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Short and medium chain chlorinated paraffins in atmospheric samples – Analytical challenges

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ABSTRACT

Chlorinated paraffins (CPs) is a group of organic compounds consisting of chlorinated n-alkanes of varying chain length (C10-C30) and degrees of chlorination (40 to 70% by weight). The CPs are generally divided into three groups; short-chain (SCCPs, C10-13), medium-chain (MCCPs, C14-17) and long-chain (LCCPs, C18-30). CPs are produced in large volumes and are used as plasticizers in plastics and rubbers, as additives in paints, adhesives and sealants, as metal working fluids and as a flame retardant in textiles and polymers. They have been found to be persistent in the environment, and show toxicity in aquatic ecosystems. This study evaluated an analytical method for quantification of SCCPs and MCCPs in air samples with regard to blank contributions from various pathways, including storage of sampling material, sample collection in the field, reagents used, and the laboratory environment. In addition, instrumental analysis using gas chromatography quadropol time-of-flight (GC/Q-TOF) mass spectrometry (MS) was evaluated, and compared to an established method using a sector MS instrument. The GC/Q-TOF instrument gave comparable results to the sector instrument in the analysis of air samples. The performance of the two instruments was also compared using sediment, biota and dust samples from an interlaboratory study. The results were comparable for all samples with exception of the sediment samples, where the sector instrument indicated higher CP levels. The GC/Q-TOF gave more precise results on repeated measurements.

Recovery of the different CP homologue groups was investigated as part of the study to evaluate if their distribution in the original sample stays intact after sample extraction and preparation. The homologue group distribution was found to be intact.

The investigation of CP contamination sources showed that the indoor laboratory environment contains considerable amounts of CPs, suggesting that precautions needs to be taken in the handling of samples. The highest indoor level of SCCPs, measured using passive air samplers, was found in a lab at 55.5 ng/m^3, while the highest MCCP level was 0.3 ng/m^3 from the same lab. In dust/organic film samples the highest level of SCCPs found was 2856 ng/m^2, while the highest MCCP level was 965 ng/m^2. Considerable amounts of CPs were also found in products used in the lab, there are however suggestions that CP contamination from dust could be a factor in this find. No systematic contamination sources related to storage of sampling material, sampling in the field or the reagents used could be found.

NORSK SAMMENDRAG

Klorparafiner (CPs) er en gruppe organiske stoffer som består av klorerte n-alkaner av varierende kjedelengde (C10 til C30) og kloreringsgrad (40 til 70 vekt %). CPs er generelt delt inn i tre grupper; kortkjedede (SCCPs, C10 til C13), mediumkjedede (MCCPs, C14 til C17) og langkjedede (LCCPs, C18 til C30). CPs produseres i store volumer, og benyttes som plastmyknere i plast og gummi, som tilsettingsstoffer i maling, festemidler og tettningsmasser, som skjærevæske i metallarbeid og som flammehemmer i tekstiler og polymerer. De er persistente i miljøet, og har vist seg å være giftige i akvatiske miljø. I denne studien evalueres en analytisk metode for kvantifisering av SCCPs og MCCPs i luftprøver med hensyn på kontaminering fra ulike kilder, inkludert lagring av prøvemateriale, prøvesamling i felt, reagenser som benyttes, og innemiljø i laboratoriet. I tillegg evalueres analysen med et gass kromatografi quadropol time-of-flight (GC/Q-TOF) masse spektrometer (MS), og dette sammenlignes men en etablert metode der et sektor MS instrument benyttes. GC/Q-TOF instrumentet viste resultater som var sammenlignbare til sektorinstrumentet ved analyse av luftprøver. Instrumentene ble også sammenlignet ved analyse av sediment, biota og støvprøver fra en interlaboratoriestudie. Disse resultatene var sammenlignbare for alle prøver, med unntak av sediment, der sektorinstrumentet viste høyere resultat. GC/Q-TOF instrumentet viste mer presise resultater ved repeterte målinger.

Gjenvinningen av de ulike homologgruppene i SCCPs og MCCPs ble vurdert som en del av studien, for å undersøke om distribusjonen av disse i en prøve forholder seg intakt etter prøveopparbeidelse. Homologgruppedistribusjonen ble funnet å holde seg intakt.

Undersøkelsen av CP kontamineringskilder viste at innemiljøet i laboratoriet inneholder betydelige mengder CPs, noe som innebærer at forholdsregler bør tas under håndtering av prøver. Det høyeste nivået av SCCPs funnet i inneluft i laboratoriet ved hjelp a passiv prøvetaker var 55.5 ng/m^3, og høyeste nivå av MCCP var 0.3 ng/m^3 fra samme lab. I prøver av støv/organisk film var det høyeste nivået funnet 2856 ng/m^2, mens det for MCCP var 965 ng/m^2. Betydelige mengder SCCP ble også funnet i produkter benyttet på laben, men det er indikasjoner på at kontaminering fra støv kan være en faktor i dette funnet. Ingen systematiske kontamineringskilder knyttet til lagring av prøvemateriale, prøvetaking i felt, eller reagenser benyttet ble funnet.

ABBREVIATIONS

AAS – Active air sampling

AMAP – Arctic monitoring and assessment program

AP – Aarhus protocol

B – Magnetic sector

BTBPE – 1,2-Bis(2,4,6-tribromphenoxy)ethan

CLRTAP – Convention on long-range transboundary air pollution

CP – Chlorinated paraffins

CRM – Certified reference material

CTD – Characteristic travel distance

DDD – Dichlorodiphenyldichloroethane

DDE – Dichlorodiphenyldichloroethylene

DL – Detection limit

DDT – Dichlorodiphenyltrichloroethane

E – Electrostatic sector

ECNI – Electron capture negative ion

EHTBB – 2-ethyl-1-hexyl 2,3,4,5-tetrabromobenzoate

EIC – Extracted ion chromatogram

FWHM – Full with half measure

GC – Gas chromatography

GFF – Glass fiber filter

HBB – Hexabromobenzene

HCB – Hexachlorobenzene

HCH – Hexachlorocyclohexane

HRMS – High-resolution mass spectrometry

ISTD – Internal standard

K_{AW} – Air water partitioning coefficient

K_{OA} – Octanol air partitioning coefficient

K_{OW} – Octanol water partitioning coefficient

LCCP – Long chain chlorinated paraffins

LRT – Long range transport

MCCP – Medium chain chlorinated paraffins

MDL – Method detection limit

MS – Mass spectrometry

m/z – Mass/charge

NILU – Norwegian Institute for Air Research

OC – Organochlorine

PAH – Polycyclic aromatic hydrocarbon

PAS – Passive air sampler

PBBz – 1,2,3,4,5-pentabromobenzene

PBDE – Polybrominated diphenyl ether

PCB – Polychlorinated biphenyl

PeCB – Pentachlorbenzene

POP – Persistent organic pollutant

PTV – Programmed temperature vaporization

PUF – Polyurethane foam

Q-TOF – Quadrupole time-of-flight

RRF – Relative response factor

SC – Stockholm convention

SCCP – Short chain chlorinated paraffins

SIM – Single ion monitoring

SVOC – Semivolatile organic compound

TCDD – Tetrachlorodibenzodioxin

TCN – Tetrachloronaphthalene

TIC – Total ion chromatogram

UNECE – United Nations economic commission for Europe

UNEP – United Nations environmental program

UV – Ultra violet

CONTENT

1. INTRODUCTION

Since the emergence of synthetic organic chemistry in the 19th century, there has been a vast growth in the number of identified organic environmental pollutants. Historically, the knowledge about environmental impacts of synthetically produced organic pollutants has been limited, and this has enabled high production volumes and indiscriminate use. As information about potential risks has emerged, with events like the publication of Rachel Carson`s Silent Spring (1962) and James Lovelocks development of the electron capture detector (Lovelock 1974), one group of organic compounds known as the persistent organic pollutants (POPs) has become a particular concern.

The POPs are a group of compounds that are associated with persistency, bioaccumulation, toxicity and potential for long-range transport (LRT). POPs share some physical/chemical properties that make them industrially/agriculturally useful, but at the same time potentially harmful to the environment. The POP group includes compounds that traditionally have been used as pesticides or for industrial purposes, like polychlorinated biphenyls (PCBs), and various organochlorine (OC) pesticides, e.g. dichlorodiphenyltrichloroethane (DDT), hexachlorobenzene (HCB), chloroboranes and dieldrin, as well as some that can be formed during production and combustion of chlorinated aromatic compounds, like dioxins and HCB (Jones & De Voogt 1999). Many POPs are semivolatile organic compounds (SVOC). SVOCs, defined as compounds with vapor pressure between 10^{-9} to 10 Pa (Weschler & Nazaroff 2008), have physical/chemical properties that make them able to partition to the gas phase and the particle phase in air. The distribution between the phases depend on temperature, particle concentrations and physical/chemical properties of the individual compound. The more volatile SVOCs that mainly are found in the gas phase can travel on air currents as gas, while heavier/less volatile SVOCs are more adsorbed to airborne particles (Jones & De Voogt 1999). High persistence, due to generally low degree of susceptibility to UV irradiation, reactive trace gases and radicals (e.g. ozone, NOx and OH), low potential for microbial enzymatic breakdown in soil and other natural breakdown processes, results in high potential to spread and remain in the environment (Harrad 2001). Condensation/volatilization processes taking place with seasonal temperature changes in combination with prevailing wind patterns results in a tendency for the POPs to move from source locations in temperate regions towards the colder Polar regions where they tend to accumulate (Wania & Mackay 1996). This is known as the grasshopper effect. There is also believed to be a fractioning of emitted POPs based on this

process. This effect has been studied for PCBs, where the lighter, more volatile congeners appear to be more subject to LRT than the heavier, less volatile congeners (Gouin et al. 2004; Meijer et al. 2002).

The POPs are generally lipophilic, which is associated with a potential for bioaccumulation of the compounds in the fatty tissue in exposed organisms, and for further biomagnification in higher trophic levels in the food chain. Some of the POPs, particularly some of the dioxins like 2,3,7,8-tetrachlorodibenzodioxin (TCDD), have also been shown to be highly toxic to humans and wildlife (Poland & Knutson 1982).

Due to the toxicity and environmental harm associated with POPs, steps have been taken in order to restrict and regulate the production and use of these compounds. The Convention for Long-range Transboundary Air Pollution (CLRTAP) under the United Nations Economic Commission for Europe (UNECE) includes a protocol for POPs, the 1998 Aarhus protocol (AP) (UNECE 1998). This protocol contains a list of 16 high-risk compounds classified as POPs. The protocol bans the intentional production and use of these compounds, and obliges the signatory parties to reduce the emissions of the unintentionally produced compounds like polycyclic aromatic hydrocarbons (PAHs) to below 1990 levels. 31 states, including Norway, and the European Union have ratified the AP (UNECE 1998). Building on the AP, and after initiative form the United Nations Environmental program (UNEP), the Stockholm Convention (SC) on POPs was signed in 2001, and ratified in 2004. In contrast to the AP and CLRTAP which are regional agreements, the SC is a global treaty. To date the number of parties that have ratified the SC is 180; 179 states, including Norway, and the European Union (SC 2009).

The SC originally bans or restricts production and use of 12 POPs known as the dirty dozen (SC 2009). The AP and the SC have in the years following their implementations been expanded to include more POPs and the lists are continuously growing. To date the AP includes 23 compounds, while the SC includes 25 compounds (Table 1). One group of compounds that is currently under review as a candidate for regulation under the SC on POPs is the short chain chlorinated paraffins (SCCPs) (SC 2009). In countries affected by the AP, there is already regulations in place for SCCPs (UNECE 1998). There is a lot of work behind the inclusion of new compounds and groups of compounds to the AP and the SC. The inclusions are based on gathered data on the compounds physical/chemical properties, environmental behavior, potential for LRT and bioaccumulation, toxicity and occurrence in various environmental media. To gather reliable data on these factors for potential POPs like the SCCPs, there is a need for good methodological and analytical techniques to be established.

Table 1: List of compounds included in the original AP and SC, compounds added in amendments to AP and SC, and compounds under review for regulation.

Compounds	Regulated under	Added in amendments	Under review
Aldrin	AP, SC		
Chlordane	AP, SC		
Chlordecone	AP	SC	
Chloroboranes	AP, SC		
Decabromodiphenyl ether			SC
Dichlorodiphenyltrichloroethane (DDT) (incl. DDT group)	AP, SC		
Dicofol			SC
Dieldrin	AP, SC		
Endosulfane		SC	
Endrin	AP, SC		
Heptachlor	AP, SC		
Hexabromobiphenyl	AP	SC	
Hexabromocyclododecane		SC	
Hexachlorobenzene	AP, SC		
Hexachlorobutadiene		AP, SC	
Hexachlorocyclohexanes	AP	SC	
Mirex	AP, SC		
Octabromodiphenyl ether		AP, SC	
Pentabromodiphenyl ether		AP, SC	
Pentachlorobenzene		AP, SC	
Pentachlorophenol		SC	
Perfluorooctanoic acid			SC
Perfluorooctylsulfonate		AP, SC	
Polycyclic aromatic hydrocarbons (PAHs)	AP		
Polychlorinated biphenyls (PCBs)	AP, SC		
Polychlorinated dibenzofurans	AP, SC		
Polychlorinated dibenzo-p-dioxins	AP, SC		
Polychlorinated naphthalene		AP, SC	
Short chain chlorinated paraffins (SCCPs)		AP	SC
Tetrabromodiphenyl ether		SC	

1.1 Chlorinated paraffins (CPs)

CPs is a group of organic compounds consisting of chlorinated n-alkanes of varying chain length and degrees of chlorination. CPs are produced by forcing molecular chlorine through liquid alkane feedstocks or alkanes in solvent in the presence of UV light and/or high pressure/temperature (Muir et al. 2000). These methods of chlorination have low selectivity of positioning and stereochemistry of the added chlorine atoms, and as a result, the products are highly complex mixtures. The type of alkane feedstock used and the amount of chlorine added determine the nature of the product. C_{10} – C_{13} CP mixtures are classified as short chain chlorinated paraffins (SCCP), the C_{14} – C_{17} mixtures are classified as medium chain chlorinated paraffins (MCCP) and the C_{18} – C_{30} mixtures are classified as long chain chlorinated paraffins (LCCP). Degree of chlorination is usually between 40 and 70% by weight (Fiedler 2010). General formula for CPs is $C_nH_{2n+2-x}CL_x$. The CPs with identical sum formula are referred to as a homologue group. Figure 1 illustrates the chemical structure of CPs.

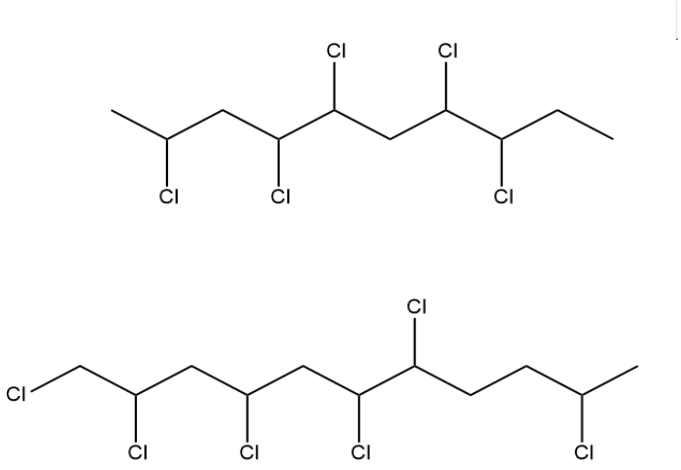


Figure 1: Illustration including two of many possible CP structures. Above: 2,4,5,7,8-pentachlorodecane, below: 1,2,4,6,7,10-hexachlorododecane.

CPs are used industrially for a variety of purposes. CPs were first produced in the 1930s as an antiseptic solution for medicinal purposes (Tomy 2009). One of the major uses of CPs since then is the application as a metal working fluid. CPs are also used as plasticizers in plastics and rubbers, as additives in paints, adhesives and sealants, and as a flame retardant in textiles and

polymers (Fiedler 2010). As such, they are ubiquitous in the anthropogenic environments including indoor environments.

The production of SCCPs has decreased in Europe, Canada and the United States during the last years due to regulations and voluntary replacements (Fiedler 2010), but in other parts of the world production of both SCCPs and other CPs still remains high. China has the largest worldwide production volumes of CPs, with a production volume of ~ 600 000 tons in 2007 (Fiedler 2010). Accurate information about production volumes is sparse, but recent estimates indicate annual production volumes of CPs of > 1 000 000 tons worldwide (van Mourik et al. 2016), and a cumulative production volume of CPs of > 7 000 000 tons between the 1930s and 2010 (Wang et al. 2010). In comparison the estimated total volume of PCBs synthesized is approximately 1 300 000 tons (Breivik et al. 2002).

The physical/chemical properties of CPs are in many ways comparable to the POPs in the AP and SC, with generally low water solubility, semivolatile behavior and high environmental persistence. There are however relatively large differences in physical/chemical properties within the CP group. Water solubility of the S/MCCP homologue groups varies from 0.029 to 1260 µg/L, where the shorter carbon chain compounds have the higher water solubility. Vapor pressure varies from 1.7×10^{-8} to 0.028 Pa, and Henrys laws constant varies from 0.01 to 51.3 Pa m^3/mol (Feo et al. 2009). As for most other POPs, the octanol-water partition (K_{OW}) coefficients are generally high, with increasing values for longer carbon chain and higher chlorinated CPs. The range of log K_{OW} for S/MCCPs is 5.06 to 8.96 (Feo et al. 2009). The variability in physical/chemical parameters is not only due to variability in chain length and chlorination degree, but also to the positioning of the chlorines. This can be illustrated with the hexachlorodecane homologue group, where some of the individual congeners have log K_{OW} varying from 5.76 to 6.17 (Muir 2010)

Table 2: Physical and chemical properties of CPs, and some selected POPs. (Feo et al. 2009; Fiedler 2010; PubChem 2016; Shen & Wania 2005)

Compound	Molecular weight (g/mol)	Water solubility (µg/L)	Log K_{OW}	Vapour pressure, 25°C (Pa)	Source
***p,p*'DDT**	354.5	0.2	6.39	$4.8x10^{-4}$	S&W
2,3,7,8-TCDD	321.9	0.2	6.80	$2.8x10^{-3}$ - 0.3	PC
PCB 77	292.0	180.0	6.70	$2.0x10^{-3}$	PC
HCB	284.8	0.4	5.64	$9.4x10^{-2}$	S&W
PBDE 209	959.2	<0.1	9.97	$9.3x10^{-9}$	PC
S/MCCP	314.5~600	0.03 - 1260	5.06 - 8.96	$1.7x10^{-8}$ - $2.8x10^{-2}$	Fe, Fi

Table 2 shows physical/chemical properties associated with CPs and some selected POPs. The large range of physical/chemical properties associated with CPs imply that there is also a large variety of environmental behavior within the CP group. As one can see from the data, CPs can be comparable both to lighter SVOCs like HCB, and to heavier compounds like the higher brominated polybrominated diphenyl ethers (PBDEs). Figure 2 (left) shows a chemical space plot including SCCPs and some selected POPs (Halse 2014). The compounds are plotted according to partitioning coefficients; the air-water partitioning coefficient; $K_{AW,}$ the octanol-air partitioning coefficient; $K_{OA,}$ and the octanol-water partitioning coefficient; K_{OW}. The SCCP points represent the average properties of each homologue group included. The distribution of the points gives an illustration of the wide range of properties associated with SCCPs. Figure 2 (right) display the partitioning of some MCCPs, and show a parallel trend to the SCCPs, only slightly more to the right in the chemical partitioning space plot. This is a consequence of a more hydrophobic and less volatile nature as the chain length increase. The points in the MCCP plot are also based on the average properties of the homologue groups (Muir 2010).

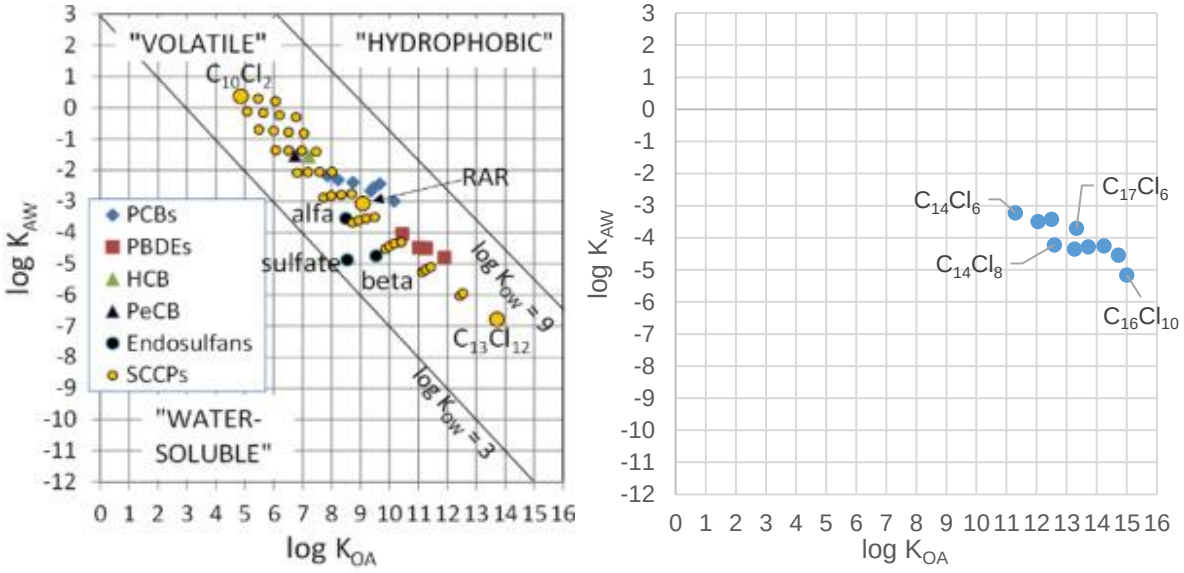


Figure 2: Left: Chemical partitioning space plot including SCCPs and some selected POPs (Halse 2014) Right: Chemical partitioning plot showing some MCCPs. Based on data from Muir (2010).

