-ECNI-LRMS.** Sediment samples after 1961 were analyzed by GC-ECNI-LRMS to determine “ECNI chlorine content” and chain length. The total ECNI chlorine contents of these sediment slices are shown in Figure 2. The degrees of ECNI chlorination of SCCPs were between 63.7 and 69.5% (surface: 67.5%). A very rapid increase could be observed during the 1980s. Obviously, these ECNI chlorine contents were rather high as compared to the chlorine contents of technical SCCP mixtures, being in the range 49–71%. Typically, CPs with high chlorine content are used as additives in plastics, paints, and coatings and not in metal working fluids. From these open system applications CPs can easily be released into the environment, including water systems. This change in chlorine content could be indicative for a change in the application of CPs.

The degree of ECNI chlorination of MCCPs was between 53.3 and 56.6% (surface: 56.1%).

A continuous increase of the ECNI chlorine content of SCCPs and MCCPs could be observed for the past 20 years. It is not possible to decide whether this shift is a consequence of increased usage of technical CP mixtures with higher chlorine content in recent years or if there is a significant dechlorination/biotransformation of CPs in older sediments.

**SCCP and MCCP Concentrations.** SCCPs and MCCPs were detected in all analyzed sediment slices (Figure 3). Comparison of the time profiles of totCPs, SCCPs, and MCCPs revealed that the rapid increase of totCP concentrations in the 1980s is mainly caused by SCCPs, whereas MCCP levels changed much less. The maximum SCCP concentration was 33 ng g<sup>-1</sup> dw in 1986 (Figure 3), and the level of the surface sediment was 21 ng g<sup>-1</sup> dw of SCCPs. MCCP concentrations increased since 1965 and reached a maximum in the surface

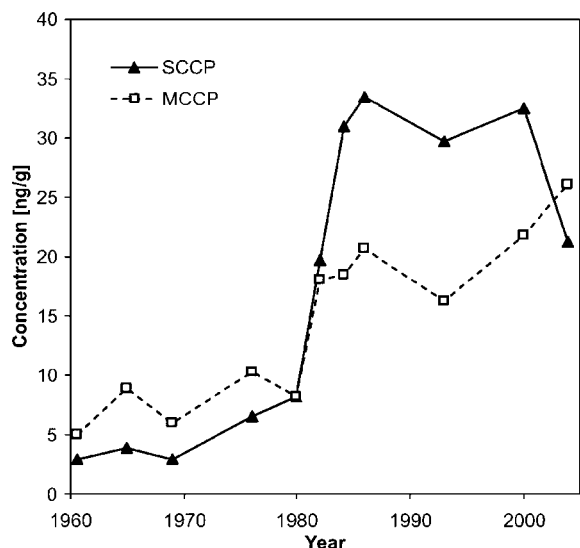


FIGURE 3. Historical time trends of SCCP (solid line) and MCCP (dashed line) concentrations obtained by GC-ECNI-LRMS.

sediment ( $26 \text{ ng g}^{-1} \text{ dw}$ ) (Figure 3). SCCP and MCCP concentrations are compared in Figure 4A. The SCCP/MCCP ratio increased continuously from 1965 to 1993. A decrease of SCCPs and a shift to more MCCPs in the SCCP/MCCP ratio were observed after 2000 in the surface slice. Future research is planned to verify this decrease, which could be attributed to an effect of the regulations of the EU Water Framework Directive and the preceding discussions about a general ban of SCCPs.

The few data available for SCCP levels in surface lake sediments are from Canada (7, 8). The SCCP concentration in the Lake Thun surface sediment was considerably lower than in Lake Ontario (lake-wide average  $49 \text{ ng SCCPs g}^{-1} \text{ dw}$ ) (7), the southern basin of Lake Winnipeg ( $176 \text{ ng SCCPs g}^{-1} \text{ dw}$ ) and Fox Lake ( $257 \text{ ng SCCPs g}^{-1} \text{ dw}$ ) (8). Only concentrations of Lake Nipigon are similar to Lake Thun ( $18 \text{ ng SCCPs g}^{-1} \text{ dw}$ ) (8). Three Canadian lakes had lower sediment concentrations (Ya Ya Lake  $1.6 \text{ ng SCCPs g}^{-1} \text{ dw}$ , Hazen Lake  $4.5 \text{ ng SCCPs g}^{-1} \text{ dw}$ , and the northern basin of Lake Winnipeg  $8.0 \text{ ng SCCPs g}^{-1} \text{ dw}$ ) (8).

For MCCPs in lake sediments there are even less studies available. Tomy and Stern reported a MCCP concentration in a surface lake sediment (Lake Erie, Canada,  $68 \text{ ng MCCPs g}^{-1} \text{ dw}$ ) (10), which was about three times higher than the maximum MCCP level in the surface sediment from Lake Thun. In 1985, Schmid and Müller found  $5 \text{ ng MCCPs g}^{-1} \text{ ww}$  in surface sediment from Lake Zürich (11). The ww level in the respective sediment layer of Lake Thun is about four times higher, but these data cannot be directly compared because of a different analytical quantification method and not well-documented sampling.

Studies on river sediments revealed higher CP concentrations than surface sediment from Lake Thun, mainly due to the industrial catchment areas of these rivers (various rivers in the Czech Republic  $<2\text{--}347 \text{ ng g}^{-1} \text{ dw SCCPs}$  and  $<2\text{--}5575 \text{ ng g}^{-1} \text{ dw MCCPs}$  (28); river Besos, Spain  $0.25\text{--}3.04 \mu\text{g g}^{-1} \text{ dw SCCPs}$  (29); various rivers in Germany, France, and Norway  $21\text{--}75 \text{ ng g}^{-1} \text{ dw SCCPs}$  and  $24\text{--}153 \text{ ng g}^{-1} \text{ dw MCCPs}$  (30)).

So far, the only available data on historical profiles in sediments are findings on SCCPs in sediments from Canadian lakes. One profile from Lake Ontario (station 1007) exhibited a maximum in 1970 with a concentration of about  $800 \text{ ng g}^{-1} \text{ dw SCCPs}$ , which decreased to  $410 \text{ ng g}^{-1} \text{ dw SCCPs}$  in the surface layer of 1996 (7). The other one (station 1034) has its maximum in the surface sediment ( $19 \text{ ng g}^{-1} \text{ dw SCCPs}$  in 1998) (7). In an investigation of six sediment cores from Canadian lakes, Tomy et al. reported concentration maxima

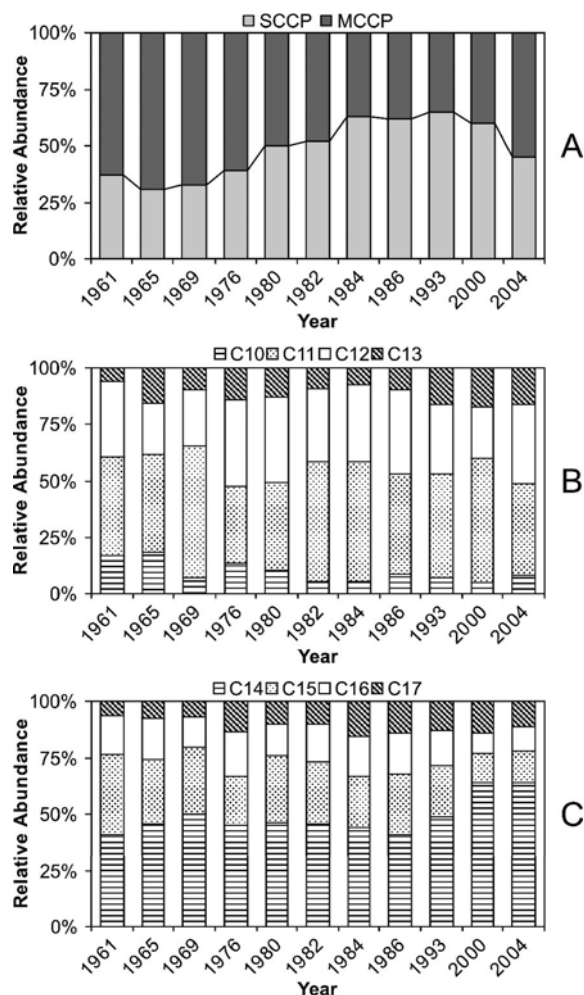


FIGURE 4. Chain length composition (A) as well as SCCP (B) and MCCP (C) homologue patterns of the sediment core from Lake Thun obtained by GC-ECNI-LRMS.

between the 1980s and the 1990s that were in the same range as in the sediment core from Lake Thun, but no clear temporal trend could be observed (8).