Of the three CP categories (SCCP, MCCP and LCCP), SCCPs have received most attention with regard to research and regulation. This is due to greater potential for LRT as well as suspected ecological and toxicological risks (Ali & Legler 2010). The known risks associated with SCCPs include toxicity to aquatic life, potential for bioaccumulation and biomagnification, and potentially carcinogenic properties (classified in category 2B; possibly carcinogenic to humans) (UNEP 2012). MCCPs are also associated with toxicity to aquatic life and potential for bioaccumulation (ECHA 2005). Unlike for SCCPs, there is no international regulation in place for the production and use of MCCPs (Miljodirektoratet 2014). The higher attention for SCCPs, especially in research, is also due to a preference for SCCPs over MCCPs and LCCPs in analytical procedures as a consequence of the added analytical challenges associated with the longer chain CPs. More information regarding the latter will be discussed in section 1.3.

1.2. Air sampling of CPs

Modeling studies based on the physical/chemical properties of CPs suggest that only a small fraction of the emitted CPs will be present in gas phase or adsorbed to suspended particles in air at any given time (Muir 2010). Looking at the different homologue groups, the fraction of CP in air decreases as chain length and chlorination degree increase, which is a reflection of the

lower volatility of the heavier CPs (Muir 2010). This is consistent with the partitioning data in Figure 2. The modeling study by Muir also suggests a characteristic travel distance (CTD, the point where deposition flux has reached 37% (1/e)) in the range of ~800 to ~3000 km for SCCPs and MCCPs. In comparison, PCB-180 has a CTD of ~5000 km (Muir 2010). This implies that the SCCPs and the MCCPs are subject to atmospheric LRT. The range of CTDs associated with CPs described by Muir suggest that CPs are subject to environmental fractioning processes based on the variation in physical/chemical properties within the CP group. This has also been suggested by data from environmental (air and soil) samples (Wang et al. 2013).

CPs are found in biota in remote areas such as the Arctic (Reth et al. 2006), which support the modeling studies in that CPs are in fact subject to LRT. Local sources of CPs in Arctic areas are expected to be marginal compared to the more urbanized areas in Europe, North America and Central Asia. Air sampling with respect to CPs is of interest to gain further insight into the spatial pattern of CPs and in order to verify modeling results. Further, air sampling in combination with models can also be used to assess source regions and transportation pathways for CPs to the Arctic, and identify local sources. As for other POPs, air sampling targeting CPs is restricted by the large volumes of air needed to obtain detectable levels. This requires an up-concentration of the CPs on a sample unit consisting of an adsorbent and a filter by using active air samplers pumping high air volumes through the sample unit or passive air samplers deployed for long times. The most common and accurate method for collecting air samples is through active air sampling (AAS), using a pump to draw a known volume of air through a sample unit (Figure 3). The currently used sample units consist of a glass fiber filter (GFF) and an adsorbent material, often polyurethane foam (PUF) plugs. The CPs present in the gas phase will adsorb to the adsorbent material (the PUFs), while the particle bound CPs will be collected on the filter. More information concerning the active sampling is given in section 2.3.3.

Another sampling technique commonly used for POPs with similar physical-chemical properties to CPs is passive air sampling. A frequently used passive air sampling technique for SVOCs is the PUF disk based passive air sampler (PAS) (Harner et al. 2006) (Figure 3). Here PUF disks are placed between two metal bowls allowing air to freely flow over the sampling material, and POPs to diffuse into the PUF disks. The limitation of this method is low control over the sampling volume, and no quantitative collection of particles. The great advantage of PAS is the small size, low cost and possibility to use in areas without access to electricity, which ultimately increases the spatial coverage of air sampling compared to use of AAS. (Melymuk et al. 2014).

Figure 3: Left: High volume active air sampler (Digitel). Right: PUF based passive air sampler.

1.3 Challenges in the chemical analysis of CPs

In the ongoing processes attempting to regulate the production and use of CPs, there is a requirement for good analytical methods in order to gain information of CP occurrence and exposure potential in various environmental compartments. There are however some challenges still to overcome in the chemical analysis of CPs, relating to the nature of industrial CP mixtures, interferences from other OCs, contamination issues and lack of suitable standards.

1.3.1 STRUCTURAL COMPLEXITY

Many of the difficulties that arise in the analytical process to quantitatively determine CP content are caused by the structural complexity of industrially produced CP mixtures. The chlorination process used to produce CPs gives relatively random products within certain restrictions. Chlorine atoms have low affinity to carbon atoms that already have a chlorine substituent, which excludes the CCl_2 group as a possible component of CPs. This effect has been confirmed by the use of NMR techniques for CPs with less than 60% chlorine by weight (Muir et al. 2000). Chlorine also have less affinity for carbons adjacent to carbons containing chlorine substituents, making products containing vicinal chlorine substituents less common, but these do occur, particularly in the higher chlorinated mixtures.

Even with the restrictions mentioned above there is a vast number of structurally similar components in an industrial CP mixture. For C_{17} CPs with 5 to 17 chlorine atoms there are approximately 53 000 theoretically possible isomers (Muir et al. 2000). A homologue group contains structural isomers, and large numbers of stereo isomers due to the emergence of stereogenic centers in the chlorination process (Muir et al. 2000).

1.3.2 INSTRUMENTAL CHALLENGES

The structural complexity of CPs has consequences for the instrumental analysis. Complete chromatographic separation of the individual components in CP mixtures is unachievable due to the large number of structurally similar CPs, and consequently quantification of individual components in CP mixtures is not possible with the currently available technology. The chromatograms obtained using mass spectrometry (MS) detection tend to appear as broad heaps rather than clearly defined peaks due to the variety of compounds with varying retention times that have identical mass/charge (m/z) (see Figure 4).

The state of the art instrumental analysis of SCCPs and MCCPs is currently based on the application of high-resolution capillary gas chromatography (GC) coupled to high-resolution mass spectrometry (HRMS). Due to the high degree of complexity of CPs, often resulting in fragments with nearly identical m/z in the ion source of the MS, the use of HR rather than low resolution MS is beneficial. The ionization technique best suited for CP analysis is the electron capture negative ionization (ECNI) mode. The ECNI source create thermal electrons by means of a buffer gas. The thermal electrons in turn combine with substituents on the molecules present in the ion source which have high electron affinity, in the case of CPs the chlorine atoms. This gives negatively charged ions in the source.

A commonly used procedure for instrumental analysis and quantification is based on the work reported by Tomy (1997). This procedure relies on the optimization of the $[M-Cl]^-$ ion cluster yield in ECNI, rather than the non-homologue group specific $Cl_2^{-\cdot}$ and HCl_2^- ions. This optimization is done by keeping the ion source temperature relatively low (120℃), as this prevents excessive fragmentation. The exact maas for the most abundant isotope combination of the relevant $[M-Cl]^-$ ions are calculated, and these signals are used for the quantification. This procedure does not give congener specific information, but gives information on the quantities of the different homologue groups present in a sample. Traditionally, HR sector instruments run in single ion monitoring (SIM) mode have been used for CP analysis. Sector instruments are scanning MS instruments that consist of various configurations of electrostatic

(E), and magnetic (B) sectors. The B sectors make it possible to scan over intervals of m/z values, while the E sectors focus the ion beam. As the number of m/z relevant for monitoring is relatively large, it has been shown that it is useful to separate the run into different retention time windows, looking only for the relevant m/z values for that particular retention time, improving the duration of scan time devoted to each homologue group (Tomy et al. 1997).

Techniques employing GCxGC have also to some extent been investigated to deal with the complexity of CP separation, the progress here has however been relatively limited due to the relatively high difficulty of operation (van Mourik et al. 2015).

The number of m/z values to be monitored limits the possibility of detecting SCCPs and MCCPs in the same run on a sector instrument. An alternative approach to CP analysis is Quadrupole time-of-flight (Q-TOF) MS. Q-TOFs are hybrid instruments capable of producing HR spectra. In the Q-TOF, there is a combination of a quadrupole, which can be used as a collision cell or simply an ion guide, coupled to an orthogonal flight path TOF. In Q-TOF instruments, information of all m/z values reaching the detector during the run is collected, so all m/z are available to extract from the instruments software after the sample run. This eliminates the scan time problem, and also makes it possible to detect SCCPs and MCCPs simultaneously, improving instrument run time. This makes the Q-TOF suitable for the analysis of CPs as also shown Gao et al. (2016).

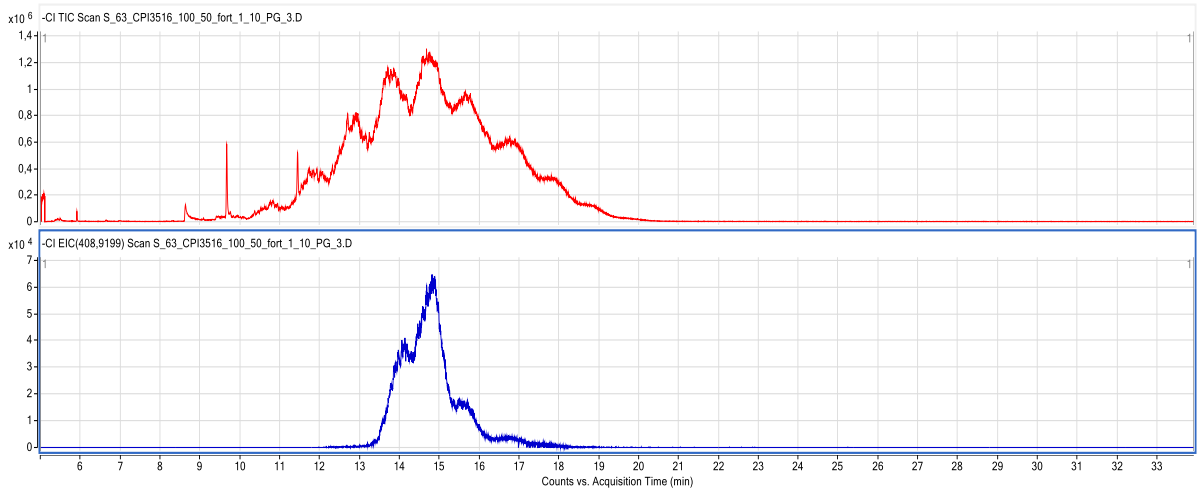


Figure 4: Above: Total ion chromatogram (TIC) of SCCP 63% Cl (by weight) technical standard. Below: Extracted ion chromatogram of mass 408.9199, corresponding to the $C_{12}H_{18}Cl_8$ homologue group, from SCCP 63% Cl technical standard

In Figure 4, two selected chromatograms from a SCCP 63% Cl (by weight) technical standard run on a GC/Q-TOF instrument is shown. The chromatogram above represents the sum of all ions produced from the technical mix, and the chromatogram below represents an extracted ion chromatogram (EIC) of mass 408,9199, corresponding to the $C_{12}H_{18}Cl_7^-$ ion, the $[M-Cl]^-$ ion from the $C_{12}H_{18}Cl_8$ homologue group.

1.3.3 AVAILABILITY OF SUITABLE STANDARDS

Standards labelled with ^{13}C has in recent years become available for use as internal standards in CP analysis, one of which consist of the single component, 1,5,5,6,6,10 hexachlorodecane ($^{13}C_{10}$) (CIL 2017). The same component is also available as an un-labelled standard. The commonly used quantification standards in CP analysis is technical standards in combination with internal standard. Technical standards have a specified concentration of SCCPs or MCCPs, and a specified chlorination degree, while the concentration of individual homologue groups and compounds is unknown. There are no standards available as ^{13}C labelled or un-labelled that contain a well-defined mix with individual components quantified, that is analogous to the industrially produced CP. Un-labeled Standards of single homologue groups and single components are available (Ehrenstorfer 2014). However, with the currently used quantification methods (see B.3 in Appendix B), these standards have limited usefulness. The lack of well-defined standards is problematic when it comes to the reliability of the quantification process. Reth et al (2005) showed that chlorination degree of the technical standard used for quantification relative to the chlorination degree of the sample is important for the validity of the results (Reth et al. 2005). In ECNI MS, the tendency for uptake of thermal electrons in the ion source will vary for CP mixture with varying chlorination degrees due to the different content of high electron affinity groups (Cl atoms). Higher chlorinated mixtures will have a higher tendency to take up thermal electrons than lower chlorinated mixtures, resulting in errors of quantification if the chlorination degree of the sample and the technical standard differs. In their 2005 study, Reth and coworkers showed that the use of three or more CP technical standards and linear regression could be of use for the quantification of SCCPs. The approach was less useful for MCCPs (Reth et al. 2005). Another method of solving the standard problem is by standard matching, where technical standards of varying chlorination degree is mixed in order to match the chlorination degree of the sample as closely as possible (Coelhan et al. 2000). This is however a highly time consuming procedure.

In addition to a lack of suitable standards for quantification, there is also currently (2017) no available certified reference materials (CRMs) for CPs. This makes it more challenging to

assess the method- and laboratory bias of the laboratory procedure in the analysis of CPs, compared to the analysis of most other POPs.

1.3.4 INTERFERENCES

The broad range of retention times on the chromatographic column of CP homolog groups makes interference from coeluting components with similar molecular masses likely (Tomy et al. 1997). Hence, occurrence of other compounds such as PCBs and OC pesticides can be a problem in CP analysis, due to possible overestimation of CPs. These issues can be dealt with in the laboratory, with the application of clean-up techniques such as silica/florisil chromatography, in order to separate the CPs in the sample from potential interfering OCs (van Mourik et al. 2015). The use of high-resolution MS techniques is another possible solution to the problem of interferences (Gao et al. 2016; Tomy et al. 1997). The necessity and applicability of these strategies depend on the sample matrix, and they are often used in combination, i.e. using both separation techniques in the laboratory, and high resolution MS to avoid interferences (Bayen et al. 2006).

In addition to possible interferences from other compounds, CPs have potential to cause self-interference. This is due to the likelihood of getting identical (or nearly identical) m/z from fragmentations of CPs from different homologue groups in the ion source, and different isotopic combinations in the molecules. As with most of the other challenges in CP analysis, this issue is related to the high degree of complexity of CP mixtures (Tomy et al. 1997).

1.3.5 CONTAMINATION ISSUES

As mentioned in section 1, regulation is in place for the production and use of SCCPs in Europe, however, SCCPs can still be present in imported goods from other parts of the world, for example China, or in products produced and bought before regulation came into force. It is therefore likely to find content of SCCPs as well as other CPs in various products and materials especially in indoor environments (see section 2.1.4 for more details). There is little control over the content of CPs in products like plastics and building materials that may be present in indoor environments such as analytical laboratories. Leaching from CP containing materials may occur to indoor air, dust and surface organic films. MCCPs are still unregulated, and is widely used in Europe. It has previously been shown that SCCPs and MCCPs are present in indoor air and house dust in domestic conditions (Fridén et al. 2011). These factors combined make CP contamination of samples during collection, storage, laboratory procedure and analysis a challenge in CP analysis.

1.4 Goals and objectives of master thesis

In this master thesis, the main goal was to study the procedure for the analysis of SCCPs and MCCPs in air samples. The study was performed at the Norwegian Institute for Air Research's (NILU's) laboratories. The goal of the study was approached through the following objectives:

- Investigation of possible contamination sources in the field/laboratory procedure as applied in the routine analysis of air samples for SCCPs and MCCPs at NILU's laboratories
- Assessment of the instrumental performance on a GC/Q-TOF including:
    - Comparing the GC/Q-TOF performance with an established method of HRMS on a sector instrument
    - Investigation of interferences from other OC compounds present in samples
- Testing relevant parameters associated with the method, like recovery, method detection limit, and application of the method to air samples collected at some of NILU's monitoring stations.

2. METHOD AND MATERIALS

In order to achieve the goals and objectives of the thesis, the following experimental design was applied.

2.1 Investigation of contamination sources

The investigation of contamination sources included a range of blank samples as well as materials and instruments used during sampling and analytical steps, together with air and dust samples from the chemical laboratories. Blank samples were prepared and analyzed in order to gain an understanding of any possible contamination pathways in the sampling and analytical procedures for CPs. The blanks were divided in four groups depending on their nature; method blanks, reagent blanks, storage blanks and field blanks. In Table 3, a summary of the types of blanks used, and their purpose can be found.

Table 3: Summary of blank sample types prepared for the study, and their intended purpose.

Category	Subgroup	Purpose
Method blanks	Laboratory blank (including sampling material)	To determine if the laboratory method contributes to CP levels
	Laboratory blank (without sampling material)	To determine if any contribution to the CP levels are matrix or method related (in combination with blank including sampling material)
Reagent blanks		To determine whether chemicals/adsorbents in the laboratory procedure contributes to CP blank values (see 2.1.3)
Storage blanks		To determine if CP blank problems are related to storage conditions (see 2.1.1)
Field blanks		To determine whether the sampling process is related to blank contributions of CPs (see 2.1.2)

Table 4 shows a summary of the tests performed for the investigation of contamination sources, number of parallels performed and reference to the section in the text where further information can be found.

Table 4: Experiments performed to study potential contamination sources.

Tests	Description	Parallels	See section
Storage test of sampling material (PUFs)	PUFs stored at -18°C 5 weeks	3	2.1.1
	PUFs stored at ambient temp 5 weeks	3	
	PUFs stored at -18°C 9 weeks	3	
	PUFs stored at ambient temp 9 weeks	3	
	Method/laboratory blanks (no PUFs)	4	
Field test of sampling material (PUFs)	PUFs stored in cool box (4°C) during transport	3	2.1.2
	PUFs stored in ambient temp during transport	3	
	PUFs given worst case treatment (see 2.1.1.2)	3	
	Method/laboratory blanks (incl. PUFs, same pre-cleaning batch)	4	
	Method/laboratory blanks (no PUFs)	2	
	Air sample from car	1	
Sulfuric acid test	Acid from 1L glass bottle	2	2.1.3
	Acid from 1L plastic bottle	2	
	Acid from flask in daily use	2	
	Method/laboratory blanks (no acid)	2	
Adsorbent test	Newly activated silica/sodium sulfate	4	2.1.3
	Silica/sodium sulfate close to expiry date	4	
Test of materials	Laboratory gloves (new/from lab)	2	2.1.4
	Fume hood bench covers (new/from lab)	2	
	Latex pipette tops (new/from lab)	2	
	Ziploc bag	1	
	Aluminum foil	1	
	Sample vial caps (new/from lab)	2	
	Plastic from micropipette pack (new/from lab)	2	
	Method/laboratory blanks (no “materials”)	2	
Turbovap system	Turbovap cleaned between samples	4	2.1.5
	Turbovap not cleaned between samples	4	
Indoor air	Laboratory used for PUF cleaning/storage	1	2.1.6
	Clean room	1	
	Laboratory used for sample extraction	1	
	Field blank	1	
	Method/laboratory blank (incl. PUF)	1	
	Method/laboratory blank (no PUF)	1	
Dust/organic film	Laboratory used for PUF cleaning/storage	1	2.1.7
	Clean room	1	
	Laboratory used for sample extraction	1	
	Field blank	1	
	Method/laboratory blanks (incl. wipes)	2	

2.1.1 STORAGE TEST OF SAMPLING MATERIAL

In routine laboratory procedures for air samples, the sampling material is stored for varying lengths of time after pre-cleaning and prior to use. The effect of this storage period and the storage conditions on uptake of CPs from packing material and surroundings was investigated by preparing some storage blanks. One set of PUF plugs were stored in ambient temperature covered in one layer of aluminum foil and a Ziploc bag in a plastic storage container, which is the norm for PUF storage when used in the established method. A second set of PUF plugs from the same batch were stored at -18℃. The packing material was identical, one layer of aluminum foil and a Ziploc bag. One lot of each of the stored PUF plugs was extracted after 5 weeks, while a second lot was extracted after 9 weeks in storage. The storage times in the test were representative of storage times for PUF plugs used in routine procedures. The treatment of the storage blanks was from this point identical, following the steps described in sections B.1.3.1, B.1.4, B.1.5, B.1.6 and B.1.7 in Appendix B. Two laboratory blanks, where no PUF sampling material was added to the soxhlet extractor, were run in parallel with these storage blanks.