**Homologue Patterns of CPs.** In all sediment layers,  $C_{11}$  and  $C_{12}$  were the most abundant homologue groups within SCCPs (range: 66–87%; average: 79%; surface layer: 76%; see Figure 4B), which corresponds to technical SCCP mixtures (31). Within MCCPs, the  $C_{14}$  homologue group was most abundant (range: 41–64%; average: 48%; surface: 64%; see Figure 4C), which is also typical for technical mixtures.

**Congener Patterns of CPs.** Since the 1960s, a significant shift from lower to higher chlorinated congeners is observed in the pattern (see Figure 5 and Supporting Information Figures S2–4). Figure 5 shows the SCCP congener group pattern of sediment from 1961 (A) and of surface sediment from 2004 (B). SCCPs ( $C_{10\text{--}13}$  chains) with eight chlorine atoms were predominant in 1961, whereas SCCPs with 9–10 chlorine atoms prevailed in surface sediment.

**Comparison with PCB.** Figure 6A shows the historical time profiles of CPs and PCBs (sum of the six indicator PCBs No. 28, 52, 101, 138, 153, and 180) in the sediment core from Lake Thun. PCBs emerged after 1940, and levels culminated around 1968, reaching a maximum concentration of  $18 \text{ ng g}^{-1} \text{ dw}$ . Thereupon, the concentrations decreased continuously to  $1.3 \text{ ng g}^{-1} \text{ dw}$  in the most recent surface layer from 2004. The swift decline after 1968 reflects the restrictions of PCB use. In Switzerland, the usage of PCBs in open systems was banned in 1972. At the same time, CP production started

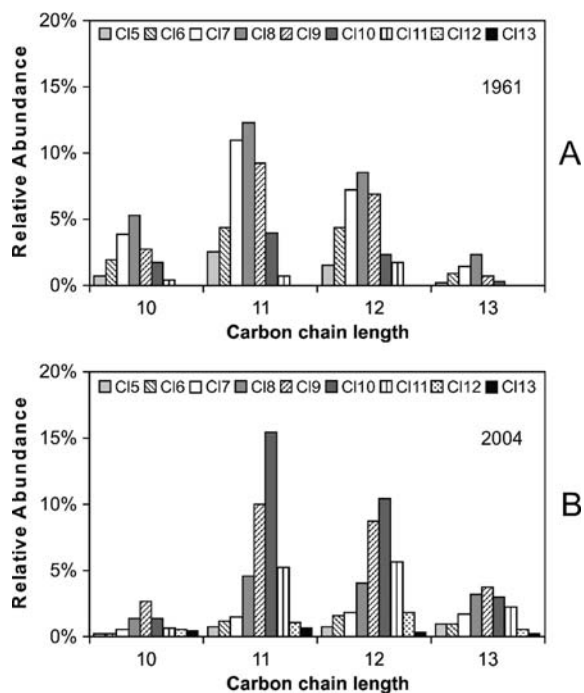


FIGURE 5. SCCP congener group patterns of the 1961 (A) and surface sediment slice (B) from Lake Thun determined by GC-ECNI-LRMS.

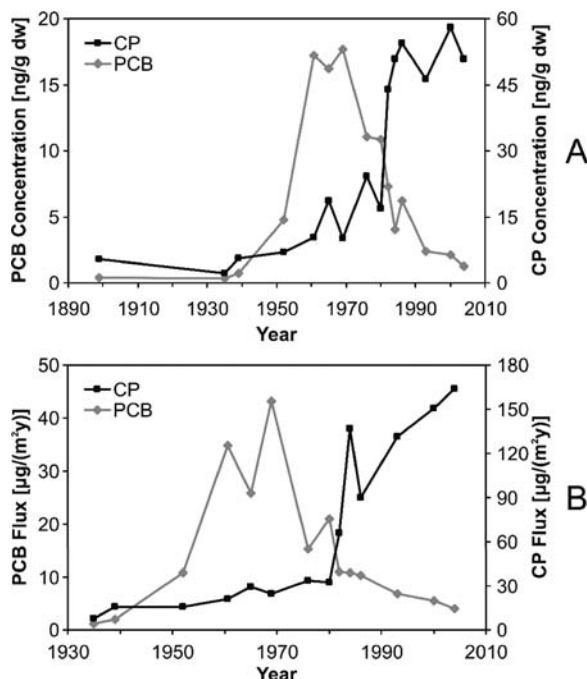


FIGURE 6. (A) Historical time trend of the sum concentration of CPs and PCBs in a sediment core from Lake Thun. Analysis was performed by GC-EI-HRMS and GC-EI-MS/MS, respectively. (B) Flux profiles of sum PCB (grey continuous line) and total CP (black continuous line) from 1937 to 2002.