2.1.2 FIELD TEST OF SAMPLING MATERIAL

In order to monitor potential CP exposure levels for air samples during transport and deployment (mounting/dismounting), a number of field blanks were used. In this study, a test scheme related to field blanks from passive air sampling was devised. The choice of passive over active sampling was based on opportunity and accessibility; see section 1.2 and 2.3.3 for further details. In cooperation with the Norwegian Research Council project; Nordic Exposure Model (NEM), PUF disks were brought out in the field on an 8 day sample collection trip around southern Norway. The PUF disks were briefly exposed to air on a selected sampling location (Ulvik, 07.10.16). This exposure involved removing the aluminum foil wrapped PUF disk from a double Ziploc bag cover, unpacking the aluminum foil, and leaving the PUF exposed to air for approximately one minute to replicate the time required to mount/dismount a sample. This exposure is done in order to evaluate whether the exposed samples were contaminated during deployment. In addition to the deployment exposure, it is also plausible that storage conditions during transport might affect the potential for CP contamination of samples. To study this, some field blanks were stored cold (4℃) during transport in a cool box, while other field blanks were stored at ambient temperature during transport. To represent a worst-case scenario, some field blanks were treated roughly when being exposed (PUF handled directly, using the same gloves as were used for the unwrapping of the aluminum foil/Ziploc cover), and were stored at ambient temperature. Additionally, one PUF disk was mounted in a

passive air sampler and deployed inside the car during the whole sample collection trip. This PUF disk was exposed to the air inside the car environment for 8 days, in order to get an image of the present CP level. On arrival at the laboratory facility after the field trip, all field blanks were stored in freezer conditions (-18℃). All field blanks were from the same batch of cleaned PUF disks, and PUF disks from this batch were also stored (freezer, -18℃) for use as laboratory blanks. Two laboratory blanks without PUF sampling material was also included. The field blanks and laboratory blanks were prepared for analysis in the laboratory according to the steps described in sections B.1.3.1, B.1.4, B.1.5, B.1.6 and B.1.7 in Appendix B.

Field blanks were also collected during the sampling of indoor air, and the sampling of dust/surface organic film. These will be described in more detail in sections 2.1.6 and 2.1.7.

2.1.3 REAGENT BLANKS

Two cleaning steps are used in the routine method for CPs in air and dust samples; 1) cleaning with concentrated sulfuric acid (H_2SO_4) and 2) silica clean-up. Each of these steps were studied with respect to possible contamination.

Acid cleaning using sulfuric acid is done in the laboratory procedure for the analysis of CPs in air and dust samples. This clean-up step is used in order to remove matrix components and acid labile potential interferences from the samples. To investigate whether the concentrated sulfuric acid contributes to blank levels of CPs, the acid process was investigated by adding the acid to approximately 1 mL n-hexane in a glass centrifuge tube. The n-hexane had previously had 50 µL CP I internal standard (see section B.1.1 for details on CP I) added. The test was subsequently performed as the acid cleaning step described in section B.1.4 in Appendix B, with the acid changed four times in total. This acid test was performed using concentrated sulfuric acid available in 1) 1L glass bottles, 2) 1L plastic bottles (see section B1.1 in Appendix B for details), and from 3) an Erlenmeyer flask containing sulfuric acid in daily use, with content originating from the glass bottle. To evaluate if there were any contributions of CPs in the solvent, two laboratory blanks with no acid added was included with the (acid) reagent blanks (see Table 4). Each of the tests, including laboratory blanks, was done in two parallels. After acid treatment, the test samples were treated according to sections B.1.6 and B.1.7 in Appendix B.

Silica cleanup is performed in order to remove any polar impurities in the samples for analysis of CPs. Polar impurities can originate from the acid cleanup treatment, in the form of broken down polymeric material, or breakdown products from other acid labile organic compounds

that remain in the organic phase. In order to establish if the silica contributes to CP levels in samples, either by CP residue from production or packaging of the silica, or from the laboratory environment with repeated opening and closing of the storage container, a test was devised. Two portions of silica were tested, one near its expiry date, one recently activated (see section B.1.2 in Appendix B, and Table 4). These two portions of silica were tested for CP content by creating test samples with approximately 0.5 mL pure solvent (n-hexane) added 50 µL CP I internal standard. The solvent/internal standard mix was transferred to a silica column packed as described in section B.1.5 in Appendix B, using silica from the two portions. Following this, the test samples were treated according to sections B.1.6 and B.1.7 in Appendix B.

2.1.4 MATERIALS USED IN THE LABORATORY

CPs are used in many indoor related materials, as plasticizers in plastics and rubbers, as additives in paints, adhesives and sealants, and as flame retardant in textiles and polymers. The use in plastics and rubbers as plasticizers makes packing material, vial caps, gloves, and other common material used in the field, during transport/storage and in the laboratory possible sources of CP contamination in samples. It was therefore of interest to investigate the CP content in plastic and rubber materials used in the lab and in the field, in order to evaluate the possible contributions to sample CP quantities from contact with these materials.

The laboratory procedure for testing the CP content in materials used in the lab involved using ultrasonic extraction for 10 minutes with no repetitions, as described in section B.1.3.2, following the steps described in sections B.1.4, B.1.5, B.1.6 and B.1.7 in Appendix B. Materials tested in this way was 1) Ziploc bags that are used for storage of PUF disks and plugs before and after samples are collected, 2) lab gloves that are in direct contact with the PUF at several points in the procedure, 3) vial lids including septum, 4) plastic backed paper covering for fume hoods, 5) latex tops used on Pasteur pipettes and 6) plastic material from the packaging of micropipettes. In addition to plastic materials, the test also included 7) a piece of aluminum foil. Two laboratory blanks (no “material”) were prepared, which consisted of 10% diethyl ether in n-hexane with CP I internal standard added, in identical glass sample vials. Further treatment of the laboratory blanks was identical to the test samples. See Table 4 for details on the materials test.

2.1.5 THE TURBOVAP SYSTEM

All samples in the study was reduced in volume by use of a TurboVap system, an evaporation unit, which was considered to be a likely source of cross contamination in the laboratory. Cross contamination is conceivable due to residues from one sample remaining in the condenser part

of the system, and transferring to the next sample that is volume reduced. A test setup was devised in order to test the relevance of cross contamination with regard to CP analysis. In this setup 200 mL 10% diethyl ether in n-hexane was spiked with 250 ng SCCP from a technical standard (51% Cl by weight) and 250 ng from a MCCP technical standard (52% Cl by weight). The solutions were reduced to 0.5 mL in each of the two compartments of the TurboVap, and discarded. One compartment of the TurboVap was subsequently cleaned using acetone, while the other was left uncleaned. Two TurboVap glasses were prepared with approximately 200 mL of 10% diethyl ether in n-hexane, and 20 µL of the CP I internal standard. These were reduced in volume to 0.5 mL, one using the cleaned compartment, one using the uncleaned compartment of the TurboVap system. This was repeated in 4 parallels, before the test samples were prepared for instrumental analysis as described in section B.1.7 in Appendix B.

2.1.6 INDOOR AIR SAMPLES

To assess the possibility of CP sample contamination from the indoor air in the laboratory, due to ubiquitous usage of CPs in indoor related materials (see section 2.1.4), PUF-based PAS were deployed in NILU's facilities. The PAS used indoors was a modified version of the PAS depicted in Figure 3, where the lower metal bowl is removed. PAS were deployed for 96 days in three rooms, 1) a laboratory used for storage, cleaning and packing of PUF plugs/disks, 2) a clean room (class 100000 parts/foot^3), and 3) a laboratory used for sample extraction. After collection, the samples were stored in a freezer at -18℃. A field blank was collected at the time of sample collection, and stored with the indoor air samples. A laboratory blank including PUF disk and a laboratory blank without PUF was run in parallel with the samples. The samples and blanks were treated according to the steps described in sections B.1.3.1, B.1.4, B.1.5, B.1.6 and B.1.7 in Appendix B.

As part of a separate study, the indoor air samples were used to determine the content of some other POPs present in indoor air. Therefore, in addition to 50 µL of the CP I internal standard, these samples also had 20 µL of the POP I, PBDE I and the new-bromine standards added. The content of these standards is described in Tables B3 to B5 in Appendix B.

2.1.7 DUST/SURFACE ORGANIC FILM SAMPLES

In addition to the indoor air samples, dust/organic film samples were collected from horizontal surfaces in the same locations (see section 2.1.6 and Table 4). Dust/organic film samples were collected using wipes wetted with isopropanol, and the surface area of the sampled areas were measured. After collection, the dust/organic film samples were stored in a freezer (-18℃). A

field blank was included, and stored with the samples. Additionally, two laboratory blanks consisting of new unused wipes were extracted in parallel with the samples. Extraction of the samples was done using ultrasonication as described in section B.1.3.2 in Appendix B, for 15 minutes in three repetitions. Further, the extracts were treated as described in sections B.1.4, B.1.5, B.1.6 and B.1.7 Appendix B.

As part of a separate study, the dust/organic film samples were used to determine the content of some other POPs present in the indoor environment. Therefore, in addition to 50 µL of the CP I internal standard, these samples also had 20 µL of the POP I, PBDE I and the new-bromine standards added. The content of these standards is described in Tables B3 to B5 in Appendix B.

2.1.8 STATISTICAL ANALYSIS ON HOMOLOGUE GROUP DATA

The relative abundances of CP homologue groups in air samples can potentially be of use in source elucidation (Marvin et al. 2003; Wang et al. 2013). In addition, it is possible that homologue group distributions can give indications of sources of CP contamination in blank samples. The number of homologue groups included in this study (39, see Table A9 and A10 in Appendix A), and a large number of samples and blanks, makes visual inspection looking for similarities in homologue group data challenging. In order to detect similarities in data for the relative homologue group abundances using statistics, a hierarchical clustering analysis was performed, using the statistical software R studio. The clustering analysis included the 84 samples and blanks described in table 4, in addition to eight air samples and blanks described in section 2.3.3.

2.2 Assessment of instrumental performance

At NILU, the instrument of choice for CPs analysis in air samples has traditionally been a GC/HRMS, where the MS is a Waters Autospec sector instrument with EBE geometry. This is associated with some limitations, as mentioned in section 1.3.2, so it was of interest to transfer the instrumental part of the analytical procedure from the Autospec to a modern Agilent GC/Q-TOF instrument. To assess the instrumental performance of the GC/Q-TOF, a comparison test with the Autospec was performed. In addition, and a test investigating the potential for OC interference in the instrumental analysis was carried out. A summary of these tests can be found in Table 5.

Table 5: Tests performed for instrumental assessment

Tests	Description	Parallels	See section
Comparison test	AMAP air samples	4	2.2.1
	Interlaboratory SCCP solution	6	
	Interlaboratory dust extract	6	
	Interlaboratory sediment extract	6	
	Interlaboratory biota extract	6	
Interference test	CP technical standard + Dechlorane solution	1	2.2.2
	CP technical standard + PCB solution	1	
	CP technical standard + DDT solution	1	
	CP technical standard + pesticide solution	1	
	CP technical standard identical to above	1	

In addition to the testing done to assess instrumental performance, some adaptations of the quantification method were performed. The non-ideal chromatographic peaks produced by CPs (see Figure 4) makes automatic integration and quantification challenging. An automated procedure in Agilent's quantification software MassHunter quant was set up. The procedure involved instructing the software to integrate the signal in a pre-programmed retention time interval for each of a set of pre-programmed masses representing relevant homologue groups, as previously done by Gao et. Al. (2016). The equation used in the quantification process is described in appendix B.

The ions used for quantification of relevant homologue groups was the $[M-Cl]^-$ ion. However, in the instances where the $[M-HCl]^-$ ion was more prominent, this was used. The exact masses of the $[M-Cl]^-$ and the $[M-HCl]^-$ ions were determined, along with their isotopic abundances. A table of quantification ions, exact masses, isotopic abundances, retention times and integration intervals can be found in Tables A9 and A10 appendix A

2.2.1 COMPARISON STUDY

To confirm comparable performance of the GC/Q-TOF instrument to the established method of analysis on the Autospec instrument, a series of samples was run on both the instruments for comparison purposes. The air samples collected at NILU's monitoring stations (section 2.3.3) were intended for this purpose. However, due to unforeseen technical difficulties with the Autospec instrument, alternative arrangements for the comparison testing became necessary. These circumstances led to only SCCPs (not MCCPs) being included in the comparison study.

A set of samples prepared for an interlaboratory study on SCCPs previously analyzed using the Autospec, was used as replacement samples for the comparison. The samples originate from a variety of matrices; 1) a solution containing an unknown quantity of SCCPs, 2) a dust extract, 3) a sediment extract and 4) a biological extract. Two aliquots of each matrix were analyzed in triplicate. Air samples were not included in the interlaboratory set, so in addition to the interlaboratory samples, four air samples from the Arctic Monitoring and Assessment Program (AMAP) previously run on the Autospec were re-analyzed using the GC/Q-TOF.

2.2.2 INTERFERENCES

The laboratory procedure employed to extract and clean air samples does not to any significant degree remove other SVOCs with similar physical/chemical properties. This is due to the fact that many of these compounds are being analyzed for from the same sample in the routine air monitoring samples, and hence it is undesirable to remove them. Fractioning the sample, and separate analysis of the fractions is a possible strategy, however this it is difficult due to the wide range of physical/chemical properties of CPs, as can be seen form Figure 2 and Table 2. This means that any potential interferences need to be dealt with in the instrumental part of the analytical process. The Q-TOF instrument is capable of producing mass spectra with a resolution around 16 000 FWHM (Full with half measure), which in most cases should be adequate. This was tested in the following fashion:

Standard solutions of several ^{12}C and ^{13}C POPs were run on the instrument in order to assess their potential interference with the masses and retention times used for the CP quantification. Five mixtures of standard solution were prepared, where four contained potential interferences. The potential interference standard solutions included in the mixtures were 1) a Dechlorane solution containing six ^{12}C and one ^{13}C component, 2) a PCB solution containing 15 ^{13}C PCB congeners and 32 ^{12}C PCB congeners, 3) a DDT solution containing three ^{13}C compounds from the DDT group, and three pairs of ^{12}C isomers from the DDT group, and 4) a pesticide solution containing 24 ^{13}C pesticides, one ^{2}H pesticide, and 31 ^{12}C pesticides. The exact content of these standard solutions can be found in Tables B6-B9 in Appendix B. Mixtures containing 20 µL of standard solutions one to four, 20 µL of SCCP technical mixture (51% Cl by weight), 20 µL MCCP technical mixture (52% Cl by weight), 20 µL of CP I internal standard and 50 µL iso-octane was prepared. In addition, a fifth mixture was prepared, which contained no potential interference standard solution, but an additional 20 µL of iso-octane to achieve equal volume. The quantification procedure for SCCPs and MCCPs was applied to the mixtures, to see if any significant difference could be found in the results.

2.3 Assessment of CP method

In order to assess aspects of the entire method, such as recovery of CPs, and the methods application to air samples were investigated. In addition, the method detection limit (MDL) was determined. Table 6 shows a summary of the recovery tests and the air samples collected at three of NILU's monitoring stations. The MDL was based on blanks from a variety of tests performed for the study. These are described further in section 2.3.2.

Table 6: Test performed to assess the method.

Tests	Description	Parallels	See section
Recovery test	PUFs spiked with CP technical standard	6	2.3.1
	CP mixture identical to above	1	
Air samples	Andøya	2	2.3.3
	Birkenes	2	
	Zeppelin	2	
	Method/laboratory blank (incl. PUF)	1	
	Method/laboratory blank (no PUF)	1	

2.3.1 RECOVERY

The recovery calculation of CPs after the laboratory procedure is based on the ratio of internal standard and recovery standard in the sample, compared to the same ratio in a quantification standard consisting of a known amount of both internal standard and recovery standard. As the recovery rate is based on one single CP component, it was of interest to assess whether the different SCCP and MCCP homologue groups have similar levels of recovery from the laboratory procedure. PUF plugs were spiked with 100 µL technical mixture of SCCPs (51% chlorine by weight), and 100 µL technical mixture of MCCPs (52% chlorine by weight), in addition to 20 µL CP I internal standard. The PUF plugs were subsequently extracted using soxhlet as described in section B.1.3.1 in Appendix B, and cleaned using acid and silica as described in sections B.1.4, B.1.5 and B.1.6 in Appendix B. The recovery test samples were volume reduced using N_2 gas to 120 µL, before addition of 20 µL Tetrachloronaphthalene (TCN) as recovery standard. A quantification standard for the recovery test samples was prepared by mixing 100 µL of each of the technical mixtures mentioned above, and 20 µL of

CP I internal standard. The quantification standard mix was volume reduced using N_2 gas to 120 µL, and given 20 µL TCN as a recovery standard. By this, the quantification standard was identical to the recovery test samples minus the extraction and cleanup procedure. The homologue group distribution in the recovery test samples were compared to the homologue distribution in the quantification standard.

2.3.2 METHOD DETECTION LIMIT

The determination of MDL for analysis of SCCPs and MCCPs in air samples was based on all sample blanks and field blanks that contained PUF sampling material analyzed, having removed extreme values. The MDL for air samples is not necessarily applicable to all tests performed in this study where the PUF sampling material is not included, i.e. the materials test, the Turbovap test, the reagent blanks and the dust/organic film samples. Therefore, a detection limit (DL) based on all solvent blanks (excluding extreme values) was determined and used to assess the relative CP levels in these samples. As the relative levels of CPs in blank samples is of interest in this study (and the blank samples are the basis of the detection limits) values below the detection limits are generally reported in the results for comparison purposes.

2.3.3 AIR SAMPLES

To assess the methods application to real world samples, six high volume air samples were collected and analyzed for content of SCCPs and MCCPs. The six samples were collected at NILU's background air monitoring observatories at Birkenes (South-Norway), Zeppelin (Svalbard) and Andøya (North-Norway). The observatories provide air monitoring data for the national monitoring program of long-range transported air pollutants conducted by NILU for the Norwegian Environment Agency and the Ministry of Climate and Environment (NILU 2017).

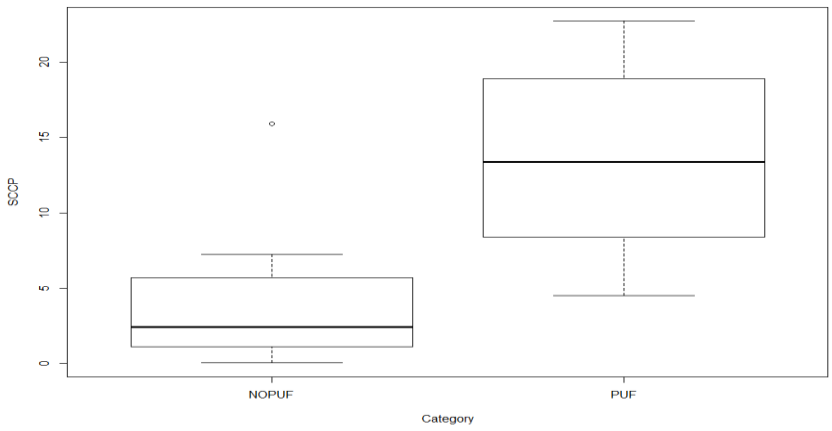
The air samples were collected using high volume active air samplers (Digitel) fitted with glass fiber filters (GFF) and PUF plugs. The sampling time was 48 hours, and the total sample volume were ~1300 m^3 for all samples, following the sampling protocol for the national monitoring program. After arrival at NILU, the samples were stored at fridge temperatures (0-4℃) until extraction. A laboratory blank including GFF and PUF, and a laboratory blank without PUF sampling material was run in parallel with the samples. In the laboratory, samples and blanks were extracted using soxhlet, as described in section B.1.3.1 in Appendix B. Further, the extracts were treated as described in sections B.1.4, B.1.5, B.1.6 and B.1.7 in Appendix B.

Field blanks from active samplers are routinely collected in ongoing monitoring programs by placing GFF holder and PUF glass container in the sampling device without activating the pumps. Otherwise they are treated identically to the exposed samples. No field blank of this type was available for analysis along with the air samples.

3. RESULTS AND DISCUSSION

3.1 Blank levels and detection limits

Two types of laboratory blanks were included in the study. Laboratory blanks including PUF/GFF or PUF sampling material were used along with air samples, indoor air samples and field blanks. Laboratory blanks without PUFs were used along with the storage test, the field blanks, materials test, indoor air samples, dust/organic film samples and air samples. The laboratory blanks containing PUF material generally showed a higher CP level than the laboratory blanks without PUF material (Figure 5). The levels of SCCPs and MCCPs in the laboratory blanks including PUFs range from 4.5 to 22.7 ng/sample (average 13.6 ng/sample, median 13.4 ng/sample) and 0.1 to 3.9 ng/sample (average 0.9 ng/sample, median 0.3 ng/sample) respectively. The SCCP and MCCP levels in the laboratory blanks without PUFs range from 0.02 to 15.9 ng/sample (average 4.5 ng/sample, median 2.4 ng/sample), and 0.02 to 1.7 ng/sample (average 0.3 ng/sample, median 0.02 ng/sample) respectively. The results are presented in box and whisker plots in Figure 5, and in Tables 7 and 8. The numbers used to create box and whisker plots are the median of the data (line inside the box), the lower and upper quartiles (25% and 75%, the upper and lower sections of the box). The whiskers represent the minimum and maximum values. Outliers are marked as points outside the whiskers.



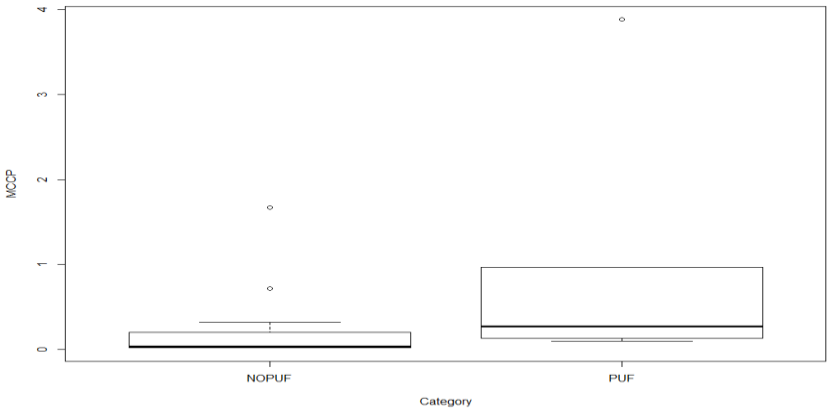


Figure 5: Above: Box and whisker plot showing SCCP results from laboratory blanks including sampling material (PUF), and laboratory blanks without PUF sampling material (NOPUF). Unit for SCCP is ng/sample. Below: Box and whisker plot showing MCCP results from laboratory blanks including sampling material (PUF), and laboratory blanks without PUF sampling material (NOPUF). Unit for MCCP is ng/sample.

Table 7: Summary of SCCP results from tests performed to investigate contamination sources. n = number of samples

	n	Average (ng/sample)	Range (ng/sample)	Median (ng/sample)	St.dev. (ng/sample)	Average concentration
Lab blanks (PUF)	6	13.6	4.5-22.7	13.4	7.0	-
Lab blanks (no PUF)	12	4.5	0.02-15.9	2.4	4.4	-
Storage blanks	12	9.0	1.9-29.4	4.9	8.4	-
Field blanks	9	17.7	5.9-33.5	17.7	7.8	-
Acid test	6	4.1	2.3-6.8	3.8	1.6	-
Adsorbent test	8	0.3	0.2-0.4	0.4	0.08	-
Materials test	12	345	0.3-3272	13.8	933	-
Turbovap test	8	2.1	0.5-7.5	0.6	2.7	-
Indoor air	3	4098	546-7461	4286	3462	30.6 ng/m^3
Dust/organic film	3	3729	118.0-6500	4569	3273	1604 ng/m^2
Air samples	6	181	56.3-336	167	116	0.1 ng/m^3

Table 8: Summary of MCCP results from tests performed to investigate contamination sources. n = number of samples

	n	Average (ng/sample)	Range (ng/sample)	Median (ng/sample)	St.dev. (ng/sample)	Average concentration
Lab blanks (PUF)	6	0.9	0.1-3.9	0.3	1.5	-
Lab blanks (no PUF)	12	0.3	0.02-1.7	0.02	0.5	-
Storage blanks	12	7.1	0.02-56.9	1.5	16.1	-
Field blanks	9	0.6	0.4-1.1	0.5	0.2	-
Acid test	6	0.02	0.01-0.04	0.02	0.008	-
Adsorbent test	8	0.01	0.001-0.1	0.01	0.002	-
Materials test	12	61.3	0.1-705	0.8	203	-
Turbovap test	8	0.003	0.001-0.01	0.003	0.002	-
Indoor air	3	20.2	8.6-35.0	16.9	13.5	0.2 ng/m^3
Dust/organic film	3	1482	173-3379	894	1682	556 ng/m^2
Air samples	6	67.4	0.6-342	5.5	136	0.06 ng/m^3

MDL for the detection of SCCPs and MCCPs in air samples was determined using the laboratory blanks including PUFs in addition to the field blanks, and the storage blanks. The level of SCCPs in these samples is shown in Figure 6 (above), in the PUF category column, and the level of MCCPs in these samples is shown in Figure 6 (below), in the PUF category column. The method for setting the MDL was based on the EMEP manual, where three times the standard deviation of blank values are added to the average value of blanks (after removal of extreme values) (Berg et al. 2002). The MDL was found to be 38.6 ng/sample (29.7 pg/m^3) for SCCPs, and 10.6 ng/sample (8.1 pg/m^3) for MCCPs The values in parenthesis are based on approximate sampled volume in AAS, 1300 m^3. Several outliers were detected in the data for the laboratory blanks, field blanks and storage blanks, these are marked as points outside the whiskers in Figure 6 (above and below, category PUF). For SCCPs, the data point at 148 ng/sample was excluded from the MDL calculation. For MCCPs there were many outliers

detected. Not all of these were excluded from the MDL calculation as it was desirable to contain the variation in blank values in the MDL. Only the point at 56.9 ng/sample was excluded.

In order to assess the relative CP levels in blank samples and tests performed where no PUF sampling material was included, a detection limit (DL) based on the laboratory blanks without PUF sampling material, and the reagent blanks was determined. The SCCP level in these blanks is illustrated in Figure 6 (above, category NOPUF), and the MCCP level in these blanks is illustrated in Figure 6 (below, category NOPUF). This DL was found to be 8.8 ng/sample for SCCPs, and 0.7 ng/sample for MCCPs. Extreme values removed for the calculation of this DL was three SCCP data points (15.9, 15.9 and 17.5 ng/sample, marked as outliers in Figure 6, above, category NOPUF).

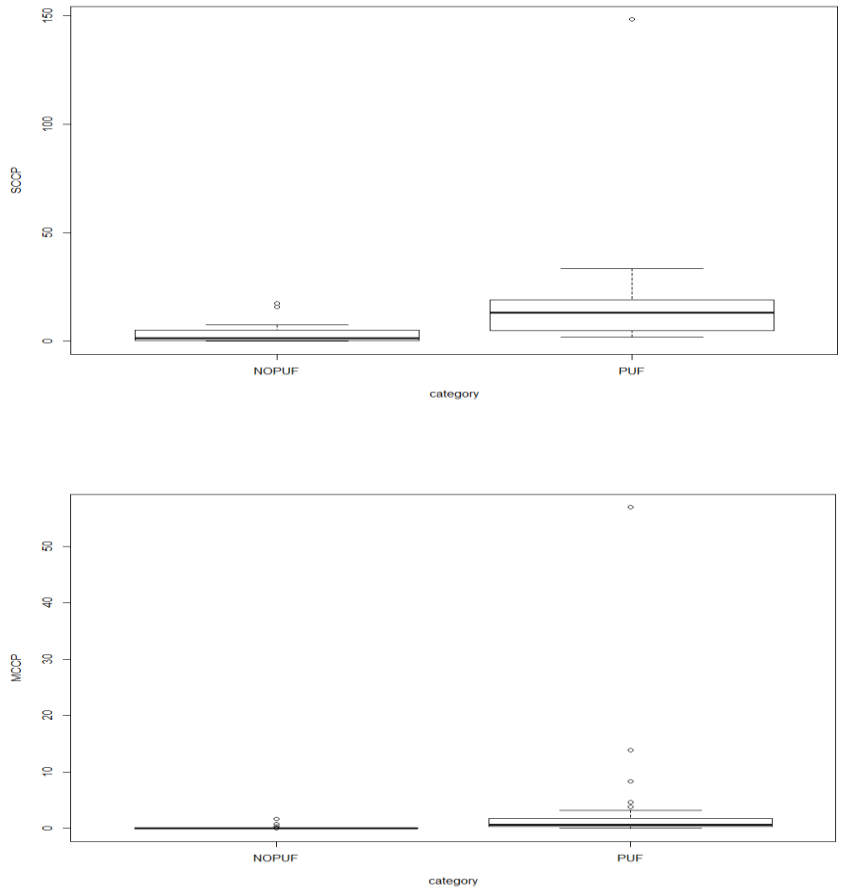


Figure 6: Above: Box and whisker plot showing the SCCP results from blank samples (laboratory, storage and field blank) in the study with sampling material (PUF), and blank samples (laboratory and reagent blank) in the study without PUF sampling material (NOPUF) Unit for SCCP is ng/sample. Below: Box and whisker plot showing the MCCP results from all blank samples in the study with sampling material (PUF), and all blank samples in the study without PUF sampling material (NOPUF). Unit for MCCP is ng/sample.

The standard approach to determining instrumental limit of detection (LOD) is by integrating the noise in the chromatogram next to the peak of interest. This is not a useful approach in CP analysis using GC/Q-TOF, as the peaks of interest are not ideal, and the baseline noise is ~zero (see Figure 4). As no meaningful method of setting the instrumental LOD in CP analysis could be determined, this has been excluded from the study.

Figure 7 and 8 show examples of typical homologue group distribution in blanks including PUFs, and blanks withot PUFs respectively. Generally, SCCPs domonated over MCCPs. The SCCP distributions were dominated by the C_{11} groups, and the MCCP distributions were dominated by the C_{14} groups. The Figure headings contains the SCCP and MCCP content given in ng/sample, to enable assessment of the relative SCCP/MCCP level in the sample.

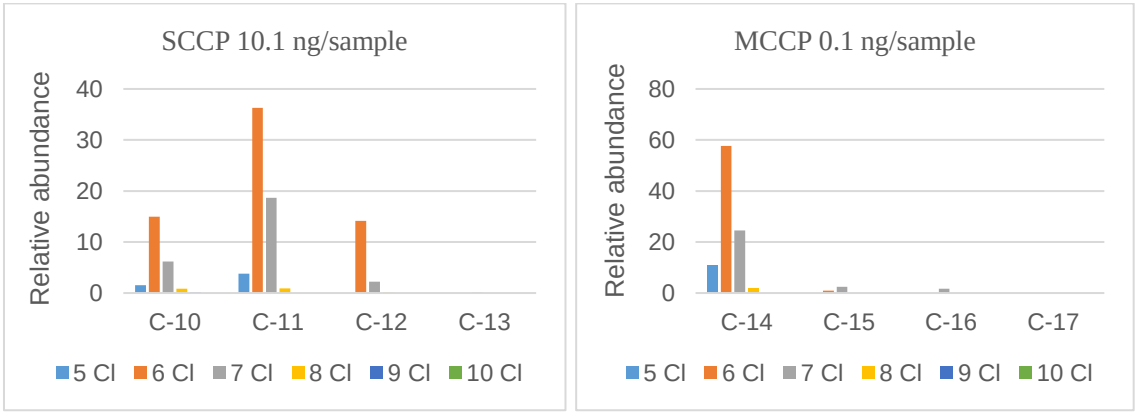


Figure 7: Typical homologue group distribution in laboratory blank including sampling material (PUF). From a laboratory blank from the field tests. (Lab blank (PUF) P4)

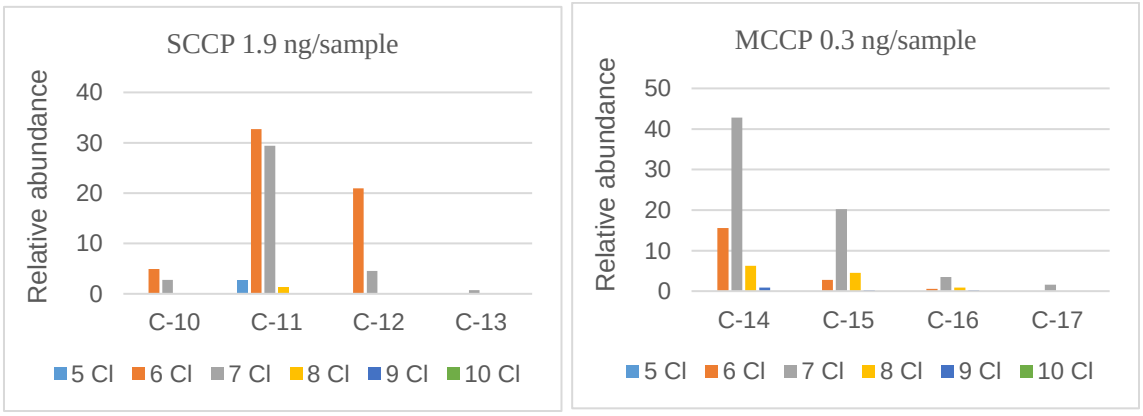


Figure 8: Homologue group distribution in laboratory blank without PUF sampling material. From a laboratory blank from the field test. (Lab blank (no PUF) P1)

3.2 Investigation of contamination sources

3.2.1 STORAGE BLANKS

The test of storage conditions and times is described in section 2.1.1, and Table 4. The levels of SCCPs and MCCPs in the storage blanks range from 1.9 to 29.4 ng/sample (average 9.0 ng/sample, median 4.9 ng/sample) and 0.02 to 56.9 ng/sample (average 7.1 ng/sample, median 1.5 ng/sample) respectively (Tables 7, 8, and A1 in Appendix A). The levels of SCCP was similar to the SCCP levels in the laboratory blanks including PUFs. The levels of MCCPs were above the level in laboratory blanks in four cases, two of which were stored at ambient temperature, and two stored in freezer conditions. The total CP content were highest in blanks stored for long time in ambient temperature and for short time in cold temperature (Figure 9). This inconsistent result indicates that the storage time and temperature do not have a clear effect on blank levels.

One of the storage blanks (Freezer P1, see Table A1 in Appendix A) showed particularly high levels of MCCPs, at 56.9 ng/sample.

Storage blanks were analyzed using a two-factor analysis of variance (ANOVA) model, with total CP content as response variable, and storage time (short or long) and storage conditions (ambient or freezer) as factors. The results show no significant difference in CP levels for PUF sampling material stored in freezer condition or at ambient temperature ($p>0.05$). No significant difference was found for storage times (5 weeks vs. 9 weeks) either ($p>0.05$). Further details on statistical testing on these samples can be found in section C.1 in Appendix C. Storage temperature and storage time (up to nine weeks) do not significantly affect the blank levels compared to laboratory blanks.

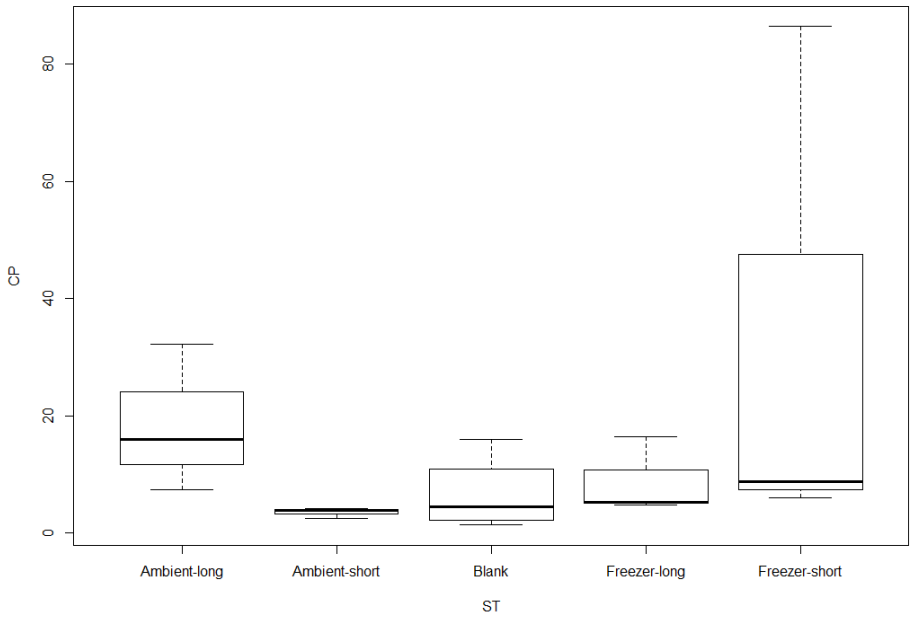


Figure 9: Box and whisker plot representing levels of sum SCCPs and MCCPs (total CP content) in storage blanks. The storage blanks are grouped according to Table 4, labeled by conditions (ambient or freezer) and storage time (long or short), and laboratory blanks (labeled as blanks in the plot). Unit for CP is ng/sample.

3.2.2 FIELD BLANKS

The test involving field blanks is described in section 2.1.2, and Table 4. The levels of SCCPs and MCCPs in the field blanks range from 5.9 to 33.5 ng/sample (average 17.7 ng/sample, median 17.7 ng/sample) and 0.4 to 1.1 ng/sample (average 0.6 ng/sample, median 0.5 ng/sample) respectively (Tables 7, 8, and A2 in Appendix A).

The field blanks were analyzed using ANOVA, with total CP content as response variable, and with treatment (ambient, cold, worst case or blank) as a factor. The p-value for the field blanks stored at ambient temperature was <0.05, indicating significant difference from at least one of the other groups, see Figure 10. The lower CP values for the worst-case group suggest that treatment in the field (precautionary vs. clumsy) is of little relevance for CP blank levels. Instead the temperature during storage/transportation seem to be of higher importance. The higher levels in the ambient samples could be a consequence of contamination from the car environment, as the cold stored samples had an additional barrier in form of the closed cool box. The worst-case group was however stored under identical conditions to the ambient group. This group does not differ significantly from the cold group, making firm conclusions difficult.

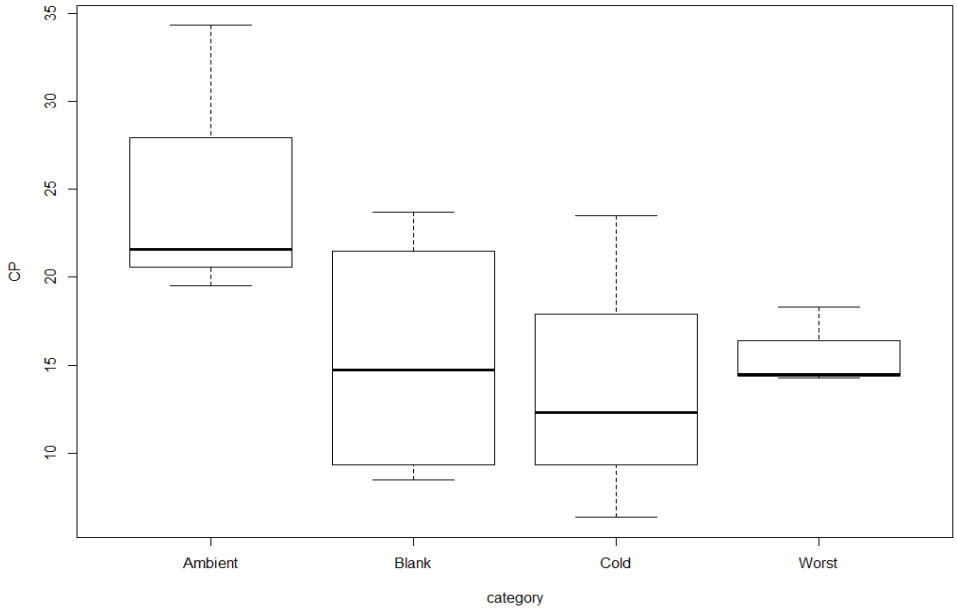


Figure 10: Box and whisker plot representing levels of sum SCCPs and MCCPs (total CP content) in the field blanks grouped according to Table 4, with ambient storage temperature (ambient), laboratory blanks incl. PUF (blank), cold storage temperature (cold) and worst-case conditions (worst). Unit for CP is ng/sample.

Data from the PUF passive air sampler deployed in the car was converted from ng/sample to ng/m^3 using an uptake rate of 1.4 m^3/day, and a sampling time of 8 days. The uptake rate used is based on average uptake rates of PCBs in PUF based PAS (Bohlin et al. 2014), as no equivalent estimate could be found for CPs. The car environment sample showed levels well above the laboratory and field blanks. SCCPs was found at 29.3 ng/m^3 (328 ng/sample), and MCCPs at 0.02 ng/m^3 (0.2 ng/sample) (Tables 7, 8, and A2 in Appendix A).

3.2.3 REAGENT BLANKS

The tests of reagents for CP content are described in section 2.1.3 and Table 4. The levels of SCCPs in the acid tests range from 2.3 to 6.8 ng/sample (average 4.1 ng/sample, median 3.8 ng/sample). The MCCP levels range from 0.01 to 0.04 ng/sample (average 0.02, median 0.02) (Tables 7, 8, and A3 in Appendix A). These levels are below the DL (based on no PUF blanks), 8.8 ng/sample for SCCPs, and 0.7 ng/sample for MCCPs. This suggests that the acid is not a source for CP contamination.

Interestingly, the corresponding laboratory blank samples where no acid was added, had SCCP levels of 15.9 and 17.5 ng/sample, see Figure 11. MCCPs were not found in the laboratory blanks at significant levels (0.02 and 0.03 ng/sample). The laboratory blank samples were treated identically to the acid test samples, with exception of the addition of acid. A suggested explanation for the higher SCCP levels in the laboratory blanks can be an acid labile interference that is removed in the acid samples, and remains in the non-acid treated laboratory blanks.