to rise, partially as a consequence of its use as a substitute for PCBs and mainly due to the increased application of CPs as metal working fluids, plasticizers, and flame retardants. This change is reflected in the temporal trend of the CP levels shown in Figure 6A, as well. Furthermore, the peak concentration of  $58 \text{ ng g}^{-1} \text{ dw}$  CPs is about 3 times higher than for PCBs ( $18 \text{ ng g}^{-1} \text{ dw}$ ), which correlates well with the higher global production of CPs. A similar concentration profile of PCBs in a sediment core from the lake Greifensee located

near Zürich was reported by Zennegg et al. (32); however, the maximum concentration ( $130 \text{ ng g}^{-1} \text{ dw}$ , sum of the six indicator PCBs) was about 7 times higher, which is well compatible with more the urban and industrialized catchment area of this lake.

**Fluxes and Inventory of CPs and PCBs.** Annual CP and PCB (sum of the six indicator congeners) fluxes based on the respective concentrations measured in the sediment core from Lake Thun (see Figure 6B) were calculated using eq 1. The deposition flux of PCBs reached its maximum around 1969 ( $43 \mu\text{g m}^{-2} \text{ y}^{-1}$ ). This corresponds to a total annual PCB input of  $2 \text{ kg y}^{-1}$  into the sediment of the whole lake. Maximum deposition of CPs was observed in the most recent sediment layer, with  $164 \mu\text{g m}^{-2} \text{ y}^{-1}$ , corresponding to  $8 \text{ kg y}^{-1}$  for the whole lake. Total inventories estimated on the basis of these fluxes were  $49 \text{ kg}$  for PCBs and  $185 \text{ kg}$  for CPs. These data are in line with relative production amounts of the two chemicals for the whole period between 1935 and 2004 as given in the Introduction.

The calculated flux from the surface layer ( $164 \mu\text{g m}^{-2} \text{ y}^{-1}$ ) was higher for Lake Thun than for the Canadian lakes ( $0.45\text{--}147 \mu\text{g m}^{-2} \text{ y}^{-1}$ ) (7, 8). Only one lake (Lake Ontario,  $170 \mu\text{g m}^{-2} \text{ y}^{-1}$ ) was comparable (7). Moreover, the SCCP flux was estimated for a sediment core from a lake in the Canadian Arctic (Devon Island). It showed a similar increase during the past 20 years (9). However, a maximum as observed for 1957 could not be detected for Lake Thun.

In conclusion, the sediment core from Lake Thun revealed a considerable deposition of CPs during the past 30 years. Comparison of the temporal trends of PCB and CP levels showed an increase of CPs when PCB levels declined. This is in line with a partial replacement of PCBs by CPs. The calculated fluxes and the high chlorine content provided an indication of a possible contamination by weak local sources releasing technical CP mixtures. However, further studies analyzing sediments from a defined spatial distribution and from the feeding rivers are necessary to obtain more information about local sources and possible transformation pathways.

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### Supporting Information Available

$^{137}\text{Cs}$  and unsupported  $^{210}\text{Pb}$  activity as a function of depth for the dating of the sediment core is shown in Figure S1. Figures S2–S4 show SCCP and MCCP congener group patterns of the sediment slices from Lake Thun between 1961 and 2004. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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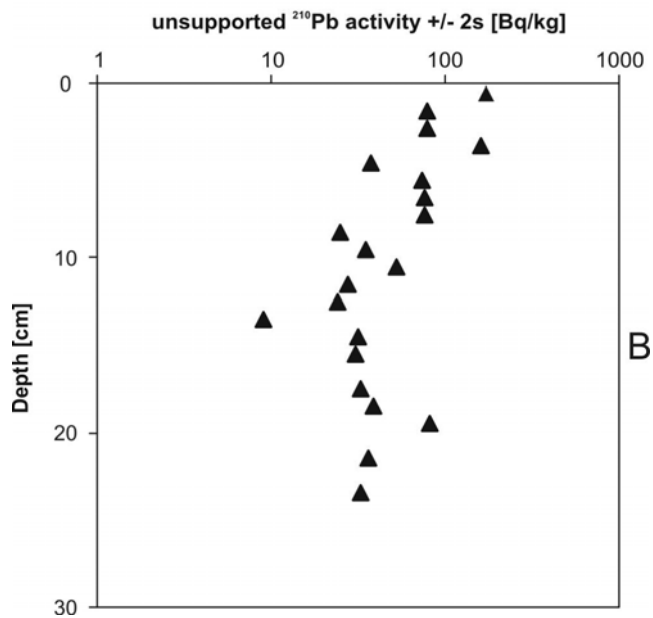
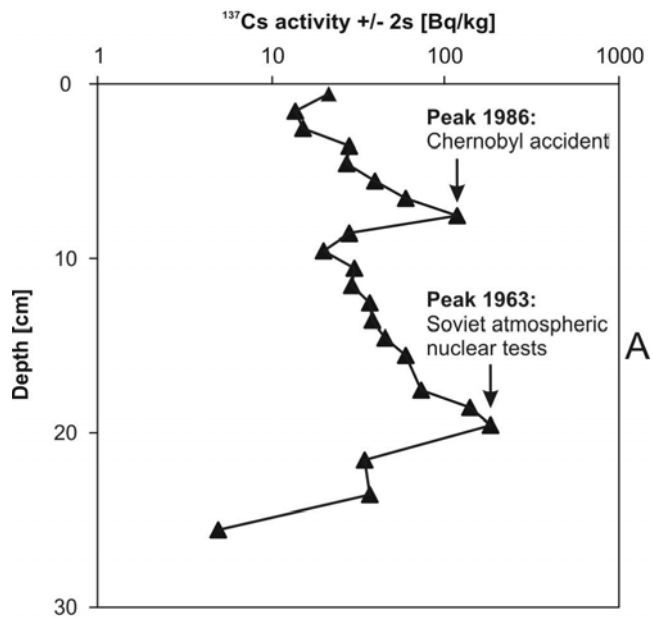
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# Supporting Information

## **Historical profiles of chlorinated paraffins and polychlorinated biphenyls in a dated sediment core from Lake Thun (Switzerland)**

*Saverio Iozza*<sup>1, 2</sup>, *Claudia E. Müller*<sup>1</sup>, *Peter Schmid*<sup>1</sup>, *Christian Bogdal*<sup>1</sup>, *Michael Oehme*<sup>2, \*</sup>