The acid test was performed in 2 parallels. The results are presented in a box plot (Figure 11) showing the median CP level (line in the box), and the CP level of each of the two parallels (the upper and lower edge of the box).

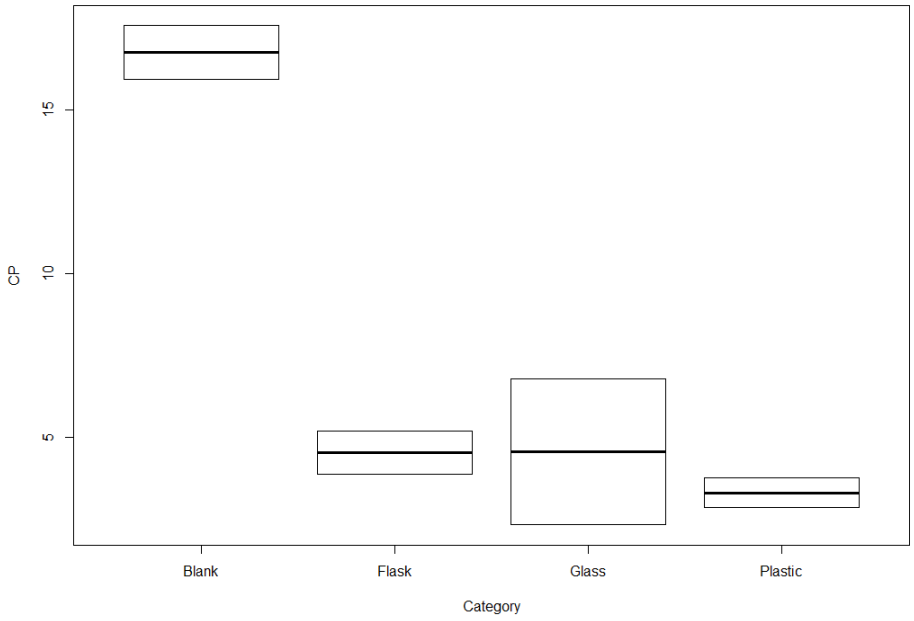


Figure 11: Boxplot representing levels of sum SCCPs and MCCPs (total CP content) in the acid test samples grouped according to Table 4, with laboratory blanks (blanks), acid from flask (flask), acid from glass bottle (glass) and acid from plastic bottle (plastic). Unit for CP is ng/sample.

The levels of SCCPs and MCCPs in the adsorbent tests range from 0.2 to 0.4 ng/sample (average 0.3 ng/sample, median 0.4 ng/sample) and 0.001 to 0.1 ng/sample (average 0.01 ng/sample, median 0.01 ng/sample) respectively (Tables 7, 8, and A4 in Appendix A). The test samples from recently activated adsorbents, and the test samples from adsorbents near their expiry date were all below the DL, as described in section 3.1. This suggests that the silica

adsorbent is not a source for CP contamination. Figure 12 shows a box and whisker plot of the adsorbent test results.

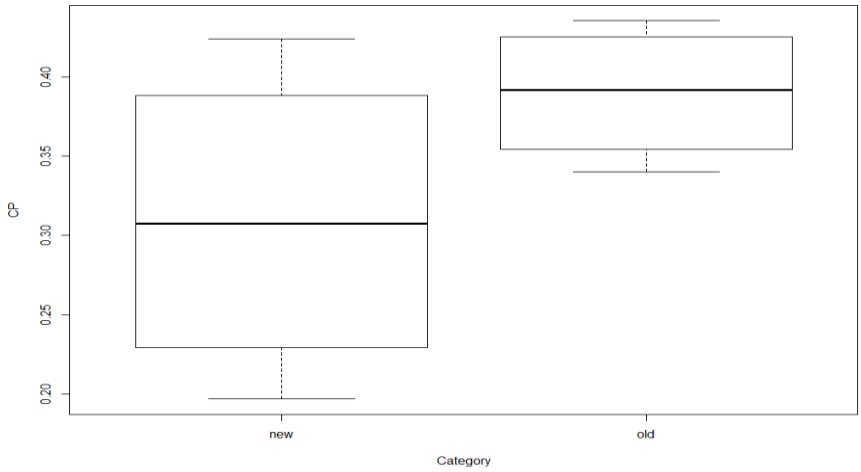


Figure 12: Box and whisker plot representing levels of sum SCCP and MCCP (total CP content) in the adsorbent tests, grouped according to Table 4, with newly activated silica (new) and silica near expiry date (old) Unit for CP is ng/sample.

3.2.4 TEST OF MATERIALS USED

Results from the tests of SCCP and MCCP content in laboratory materials are presented in Figure 13. The test is described in section 2.1.4 and in Table 4.

The results from the test performed to assess the presence of CPs in laboratory materials are of a more qualitative than quantitative nature as the amount of the different materials are variable. The results show a large variability in SCCP and MCCP levels in the included materials, from 0.3 to 3272 ng/sample (average 345 ng/sample, median 13.8 ng/sample), and 0.1 to 705 ng/sample (average 61.3, median 0.8 ng/sample) respectively (Tables 7, 8, A5 in Appendix A, Figure 13). Levels of SCCPs and MCCPs were well above DL in the gloves used in the laboratory procedure. In addition, large amounts of SCCPs and MCCPs were found in a used latex top for Pasteur pipettes from the laboratory where samples are prepared. An un-used latex top was also tested for CP content, and this showed lower levels, in addition to a different distribution of homologue groups, see Figures 14 and 15. This suggests that the levels in the latex pipette top do not arise from the latex material in itself, but from contamination on the used latex top. The results for the gloves indicates that there might be CPs in the material itself as the levels were higher in the new gloves (taken from an un-opened package) than the old

gloves (taken from opened package in the laboratory). The results of the test of laboratory related materials suggest that the gloves might be a source of contamination and the storage and use of latex pipette tops also can contribute to contamination of samples.

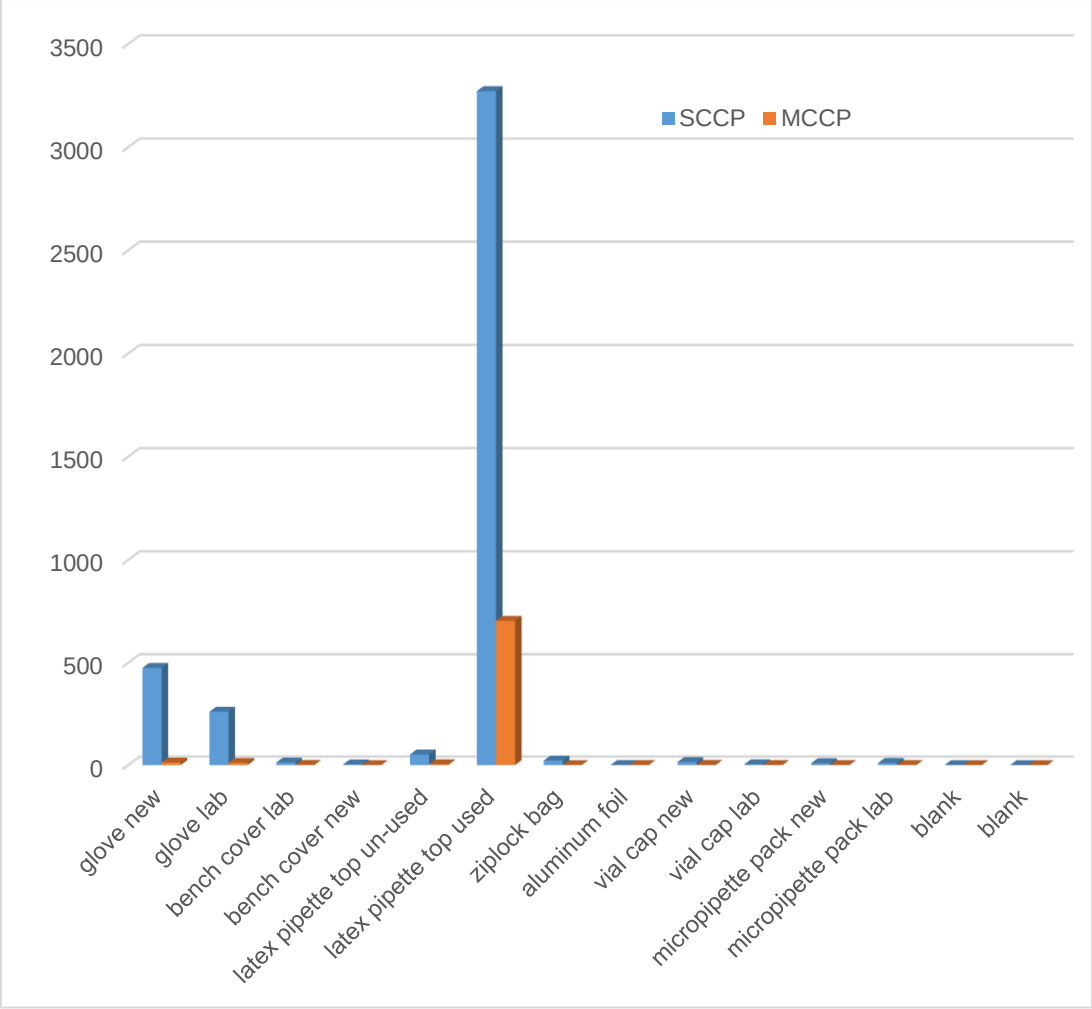


Figure 13: Levels of SCCPs and MCCPs in the test of laboratory related materials.

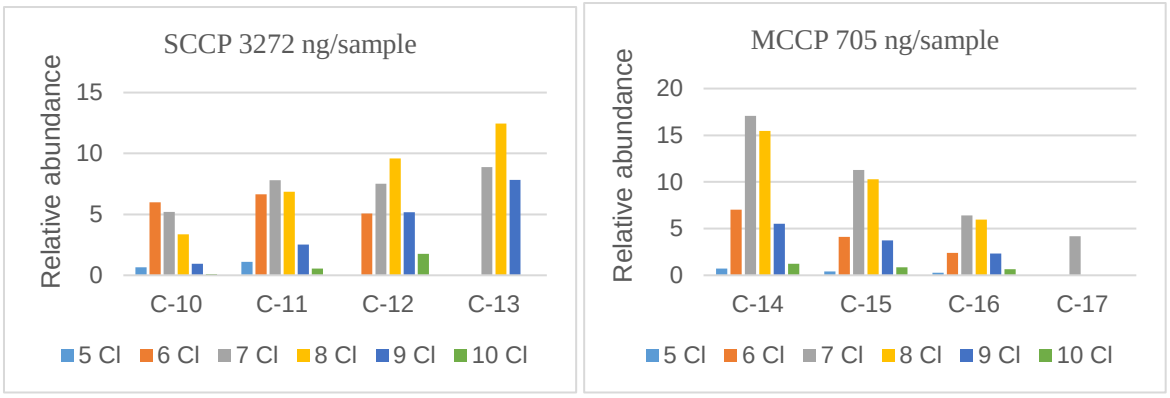


Figure 14: SCCP and MCCP homologue group distribution in sample from used latex pipette top.

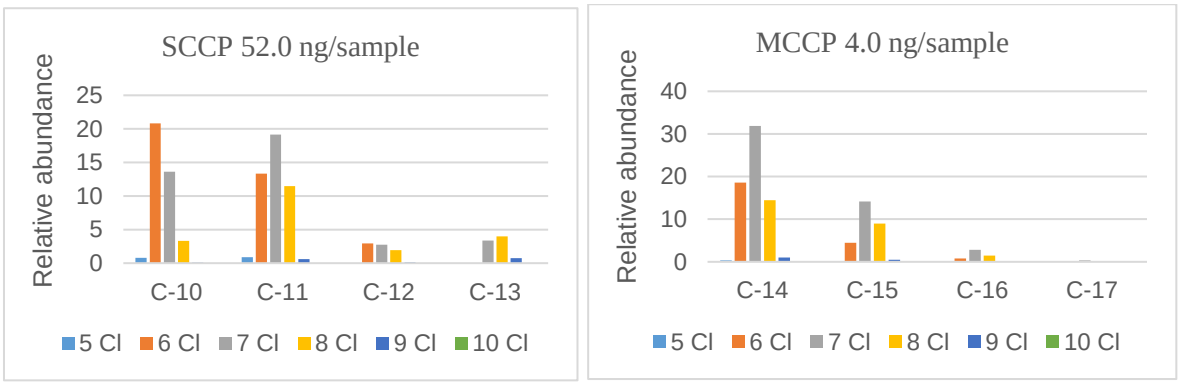


Figure 15: SCCP and MCCP homologue group distribution in sample from new latex pipette top.

3.2.5 THE TURBOVAP SYSTEM

The test of the TurboVap system is described in section 2.1.5 and in Table 4. The levels found in the samples from the TurboVap test ranged from 0.5 to 7.5 ng/sample (average 2.1 ng/sample, median 0.6 ng/sample) for SCCPs, while the MCCPs ranged from 0.001-0.01 ng/sample (average 0.003 ng/sample, median 0.003 ng/sample) (Tables 7, 8, A6 in Appendix A, Figure 16). The levels in the test samples were all below the DL.

Higher levels were expected in samples that were volume reduced on uncleaned TurboVaps, however, the results showed no clear difference in CP levels between cleaned and uncleaned TurboVaps. In fact, the two slightly higher results (7.5 ng/sample and 5.1 ng/sample) were from a cleaned TurboVap. The tests performed on the TurboVap system give no indications of CP cross contamination of samples in the volume reduction process, when CP levels are in the range normally found in air samples.

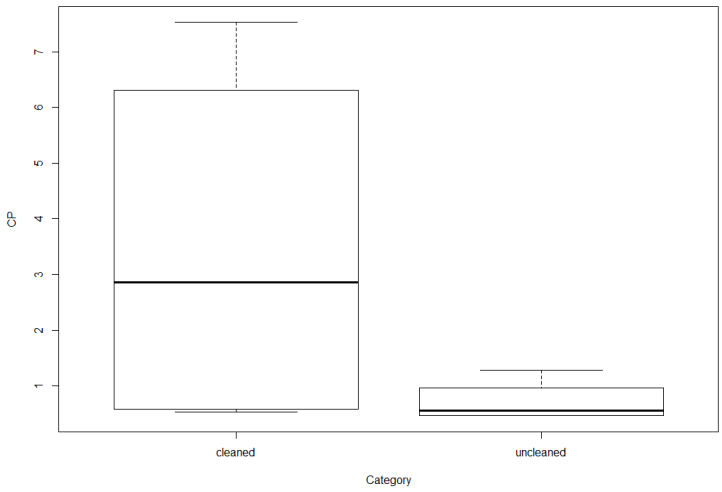


Figure 16: Box and whisker plot representing levels of sum SCCPs and MCCPs (total CP content) for the testing of cross contamination in the Turbovap system. Unit for CP is ng/sample.

3.2.6 INDOOR AIR SAMPLES

The indoor air samples are described in section 2.1.6 in table 4. Data from the PUF passive air samplers deployed indoors at NILU, were converted from ng/sample to ng/m^3 using an uptake rate of 1.4 m^3/day, and a sampling time of 96 days (Bohlin et al. 2014). The indoor air samples taken at the three locations at NILU's chemical laboratories (see Table 4) show a SCCP content of between 4.1 and 55.5 ng/m^3. The MCCP content was between <MDL (8.3 ng/sample, MDL = 10.6 ng/sample) and 0.3 ng/m^3 (see Table 7, 8 and A7 in Appendix A). The indoor air samples collected at NILU's facilities show that high levels of SCCPs are present in the building. In particular, high levels of SCCPs were observed in the room where sampling material (PUF plugs and disks) is cleaned and stored. The highest level of MCCPs in the indoor air samples was also at this location. The lowest level of both SCCPs and MCCPs were found in the clean room, with 4.1 ng/m^3 of SCCPs and <MDL for MCCPs, see Figure 17.

Fridèn and coworkers monitored indoor home environments, and the levels of sum CPs (SCCPs and MCCPs) ranged from 5 to 210 ng/m^3 (Fridén et al. 2011). The air samples were collected using a low volume active sampler, and are not directly comparable to the results from this study. Nonetheless, the highest detected levels of CPs found in the indoor air at NILU's laboratories are in the upper range of those in Fridèn and coworkers study. A study done by Barber et. al. reported a single sample from laboratory environment, sampled using PUF based PAS, showing a SCCP level of 5500 ng/sample and a MCCP level of 1600 ng/sample (deployed

for 12-13 weeks) (Barber et al. 2005). The findings give air concentration in the same order of magnitude as the levels found in the laboratory indoor air samples collected for this study for SCCPs, while the MCCP levels found in this study is approximately 50 times lower.

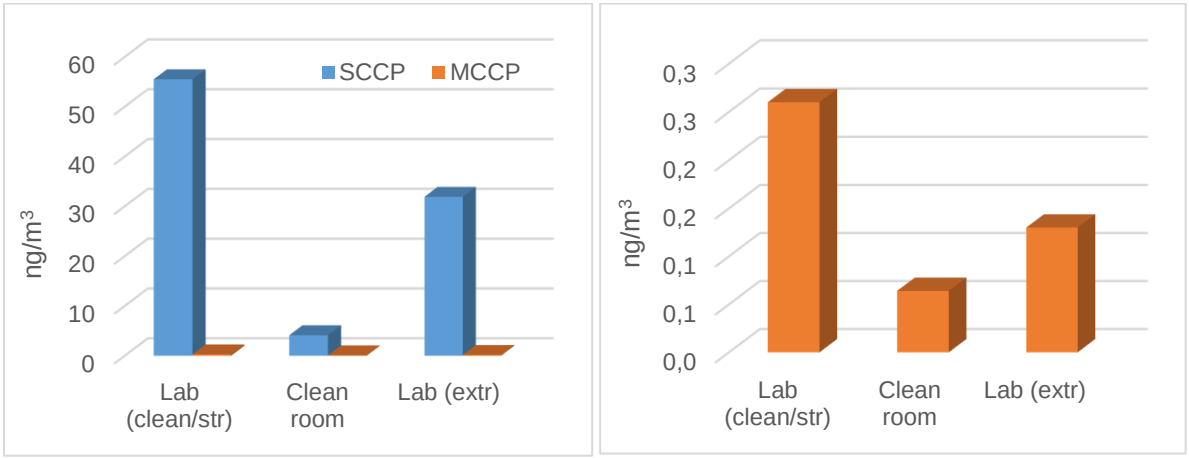


Figure 17: Left: SCCP and MCCP results from indoor air samples collected at NILU's chemical laboratories at Kjeller. Right: MCCP results from the same indoor air samples in magnified form. Lab (clean/str) is laboratory used for cleaning and storage, Lab (extr) is laboratory used for extraction.

The levels of SCCPs in the indoor air samples were > 100 times higher than the levels of MCCPs. In addition, the lower chlorinated, shorter chain groups dominate homologue group distribution within the SCCPs and MCCPs in the indoor air samples. Figure 18 show the homologue group distribution in the sample collected in the laboratory used for cleaning/storage of sampling material. These findings were anticipated as the passive air samplers mainly collect the more volatile compounds found in the gas phase, i.e. SCCPs >> MCCPs, shorter chain groups over longer chain groups and lower chlorination degree over higher chlorination degree.

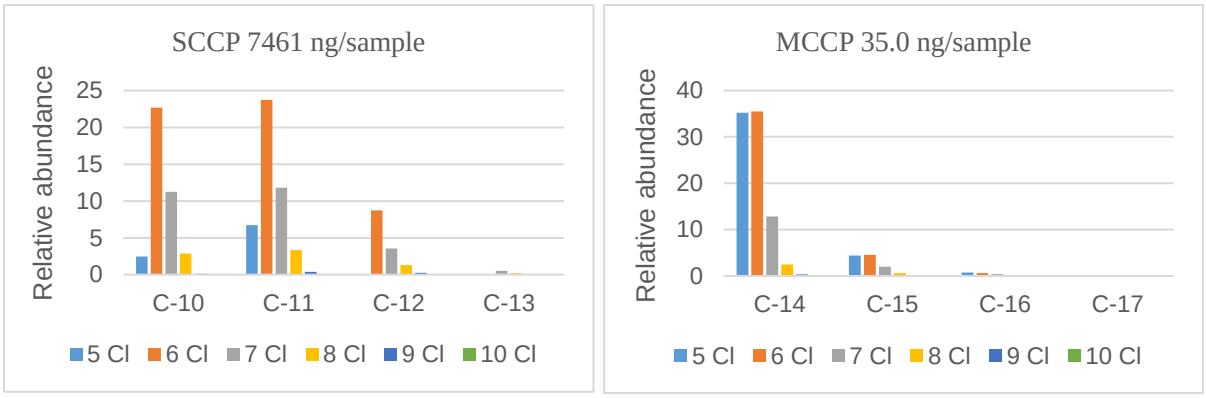


Figure 18: SCCP and MCCP homologue group distribution in indoor air sample from laboratory used for cleaning/storage of sampling material.