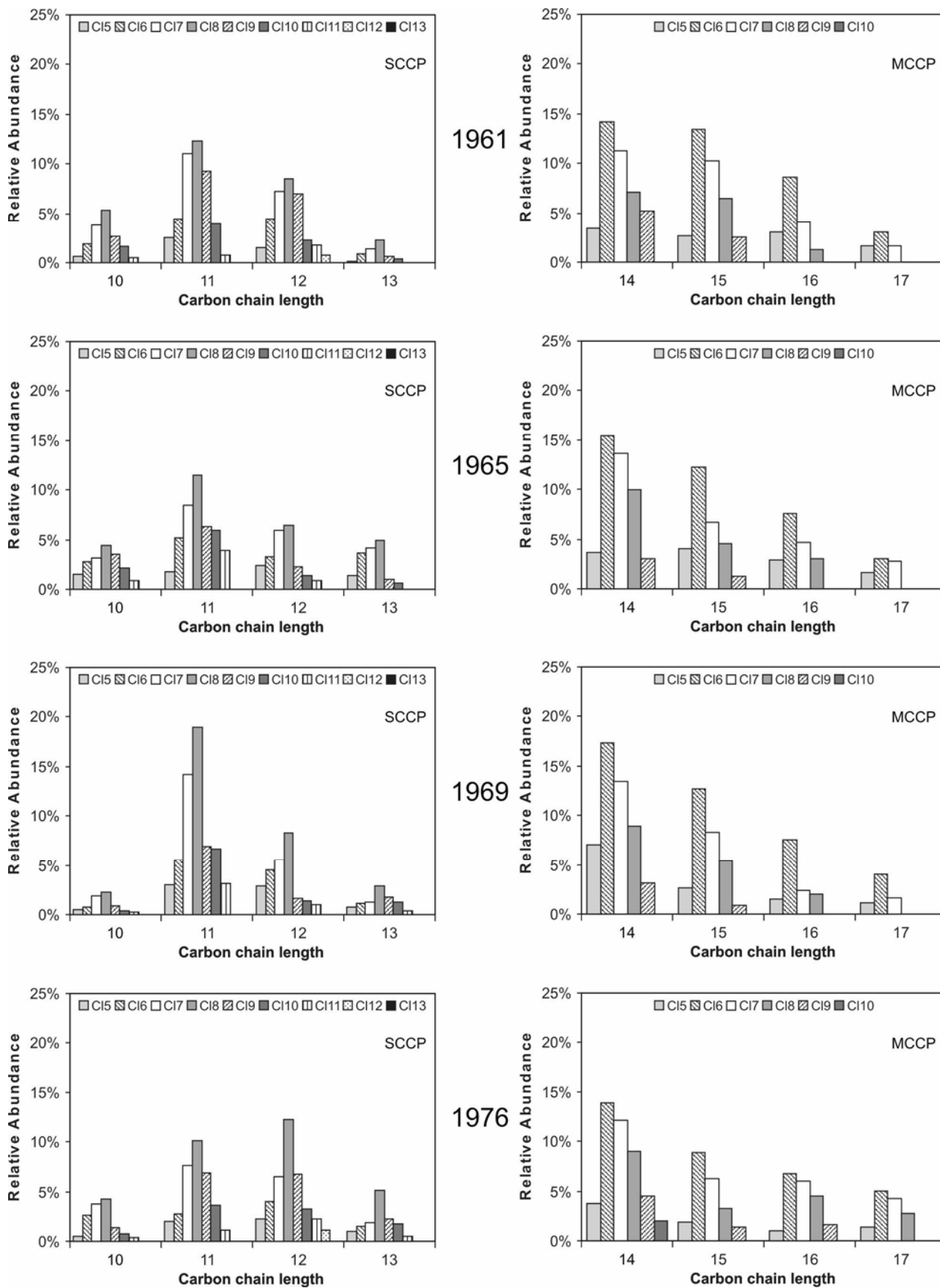
<sup>1</sup>Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Analytical Chemistry, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland; <sup>2</sup>University of Basel, Department of Chemistry, St. Johannis-Ring 19, CH-4056 Basel, Switzerland