3.2.7 DUST/ORGANIC FILM SAMPLES

The dust/organic film samples are described in section 2.1.7 and Table 4. Data from the dust/organic film samples taken indoors at NILU were converted from ng/sample to ng/m^2 using the surface area of the sampled area. The dust/organic film samples taken at three locations at NILU's chemical laboratories show a SCCP content of between 98.3 and 2856 ng/m^2. The MCCP content was between 144 and 965 ng/m^2 (see Tables 7, 8 and A8 in Appendix A). The levels of SCCPs and MCCPs are more similar in the dust/organic film samples than in the indoor air samples. The highest concentrations of SCCPs were found in a laboratory used for cleaning and storage of sampling material, while the highest concentration of MCCPs were found in the laboratory where samples are extracted. The clean room was found to have the lowest concentrations of both SCCPs and MCCPs. Figure 19 shows the distribution of the SCCP and MCCP results from the dust/organic film samples from the three sampled locations. CPs in indoor dust has also previously been reported by Fridèn and coworkers, with sum CPs ranging from 3.2 to 18 µg/g (Fridén et al. 2011). Also, Kersten and coworkers has reported CPs in dust, showing a SCCP level of 180 mg/kg (Kersten & Reich 2003). These numbers are not directly comparable to the samples collected for this study, due to difference in sampling technique and analysis, they do however confirm that CPs in fact can be present in dust.

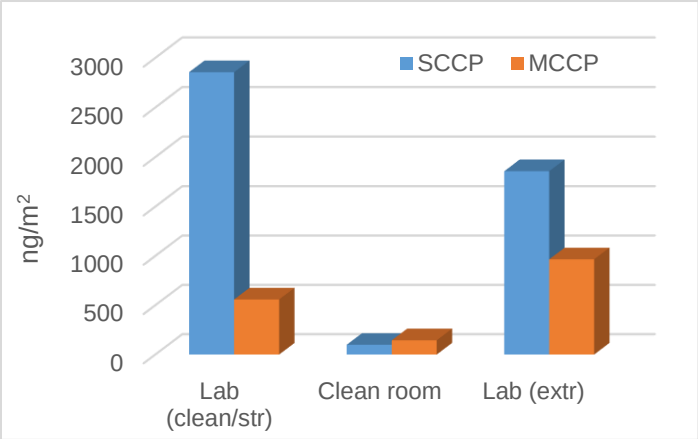


Figure 19: SCCP and MCCP results from dust/organic film samples collected at NILU's chemical laboratories at Kjeller. Lab (clean/str) is laboratory used for cleaning and storage, Lab (extr) is laboratory used for extraction.

The homologue group distribution in the dust/organic film sample from the laboratory used for cleaning/storage is shown in Figure 20. In the dust/organic film samples, there is a higher proportion of the higher mass CPs, i.e. longer chains and higher degree of chlorination compared to the indoor air samples from the same location seen in Figure 18. The difference in homologue group pattern/distribution implies a possibility to distinguish between blank sample contamination originating from exposure to indoor air and contamination originating from dust. Dust contamination is likely to result in homologue group profiles containing heavier, longer chain and higher chlorinated CPs, than contamination via indoor air.

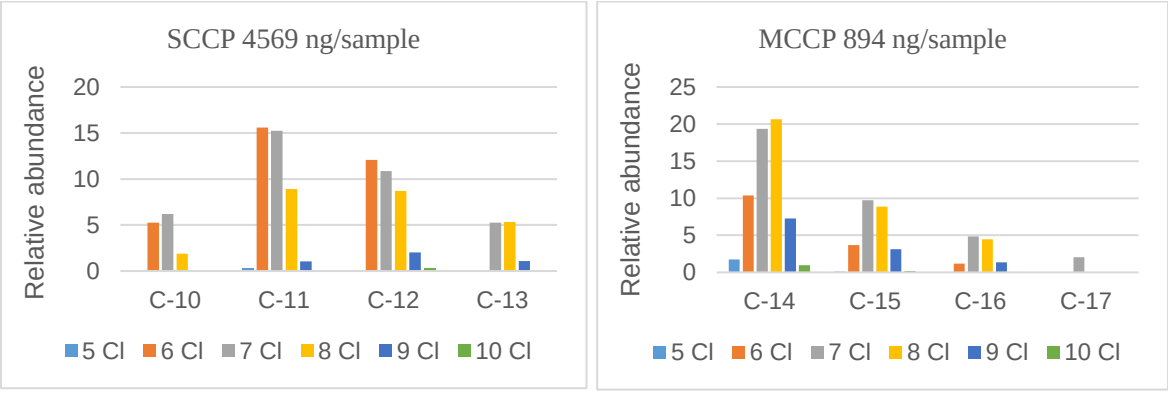


Figure 20: SCCP and MCCP homologue group distribution in dust/organic film sample from laboratory used for cleaning/storage of sampling material.

3.2.8 GENERAL DISCUSSION ON BLANK CONTAMINATION

The investigation of potential contamination sources in the field and laboratory showed that in general, there is SCCPs present in blank samples which include PUF material (Table 7). MCCPs are present to a much lower degree (Table 8). Laboratory blanks without PUF sampling material and reagent blanks show a lower level of both SCCPs and MCCPs, which is an indication that CP contamination is to a large extent related to the PUF sampling material, rather than the laboratory procedure from extraction and onwards. However, the tests performed on the reagents in this study do not fully address the within run variability. Some variability is addressed by using new/old adsorbents, and acids from different origin. There may be variations in the reagents from batch to batch, day to day variations, or variations arising from other factors. Although no blank contamination from reagents was found in this study, episodic blank contamination events due to contaminated reagents can not be excluded.

In the storage blanks and field blanks, no systematic CP contributions according to treatment of the blanks could be found. They appear to follow the general trend for blank samples containing the PUF sampling material, i.e. higher levels than blanks without PUF, and higher SCCP than MCCP levels, although with some variation (Tables 7 and 8). However, with the number of parallels included in these tests any systematic difference in CP level would need to be large to be detected in the statistical procedures. It is therefore possible that more subtle differences exist in CP levels, given the applied treatments/conditions.

The results from the samples taken from the indoor environment (indoor air and dust/organic film) show that there were sufficient levels of particularly SCCPs, but also MCCPs present for the indoor environment to represent challenge in CP analysis. The CP levels found in the three locations at NILU using PUF PAS and wipes, to a large extent confirmed each other. The relative CP levels at the three locations is similar for SCCPs and MCCPs, and for indoor air and dust/organic film. The one exception is the higher MCCP levels in the dust/organic film sample from the sample extraction laboratory than the cleaning/storage laboratory (Figures 17 and 19). The low levels of CPs found in the clean room suggest that the CPs present in the building are not caused by building materials, but rather by the room content, or people present in the room.

In order to find possible connections in the homologue group distributions of the samples and blanks, hierarchical clustering was performed on the homologue group data (see section 2.1.8). This was done on data from all blanks (laboratory blanks (PUF/without PUF), storage blanks, field blanks, reagent blanks), TurboVap tests, materials test, indoor air samples, dust/organic film samples and air samples. Close grouping indicate similarity in homologue group

distribution in the samples, and could potentially give indications of contamination pathways. The statistical procedure created two distinct groups, where the reagent blanks, the samples from the TurboVap test and one of the laboratory blanks (without PUF) were grouped together in one of the groups, and the other group contained samples and blanks including PUF sampling material, and the materials tests. A pairing appeared between the dust/organic film sample from the cleaning/storage laboratory, and the used latex pipette top (circled and marked "1" in Figure 21, see also Figure 14 and 20). This could be an indication that the majority of the CP content found on/in the latex pipette top originates from dust in the laboratory, and not from the latex material in itself. This explains the difference in CP content and homologue group distribution between the unused latex pipette top and the used latex pipette top. It also reveals a plausible route for episodic blank contamination of samples during laboratory work. Pasteur pipettes are used in several of the laboratory procedures, any dust present on the inside of a pipette top can easily be blown into the sample.

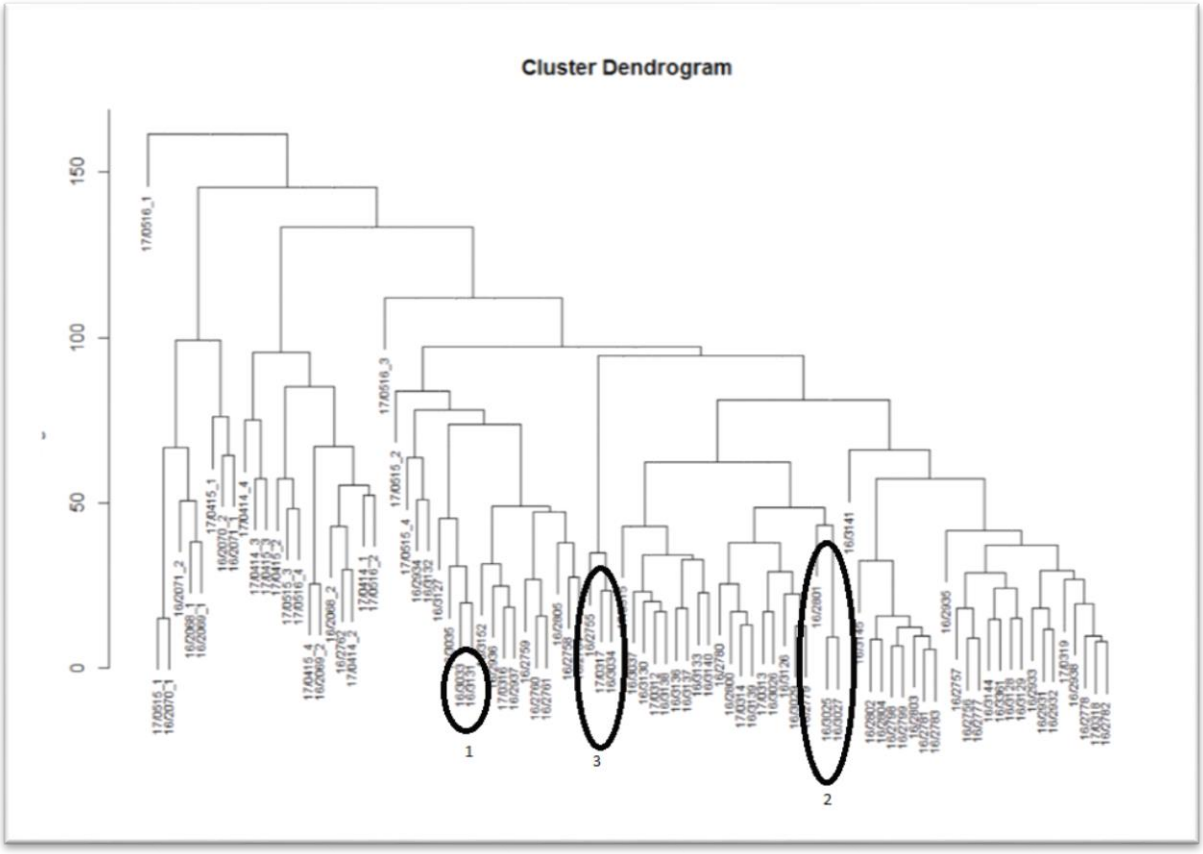


Figure 21: Cluster dendrogram from hierarchical clustering of the homologue group data from all samples and blanks included in the study. A table showing a description of each sample number included in the figure can be found in Appendix C.

The homologue group distribution in the car sample from the field study showed low similarity to the field blanks, as no close grouping to any of these could be found in the clustering study. The car sample does however show some similarity to two of the three indoor air samples (circled and marked “2” in Figure 21). Circled area marked “3” in Figure 21 will be discussed in section 3.4.3. More information on the clustering study can be found in section C.3 in Appendix C.

The majority of the blank samples (method blanks, storage blanks and field blanks) seem to have a homologue group pattern that suggest contamination via air, as relatively volatile CPs dominate (see Figure 7). However, this is not a clear conclusion, as the $C_{10}Cl_5$ and $C_{11}Cl_5$ SCCPs are less dominant than in the pattern found in indoor air samples (see Figure 18). Nevertheless, due to the high levels of SCCPs found in indoor air, it is not unlikely that this represents the main contribution to blank contamination found in this study.

3.3 Instrumental performance

3.3.1 COMPARISON STUDY

The comparison study is described in section 2.2.1 and in Table 5. The SCCP results from the comparison samples on the Autospec and the GC/Q-TOF are shown in Figure 22 and Table 9. The SCCP results on the two different instruments show comparable performance for all samples except the sediment samples, where the results from the Autospec are significantly higher. Table 9 shows the average concentration of six (five for sediment) runs on the two instruments, and the standard deviation of these results. The true concentration of SCCPs in the samples are to date unknown, so accuracy of the instrumental performance cannot be determined from these samples until the results of the interlaboratory study is presented. The results show that the precision of the SCCP results is better on the GC/Q-TOF instrument by the standard deviation of the results, as shown in Table 9. Furthermore, the same tendency is apparent in Figure 22.

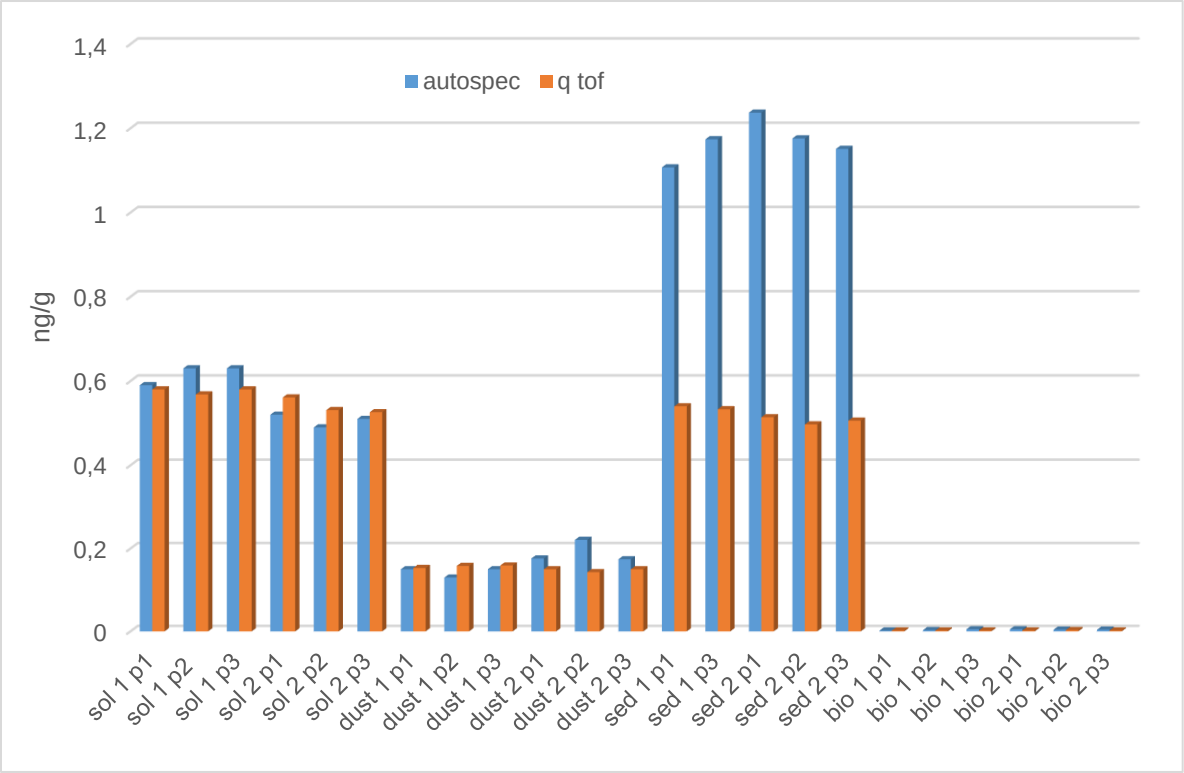


Figure 22: SCCP results from the comparison study quantified on the Autospec instrument, and on the GC/Q-TOF.

Table 9: Average concentration of SCCPs and standard deviation of the results from the comparison study. Numbers based on six samples (five for sediment)

	Solution (ng/g)	Dust (ng/g)	Sediment (ng/g)	Biota (ng/g)
Autospec average	0.6	0.2	1.2	0.004
Q-TOF average	0.6	0.2	0.5	0.002
Autospec stand. dev.	0.06	0.03	0.05	0.002
Q-TOF stand. dev.	0.02	0.006	0.02	0.0004

Four air samples from AMAP (Zeppelin Observatory) were also run on both instruments; the obtained air concentrations of SCCPs were compared (Figure 23). The difference between the results on the two instruments range from 1 to 24 %. The average difference was 12%. These results demonstrate that comparable levels can be obtained from the GC/Q-TOF and the Autospec instruments when analyzing air samples. Based on these results, the moving of the

routine analysis from the Autospec to the GC/Q-TOF is not likely to affect the comparability to previously analyzed air samples.

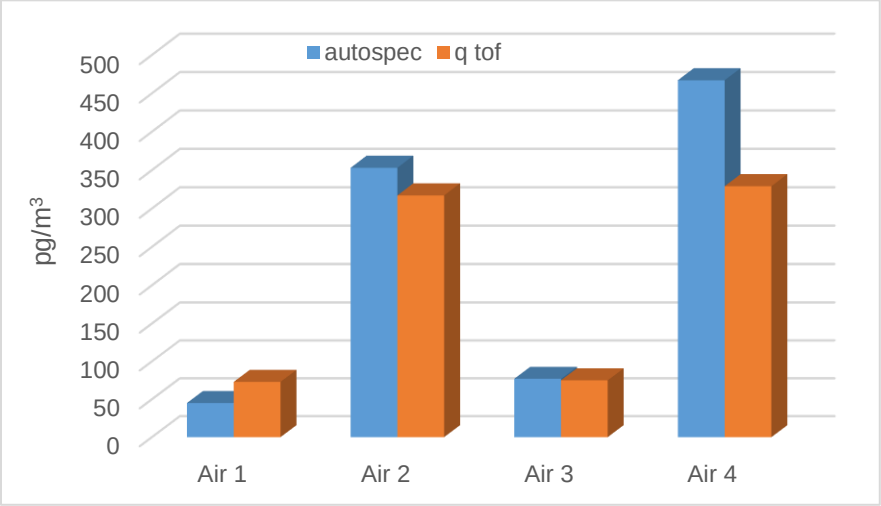


Figure 23: SCCP results from four air samples from the Arctic monitoring and assessment program, analyzed using sector instrument (Autospec) and GC/Q-TOF instrument.

3.3.2 INTERFERENCES

The test devised to assess the potential for interference in the instrumental analysis by other OCs is described in section 2.2.2 and Table 5. The selectivity of the instrumental analysis was determined by applying the CP quantification method to samples consisting of potential interferences in the form of ^{12}C and ^{13}C OC components, the results can be found in Table 10. These test samples show only low difference in SCCP level between the CP sample (1694 ng/sample) and the interference test samples (1648 to 1715 ng/sample). For MCCPs however, the differences are larger. The CP sample had a MCCP level of 1753 ng/sample, and the interference test samples ranged between 1548 and 2525 ng/sample. The interference test sample containing the dechlorane solution showed a level of MCCPs that was 772 ng/sample (44%) higher than the CP sample. On inspection of the chromatograms and mass spectra from the dechlorane mix, there were no clear signs of interference, so it remains unclear whether the high MCCP level is caused by interference or general lack of accuracy in the method. In the interference test samples containing the PCB and the DDT solutions there are several peaks appearing in the EICs which can be identified as non-CP by having ideal peak shape. These are however avoidable by using manual integration.

Table 10: Results from tests of OC interference on CP quantification.

	SCCP (ng/sample)	MCCP (ng/sample)	Diff. SCCP (ng/sample)	Diff. MCCP (ng/sample)	Diff. SCCP (%)	Diff. MCCP (%)
CP	1694	1753	-	-	-	-
Dechlorane	1710	2525	17	772	0.9	44.0
Pesticide	1715	1548	21	-205	1.2	11.7
PCB	1648	1723	-46	-30	2.7	1.7
DDT	1667	1883	-26	130	1.6	7.4

In addition to interferences from other OCs, it is also potential issues of self-interference present in the case of CPs. SCCPs and MCCPs with difference of C_5Cl_2 can potentially interfere with each other. For example the $[M-Cl]^-$ ion of the $C_{10}H_{12}Cl_{10}$ group (450.8082) and the $[M-Cl]^-$ ion of the $C_{15}H_{24}Cl_8$ group (450.9673), where a resolution of ~3000 is required to achieve separation. Resolution well above this was achieved on the Q-TOF instrument (approximately 12 000 FWHM). Interferences caused by ^{13}C containing $[M-HCl]^-$ ions interfering with the $[M-Cl]^-$ of the same homologue group will be present, and not in all cases self-cancelling, as a variation of $[M-HCl]^-$ and $[M-Cl]^-$ ions are used for quantification (see Tables A9 and A10). However, these interferences will be small, as natural abundance of ^{13}C is 1.1 % (Tomy et al. 1997).

3.3.3 GENERAL DISCUSSION ON INSTRUMENT

The assessment of instrumental performance using GC/Q-TOF highlighted both pros and cons associated with the instrument, in addition to raising some questions. Although the comparison of SCCP results on GC/Q-TOF and Autospec for air samples showed similar levels, this was not the case for sediment samples. A hypothesis for the difference is that the higher levels from the Autospec is caused by a matrix related issue on the internal standard used for quantification in the Autospec instrument. A longer GC column was used on the GC/Q-TOF which may have caused the matrix to have lesser effect on the internal standard. The reasons for this being that the matrix was separated from the internal standard in the column, and that the intensity of the matrix was lowered. The Autospec is also more vulnerable to matrix issues due to the peaks in the chromatogram being composed of fewer points. This makes it possible for parts of the peak to be left out when the peak is integrated. If this occurs on the internal standard peak, it will lead to overestimation of all homologue groups in the sample, as only one internal standard is

used for all groups. The homologue group distribution found in the sediment samples using the Autospec is similar to the distribution found using the GC/Q-TOF, making interference with the internal standard a likely explanation for the large difference in the SCCP results in these samples. The homologue group distributions in sediment sample 1, parallel 1 obtained by the Autospec instrument and the GC/Q-TOF instrument is shown in Figure 24.

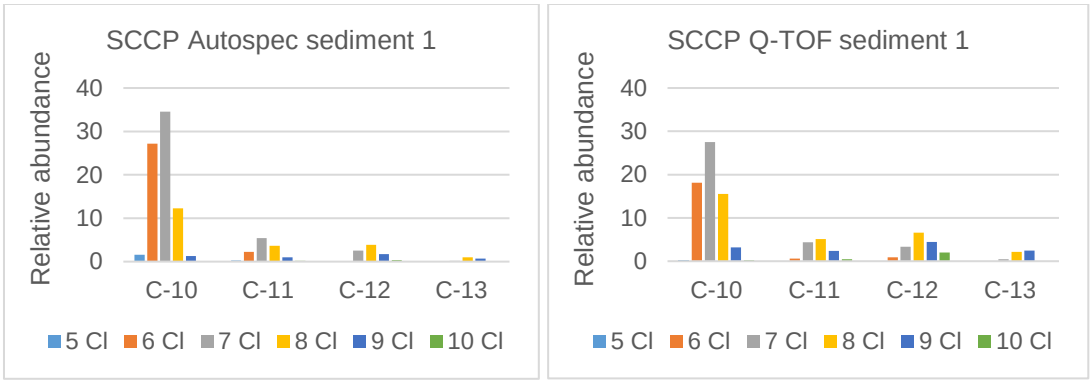


Figure 24: SCCP homologue group distribution in sediment sample obtained by the Autospec instrument and by the GC/Q-TOF instrument.

The interference test show that dechlorane compounds is candidates for causing interference in MCCP analysis, in addition, peaks from other OCs appear in EICs. This is likely to be related to a problematic feature with the GC/Q-TOF in CP analysis. The GC/Q-TOF instrument was affected by a drift of measured m/z over time. Figure 25 show EIC of m/z 374.9589 from a SCCP technical standard (63%) with three ppm intervals; 100, 50 and 10 ppm (± symmetric). With a ppm interval of ± 50 ppm, the later eluting part of the peak is blurred, leading to a lower integrated peak area. With a ppm interval of ± 10 ppm, much of the peak is lost. The practical consequence of this is that the resolution the Q-TOF instrument is capable of producing is not completely accessible in the analysis of CPs. In Figure 26 the EIC of m/z 323.0006 (from the single component internal standard) in the same ppm intervals is shown. It is apparent that single component peaks are less prone to problems from mass drift, implying that this is particularly problematic in CP analysis, where broad peaks are obtained due to a variety of individual components with identical m/z and a large range of retention times. In the quantification procedure applied to all samples and blank samples in this study, the ppm range for the integrated peaks was set at ±50 ppm. This represents a compromise, where the interest

of including as much of the peak as possible was weighed up against the interest of excluding as many interferences as possible.

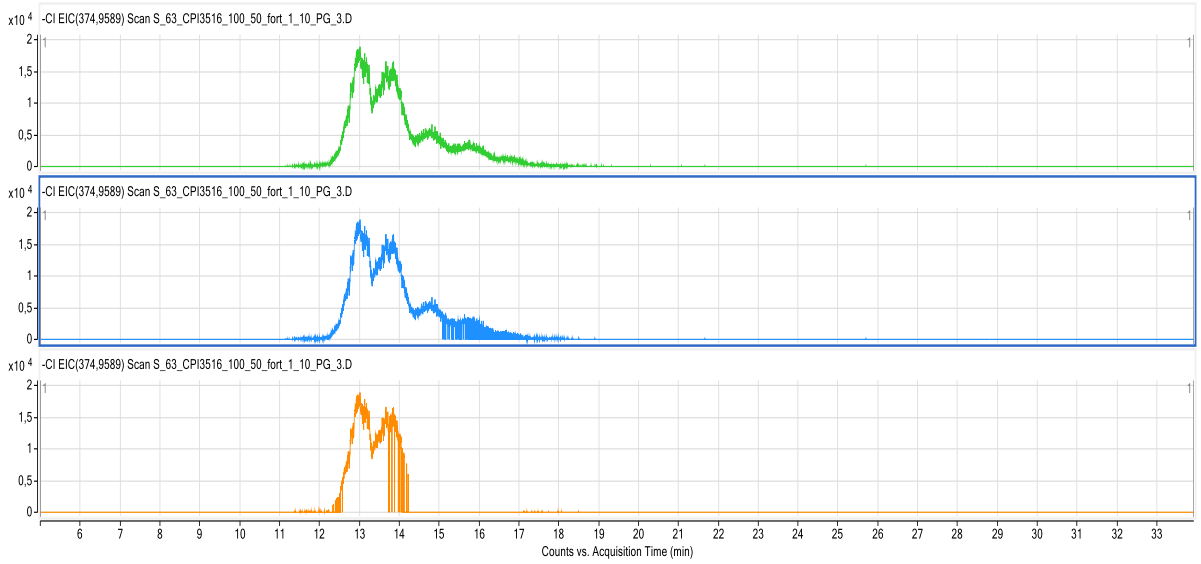


Figure 25: EIC of mass 374.9589 with ppm range (from above) 100, 50 and 10. From SCCP technical standard 63% Cl.

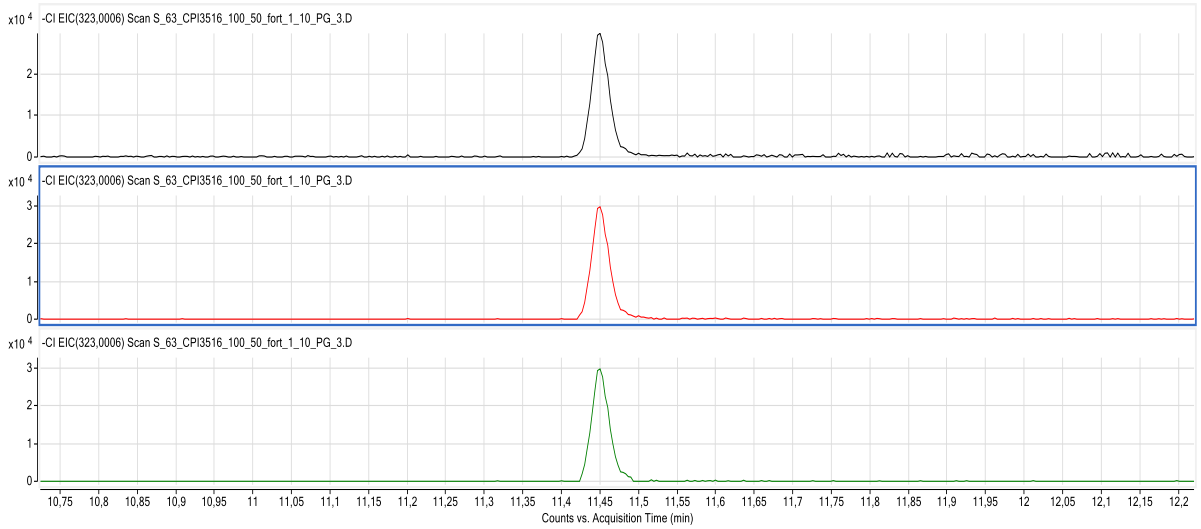


Figure 26: EIC of mass 323.0006 (internal standard) with ppm range (from above) 100, 50 and 10.

The ppm range used is likely to affect the potential for interferences, and increases the likelihood that the high MCCP result on the dechlorane interference test are caused by interference although no direct evidence of this was found. It also increases the likelihood of

self-interference of CPs. Self-interference of the C_5Cl_2 type discussed in 3.3.2, is however still avoided at the ±50 ppm interval.

Another disadvantage with the GC/Q-TOF is that the linear range of Q-TOF instruments are generally lower than the linear range in sector instruments by some margin (two orders of magnitude compared to six). The testing of linearity specifically for CPs is however complicated by their inherent complexity. It is possible to assess linear response with the use of standard solutions containing quantified amounts of single CP components in varying concentrations and constant internal standard concentration. This will however not be of great value when analyzing CP mixtures, as these do not produce ideal peaks, and are not quantified on an individual component basis, but rather as sum SCCPs and sum MCCPs (see section B.3 in Appendix B for details on the quantification procedure).

The advantage of the GC/Q-TOF instrument lie in the vast amount of data collected compared to a traditional sector instrument, i.e. all m/z are detected simultaneously. This makes it possible to analyze for SCCPs and MCCPs in one single injection on the GC/Q-TOF, as opposed to two different injections on sector instruments, which shortens the time required to perform the instrumental analysis. In addition, it makes it possible to extract EICs of all m/z after a sample is run. This gives the opportunity to choose which ion (isotopic combination) to use for quantification after inspection of the chromatograms and spectra, both for the homologue groups, and the internal standard. This makes it (in theory) possible to extend the range of the linear response area upward, as ions from lower abundance isotopic combinations can be chosen for quantification if the more abundant ion has saturated the detector. CPs, which generally contain >5 Cl atoms, is well suited for this, given the large range of isotopic combinations present. The Autospec instrument on the other hand can only provide data for a small number of pre-selected m/z values.

3.4 Assessment of CP method

3.4.1 RECOVERY

The recovery test performed is described in section 2.3.1 and in Table 6. The recovery of internal standard from PUF sample material spiked with CP technical standard was found to be 93 $\pm$ 13 % based on six parallels, see Table 11, and Table A11 in Appendix A.

Recovery of internal standard in routine CP analysis does not necessarily provide a representative view of recovery of all homologue groups present. However, the recovery test performed here show that the laboratory procedure performs very similarly for the different homologue groups of both SCCPs and MCCPs. A visual comparison of the homologue group distribution of the recovery test samples that had been through the extraction/cleanup procedure to the mix of the same technical standards that had not been through the procedure show identical patterns. This implies that the internal standard recovery is representative for all homologue groups included in the study, and that the homologue group information present in a sample is preserved through the laboratory procedure. Figure 27 show the homologue group distribution in the technical standard mixture, and one of the six parallels of the recovery test. Figure A3, showing all parallels of the recovery test, can be found in Appendix A.

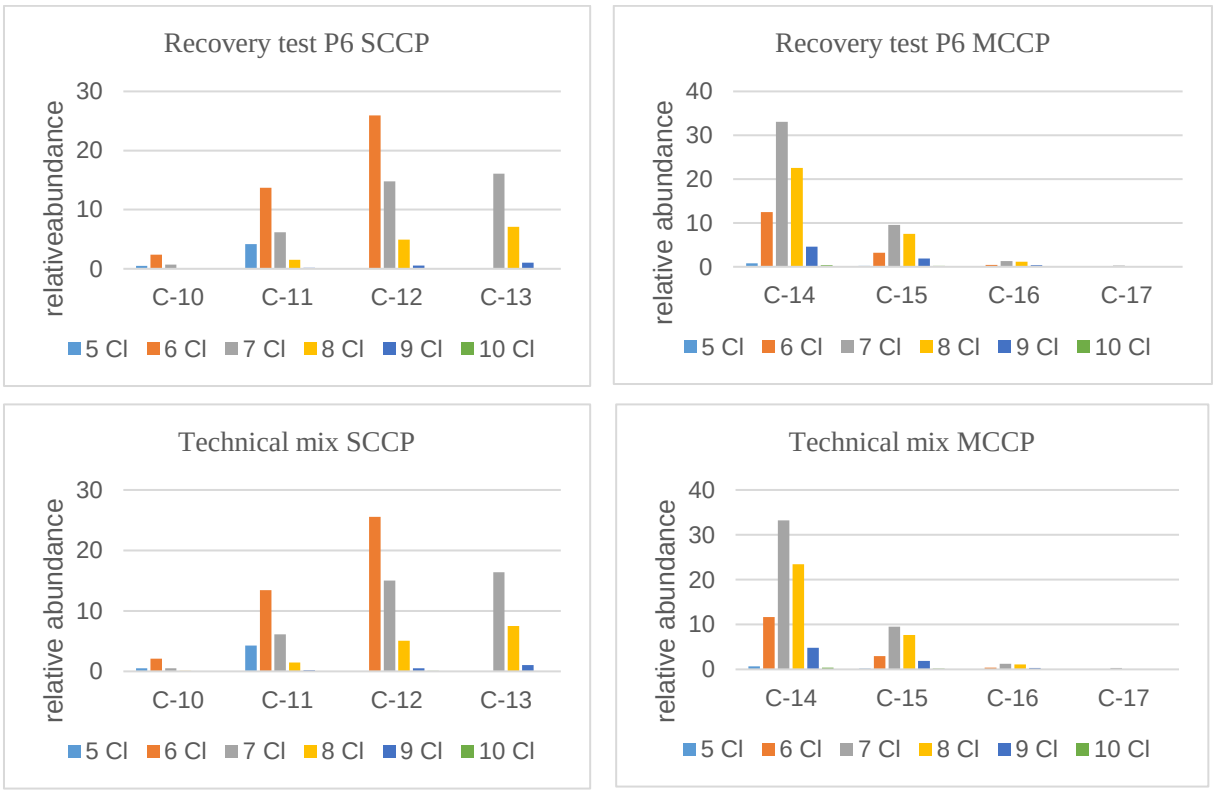


Figure 27: Distribution of SCCP and MCCP homologue groups in recovery test parallel 6, and in technical standard mix.

Table 11: SCCP and MCCP levels found in recovery test samples, and difference between expected level and found level for SCCPs and MCCPs.

	SCCP (ng)	MCCP (ng)	Diff. SCCP (%)	Diff. MCCP (%)
16/2546 P1	10520	11338	5.2	13.4
16/2546 P2	9969	9517	0.3	4.8
16/2546 P3	10423	10265	4.2	2.7
16/2546 P4	10718	12100	7.2	21.0
16/2546 P5	10026	9825	0.3	1.7
16/2546 P6	10067	10184	0.7	1.8
Average	10288	10539	3.0	7.6
Stand. dev.	309	983	3.0	7.9

In all samples and blanks analyzed for this study, the recovery of internal standard was found to be 86 $\pm$ 15 %. The data can be found in Tables A1 to A5, A11 and A13 in Appendix A. This indicates that the laboratory method as described in Appendix B, and analysis using the GC/Q-TOF provides good recovery.

3.4.2 AIR SAMPLES

The air samples analyzed for this study are described in section 2.3.3 and Table 6. The air samples from three monitoring stations in Norway showed SCCP concentrations ranging from 42.3 pg/m^3 at Birkenes to 249 pg/m^3 at Andøya. MCCP concentrations were below the MDL (MDL = 8.1 pg/m^3) at Andøya and Birkenes. At Zeppelin, however, relatively large amounts of MCCPs was found, with sample one showing 40.0 pg/m^3 and the other sample showing 284 pg/m^3. The CP levels in the air samples is summarized in Tables 7 and 8 in section 3.1, and in Tables A12 and A13 in Appendix A, in addition to Figure 28. The MCCP levels found in air samples from Zeppelin in this study is consistent with MCCP data from the national monitoring program. SCCPs and MCCPs have previously not been measured at the Birkenes and Andøya stations. Surprisingly, the lowest air concentrations of CPs were found at Birkenes, where the levels of SCCPs found were only marginally over the MDL. Birkenes is the station closest to the continent and urban environments, and as such, higher levels were expected to be found there than at the Arctic stations. The reason for this finding is not known. Further investigation into possible local sources is beyond the scope of this study.

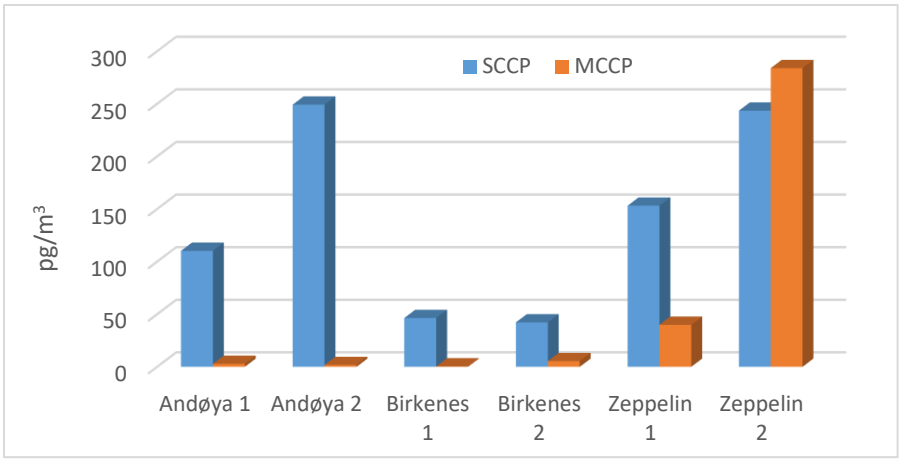


Figure 28: SCCP and MCCP results from air samples collected at background stations in Norway.

3.4.3 GENERAL DISCUSSION ON THE CP METHOD

The CP method (sampling, laboratory and instrumental analysis) is associated with challenges not only with contamination issues and instrumental challenges, but also with regard to accuracy.

The results from the recovery test can be used to assess the accuracy of the method, as a known amount of the SCCP and MCCP technical standards were added to the PUFs prior to extraction. For SCCPs the difference between measured and expected result is 3.0 ± 3.0 %. For MCCPs the difference between measured and expected result is 7.6 ± 7.9 % (Table 11). This shows that the method can have good accuracy when a technical standard with a high degree of similarity to the samples is used for quantification. However, when a quantification standard containing technical standard SCCP 55% was applied to the SCCP data from the recovery test samples the difference between measured and expected result rose to ~60% (see Table A11 in Appendix A). In analysis of air samples, the ideal similarity of standard and sample is not achieved (see Figures B3 and B4 in Appendix B). The accuracy achieved in the analysis of air samples is therefore expected to be considerably worse than the figures shown in Table 11 indicate.

Ideally, accuracy is a parameter that should be estimated using well-characterized reference materials; this is as previously mentioned not available for CPs. The use of CP technical standard rather than reference materials to estimate accuracy adds to the associated uncertainty of the results obtained using the analytical procedure for CP analysis. The accuracy and precision for the MCCP quantification is lower than for SCCPs (see Table 11), which is another

potential explanation for the high MCCP result for the dechlorane interference test (see section 3.3.2), in addition to the ppm range used in integration (see section 3.3.3).

The possibilities of assessing method and laboratory bias in the analysis of CPs are sparse. This could also be addressed using CRMs. Interlaboratory studies is another method for assessing these issues. Unfortunately, there is to date (2017) no interlaboratory study on CPs that include air samples. The results for the interlaboratory study, which samples were used as part of the comparison of instrumental performance, were not published in time to be included as part of this study. Previous results on CP analysis from interlaboratory studies show large variation in reported results. Tomy et. al. reported a coefficient of variation (CV) of up to 47 % in an interlaboratory study on SCCPs (1999), while Pellizzato et.al. reported a CV of 209 % (by removing two outliers this decreased to 18 %) in a laboratory intercomparison study on SCCPs (2009). These results show that there are challenges in the analysis of SCCPs with regard to accuracy and comparability of results. The results from the study performed for this thesis indicate that the MCCP results could be associated with even less accuracy than SCCPs on a single laboratory basis. No data from interlaboratory studies on MCCPs could be found (2017)

The air samples showed surprising results with regard to MCCPs. The MCCPs did not appear to be as relevant as SCCPs in sample contamination in the laboratory, in addition, the high levels of MCCPs were found in the samples from one location, Zeppelin. Samples from the other locations had MCCP levels below MDL, as did the laboratory blanks analyzed in parallel with the air samples (see table A 13 in Appendix A). This makes contamination of the Zeppelin samples in the laboratory unlikely. The large difference in MCCP levels between the Zeppelin station and the stations at Birkenes and Andøya might be an indication of a MCCP source in or near the Zeppelin station.