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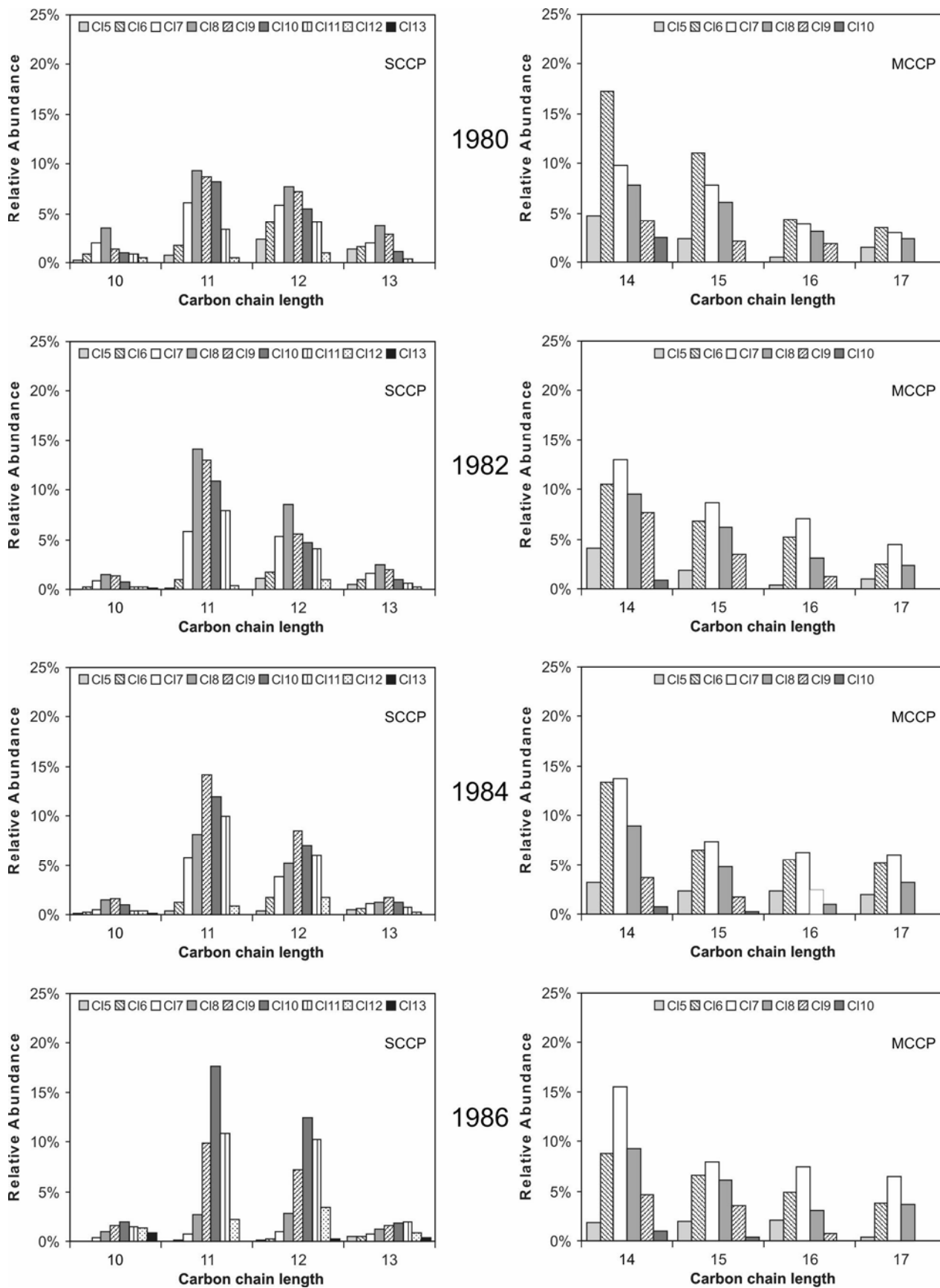
9 **FIGURE S1.**  $^{137}\text{Cs}$  (A) and unsupported  $^{210}\text{Pb}$  (B) activity as a function of depth for the dating of the  
10 sediment core.

11



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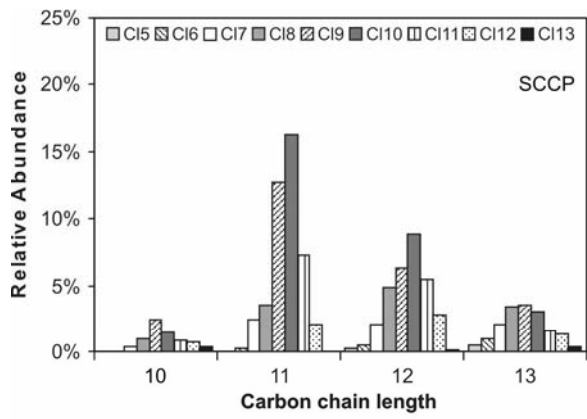
13 **FIGURE S2.** SCCP and MCCP congener group patterns of the 1961, 1965, 1969, and 1976 sediment  
 14 slice from Lake Thun determined by GC-ECNI-LRMS.



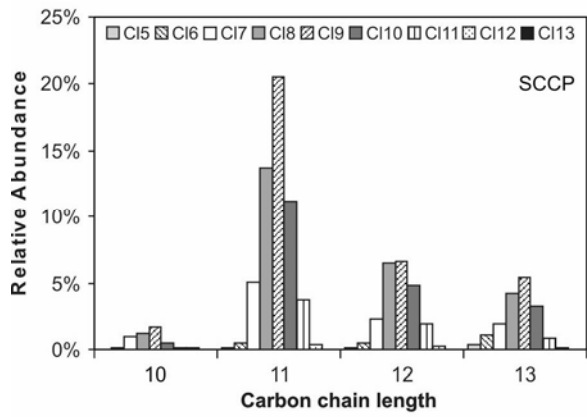
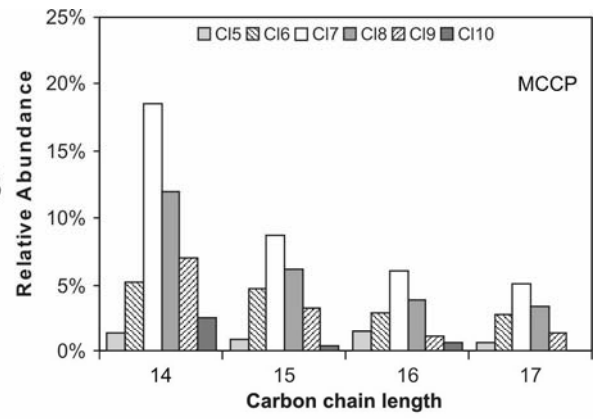
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16 **FIGURE S2.** SCCP and MCCP congener group patterns of the 1980, 1982, 1984, and 1986 sediment  
 17 slice from Lake Thun determined by GC-ECNI-LRMS.

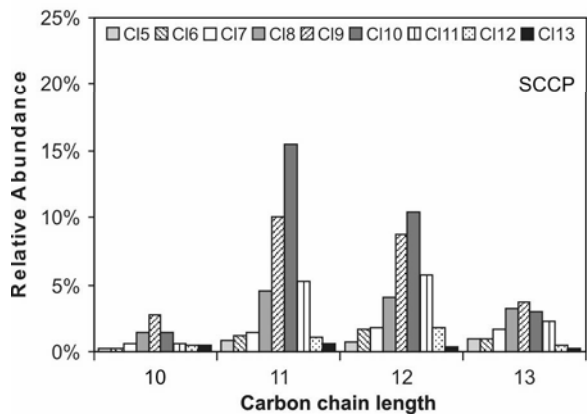
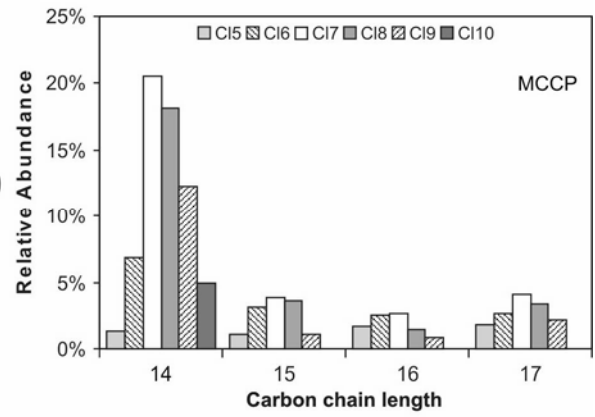




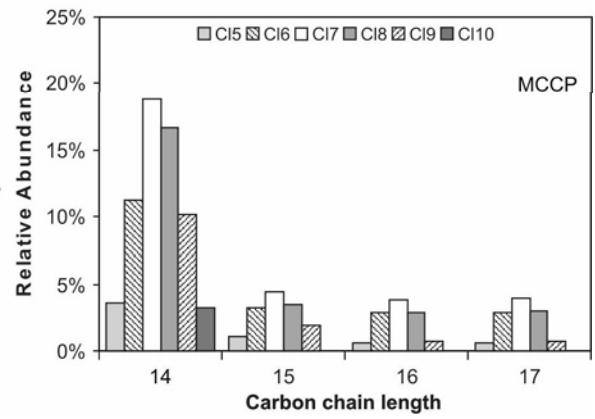
1993



2000



2004



18

19 **SI FIGURE S3.** SCCP and MCCP congener group patterns of the 1993, 2000, and 2004 sediment slice  
 20 from Lake Thun determined by GC-ECNI-LRMS.

21

22

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# CURRICULUM VITAE

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## PERSONAL INFORMATION

Name	Iozza, Saverio
Date of birth	January 26 <sup>th</sup> , 1977
Place of birth	Frankfurt, Germany
Citizenship	Italian

## EDUCATIONAL BACKGROUND

1983-1987	Primary school, Frankfurt, Germany
1987-1997	Gymnasium (Ziehenschule), Frankfurt, Germany
1997-2002	Studies in Food Chemistry, University of Frankfurt, Germany
10/2002	First state exam
2002-2003	Internships within the scope of the Food Chemistry state exam at „Amt für Lebensmittelkontrolle und Umweltschutz“, Schaffhausen, Switzerland and at „Staatliches Untersuchungsamt Hessen“, Kassel, Germany
11/2003	Second state exam
2004-2008	Ph.D. studies in Organic Analytical Chemistry under the supervision of Prof. Dr. Michael Oehme at the University of Basel, Switzerland, and since 2006 at the Laboratory for Analytical Chemistry at Empa in Dübendorf, Switzerland

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