The hierarchical clustering procedure described in section 2.1.8 and 3.2.8, found a pairing between the dust/organic film sample from the clean room, and the air sample Zeppelin 2 (see circle “3” in Figure 21, and Figure 30). These two samples are also grouped close to storage blank Freezer P1, which contained high CP levels. All these three samples/blanks have a higher level of MCCPs than SCCPs, and the SCCP content were dominated by the heavier C_{13} homologue groups. The MCCP content was dominated by the C_{14} homologue groups. This homologue group distribution was not consistent with the typical pattern found in dust/organic film samples, which contained more SCCPs than MCCPs, and a more even distribution of carbon chain lengths (see Figure 20). In addition, the MCCP distribution in typical dust/organic film samples were more dominated by higher chlorinated, longer chain homologues. The

Zeppelin 1 sample had a similar distribution for the MCCP homologue groups, but the SCCP content was dominated by the more volatile homologue groups. It is possible that the Zeppelin 1 sample is affected by CPs from the same MCCP source as Zeppelin 2 (at lower levels), plus additional SCCP sources of a more typical LRT type, making the homologue group distribution found in the Zeppelin 1 sample a sum of these (see Figure 29). The homologue group distribution from the clean room dust/organic film sample is shown in Figure 31. There are no indications that the similarities in homologue group distributions are caused by MCCP contamination in the laboratory procedure.

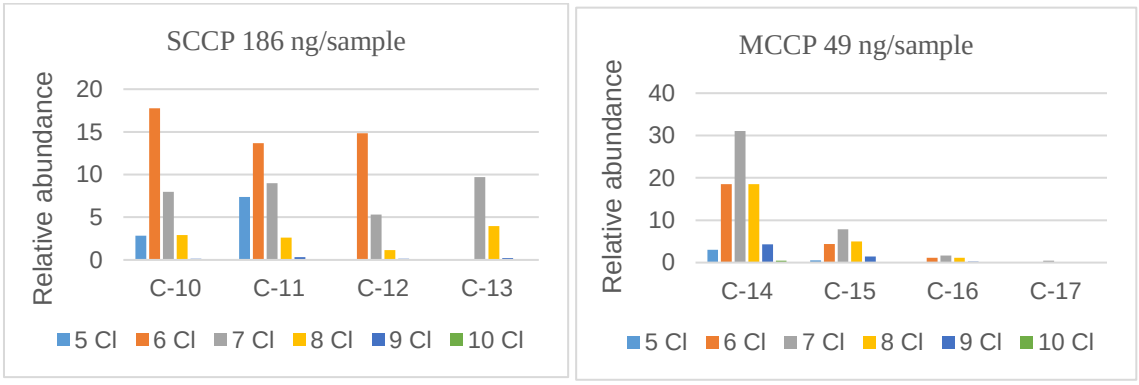


Figure 29: Homologue group distribution in the Zeppelin 1 sample.

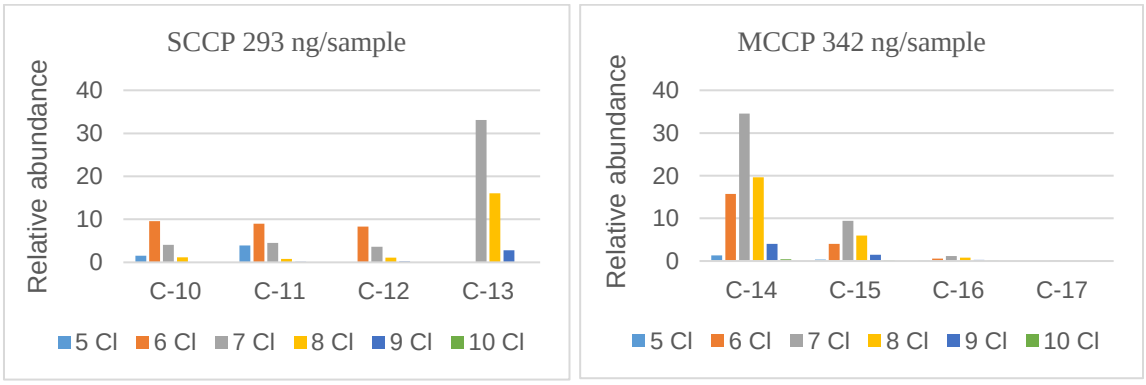


Figure 30: Homologue group distribution in the Zeppelin 2 sample.

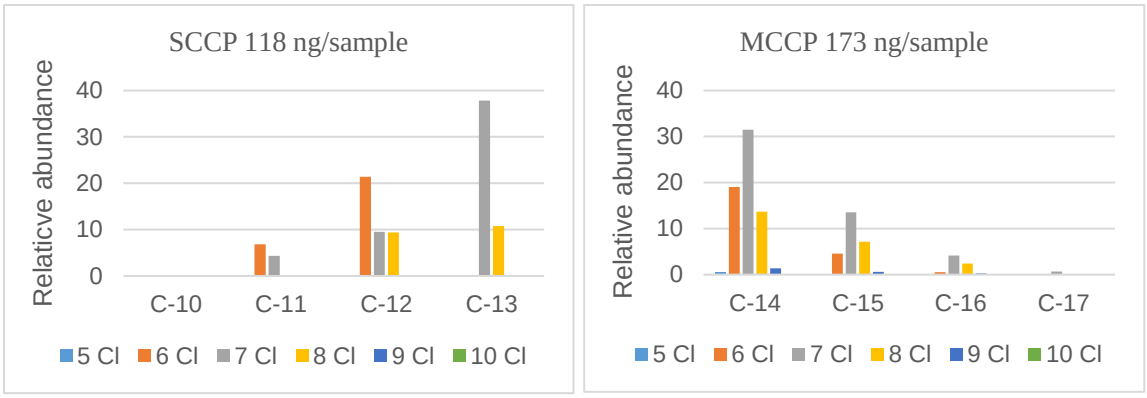


Figure 31: Homologue group distribution in dust/organic film sample from clean room.

The homologue group distributions of samples and blanks in this study were compared visually and statistically based on relative and not absolute amounts. This approach makes it easier to statistically find similarities between samples with similar patterns, and possibly identical sources. This approach has some limitations however, when the CP concentrations are very low, like they may be in most blank samples. The homologue groups with low concentration relative to the more abundant homologue groups will reach a point where they are not detectable in the instrument, hence the more abundant homologue groups will appear more abundant than they are, giving a distorted image of the distribution. Hence, it is likely that the C_{11} homologue groups are dominant in the SCCP transfer pathway of background contamination to blank samples, however not as dominant as they appear in the relative homologue group distribution charts of the blank samples (see Figures 7 and 8). This supports the conclusion that indoor laboratory air (see Figure 18) (and potentially transport vehicle) can contribute to the higher CP levels generally found in blanks containing PUF sampling material compared to the non PUF blanks.

The recovery tests show that the laboratory procedure preserve the homologue group information from the original sample. This supports the approach of looking for sources of blank contamination by comparing homologue group patterns/distributions. The situation is however complicated by the possibility of contributions from a combination of sources.

4. CONCLUSION AND FUTURE PERSPECTIVES

The results from the investigation of contamination sources show that the indoor laboratory environment and transportation vehicle can be a diffuse source of CPs to real air samples. The solvents, reagents and materials used in the laboratory do not contain significant levels of CPs. Individual high levels of CPs in materials used in the lab (latex pipette top) seem to originate from indoor dust in the laboratory, rather than from the material in itself. This type of contamination can explain the variability in blank levels found in routine CP analysis, and highlights the importance of careful sample handling at all steps in the analytical procedure, making sure the PUF sampling material has minimal exposure to indoor air. In addition, it highlights the importance of keeping a clean laboratory environment, and of keeping all glassware and equipment dust free.

The origin of the high indoor levels of CPs was not determined in this study, although there are indications that it is not the building material in itself. Further study looking more extensively at CP content in the laboratory indoor environment, including indoor environment/buildings at sampling stations is recommended.

Instrumental performance with regard to quantified results from the GC/Q-TOF is comparable to the sector instrument (Autospec) for air samples for SCCPs. The comparability for MCCP analysis need investigation. There are advantages in the possibilities of operation of the GC/Q-TOF. The GC/Q-TOF requires only one run of the samples, as opposed to two runs on the Autospec instrument. Also, if problems like detector saturation or interferences occur for a m/z used for quantification, the GC/Q-TOF has the possibility to select a different m/z to use for quantification post-sample run. However, there are issues with m/z measurement in broad peaks, which affect the CP analysis using GC/Q-TOF negatively. These issues need to be investigated further.

There were some indications that dechlorane compounds present in samples increase the quantified MCCP level, however no direct evidence of interference could be found. It is not known weather the high levels of MCCPs found in the interference test wass a consequence of a lack of accuracy in the method, which is particularly relevant for MCCPs, or a consequence of high ppm intervals used in the EICs.

Results from the analysis of CPs from air samples can be of value even if the numbers are associated with a great deal of uncertainty. If there is consistency in the method used, and

particularly important, consistency in quantification standard used, results from air samples can be comparable even if they are not accurate. Time series of measurements from background monitoring stations can show trends in CP levels over time, which is important information with regard to regulation and control strategies, and for conformation of modeling studies looking at spatial distributions of CPs, and potential source regions. In order to gain as much as possible from the CP analytical data, it is important that the CP community work toward standardization of sampling, laboratory procedure, instrumental analysis and quantification, as this would make comparison of results obtained from different laboratories possible.

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APPENDIX A

This appendix contains tables and data from the study.

Table A1: SCCP and MCCP data from storage test. Samples marked Freezer and Room temperature have 5 weeks storage time, while samples marked Freezer long and Room temperature long have nine weeks storage time.

	SCCP (ng/sample)	MCCP (ng/sample)	Sum CP (ng/sample)	Recovery (%)
Freezer P1	29.4*	56.9	86.4	47
Freezer P2	4.6*	1.5*	6.1	72
Freezer P3	4.1*	4.7*	8.8	67
Ambient P1	2.6*	1.6*	4.2	70
Ambient P2	2.0*	1.9*	3.9	60
Ambient P3	1.9*	0.5*	2.5	76
Freezer long P1	4.6*	0.2*	4.8	54
Freezer long P2	5.2*	0.1*	5.2	61
Freezer long P3	15.5*	0.8*	16.3	77
Ambient long P1	7.3*	0.02*	7.3	36
Ambient long P2	18.4*	13.8	32.2	277
Ambient long P3	12.7*	3.3*	15.9	73
Lab blank (no PUF) P1	2.9*	0.02*	2.9	58
Lab blank (no PUF) P2	1.4*	0.02*	1.4	63
Lab blank (no PUF) P3	6.0*	0.02*	6.0	63
Lab blank (no PUF) P4	15.9*	0.02*	15.9	66

**Below method detection limit as described in section 3.1*

Table A2: SCCP and MCCP data from field blanks.

	SCCP (ng/sample)	MCCP (ng/sample)	Sum CP (ng)	Recovery (%)
Cold P1	5.9*	0.4*	6.3	101
Cold P2	11.9*	0.5*	12.3	97
Cold P3	22.4*	1.1*	23.5	72
Worst case P1	14.1*	0.4*	14.5	104
Worst case P2	17.7*	0.7*	18.3	98
Worst case P3	14.0*	0.4*	14.3	105
Ambient P1	33.5*	0.8*	34.3	81
Ambient P2	21.0*	0.5*	21.6	105
Ambient P3	19.1*	0.4*	19.5	93
Lab blank (PUF) P1	22.7*	1.0*	23.7	96
Lab blank (PUF) P2	8.4*	0.2*	8.6	92
Lab blank (PUF) P3	18.9*	0.4*	19.3	113
Lab blank (PUF) P4	10.1*	0.1*	10.2	99
Lab blank (no PUF) P1	1.9*	0.3*	2.2	103
Lab blank (no PUF) P2	1.7*	0.02*	1.7	92
Air sample car	328	0.2*	328	85

**Below method detection limit*

Table A3: SCCP and MCCP data from tests on concentrated sulfuric acid

	SCCP (ng/sample)	MCCP (ng/sample)	Sum CP (ng/sample)	Recovery (%)
Glass bottle P1	6.8*	0.01*	6.8	79
Glass bottle P2	2.3*	0.03*	2.3	82
Plastic bottle P1	3.8*	0.01*	3.8	75
Plastic bottle P2	2.9*	0.01*	2.9	76
Flask P1	5.2*	0.02*	5.2	78
Flask P2	3.9*	0.02*	3.9	83
Lab blank P1	15.9	0.03*	15.9	87
Lab blank P2	17.5	0.02*	17.6	79

**Below detection limit (based on no-PUF blanks) as described in section 3.1*

Table A4: SCCP and MCCP data from adsorbent tests.

	SCCP (ng/sample)	MCCP (ng/sample)	Sum CP (ng/sample)	Recovery (%)
Old P1	0.4*	0.1*	0.5	77
Old P2	0.4*	0.01*	0.4	77
Old P3	0.4*	0.01*	0.4	71
Old P4	0.3*	0.01*	0.3	81
New P1	0.3*	0.004*	0.3	81
New P2	0.4*	0.005*	0.4	73
New P3	0.2*	0.01*	0.2	74
New P4	0.4*	0.001*	0.4	77

**Below detection limit (based on no-PUF blanks)*

Table A5: SCCP and MCCP data from test of laboratory related materials.

	SCCP (ng/sample)	MCCP (ng/sample)	Sum CP (ng)	Recovery (%)
Glove new	475	12.5	488	82
Glove lab	261	10.7	272	355
Bench cover new	3.5*	0.1*	3.6	86
Bench cover lab	12.5	1.1	13.6	100
Latex pipette top un-used	52.0	4.0	56.0	74
Latex pipette top used	3272	705	3976	72
Ziploc bag	21.9	0.3*	22.1	NA
Aluminium foil	0.3*	0.6*	0.8	92
Vial cap new	15.1	1.0	1.1	90
Vial cap lab	3.9*	0.3*	4.2	83
Micropipette pack new	9.4*	0.6*	10.0	94
Micropipette pack lab	10.4	0.3*	10.7	89
Lab blank P1	0.1*	0.1*	0.2	134
Lab blank P2	0.02*	0.02*	0.04	115

**Below detection limit (based on no-PUF blanks)*

Table A6: SCCP and MCCP data from test on cross contamination in the Turbovap system.

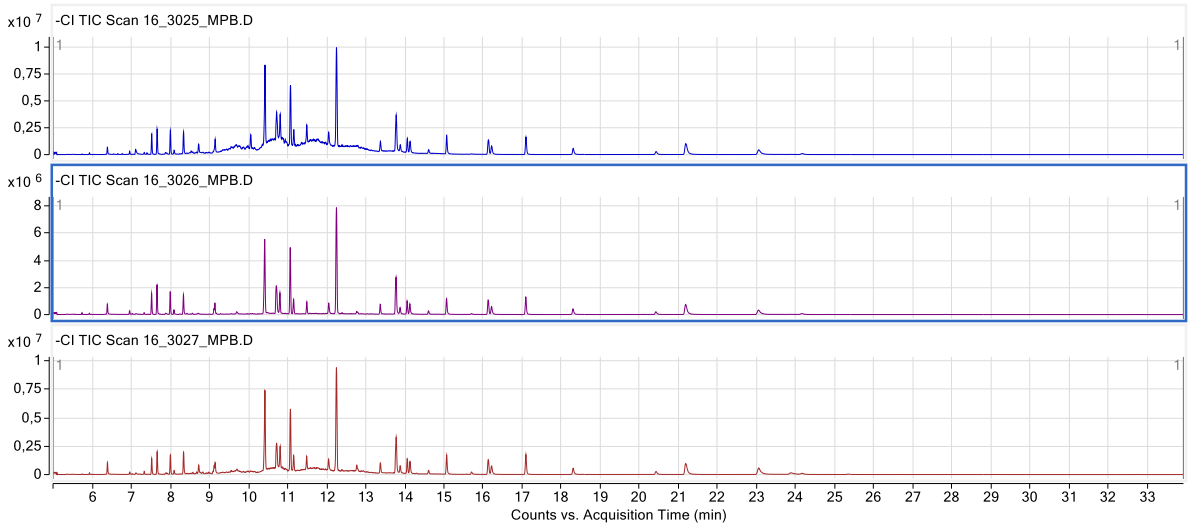
	SCCP (ng/sample)	MCCP (ng/sample)	Sum CP (ng/sample)	Recovery (%)
Cleaned P1	0.6*	0.001*	0.6	67
Cleaned P2	7.5*	0.003*	7.5	77
Cleaned P3	0.5*	0.01*	0.5	84
Cleaned P4	5.1*	0.003*	5.1	84
Uncleaned P1	0.5*	0.002*	0.5	90
Uncleaned P2	0.6*	0.003*	0.6	96
Uncleaned P3	1.3*	0.004*	1.3	98
Uncleaned P4	0.5*	0.005*	0.5	92

**Below detection limit (based on no-PUF method blanks)*

Table A7: SCCP and MCCP data from indoor air samples.

	SCCP (ng/sample)	MCCP (ng/sample)	SCCP (ng/m^3)	MCCP (ng/m^3)	Sum CP (ng/m^3)
Lab (clean/storage)	7461	35.0	55.5	0.3	55.8
Clean room	546	8.6*	4.1	0.06*	4.1
Lab (extraction)	4286	16.9	31.9	0.1	32.0
Field blank	148	8.3*			
Lab blank (PUF)	16.7*	3.9*			
Lab blank (no PUF)	5.4*	1.7*			

**Below method detection limit*



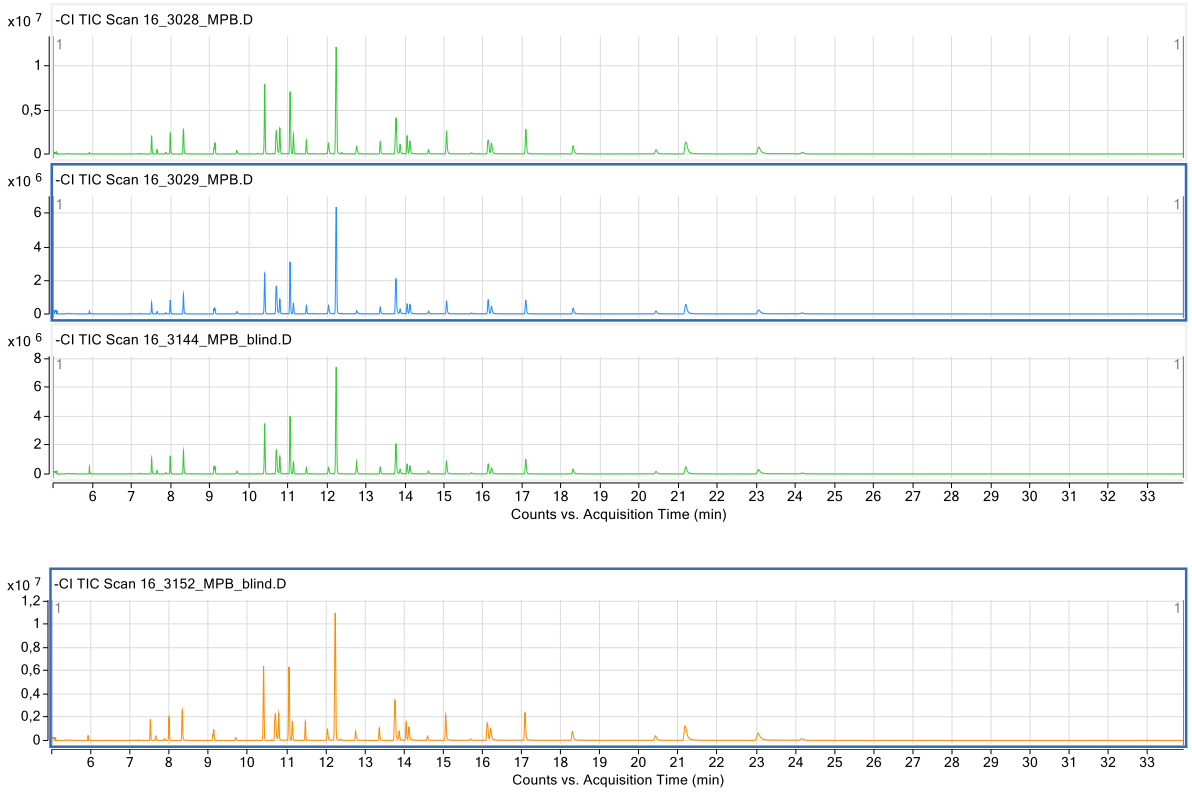


Figure A1: Chromatograms from indoor air samples

Table A8: SCCP and MCCP data from indoor dust/organic film samples.

	SCCP (ng/sample)	MCCP (ng/sample)	Sampled area (m^2)	SCCP (ng/m^2)	MCCP (ng/m^2)	Sum CP (ng/m^2)
Lab (cleaning/storage)	4569	895	1.6	2856	559	3415
Clean room	118	173	1.2	98.3	144	243
Lab (extraction)	6500	3380	3.5	1857	965	2822
Field blank	2.6*	0.3*				
Lab blank	3.2*	0.04*				
Lab blank	7.2*	1.7				

**Below detection limit (based on no-PUF method blanks)*

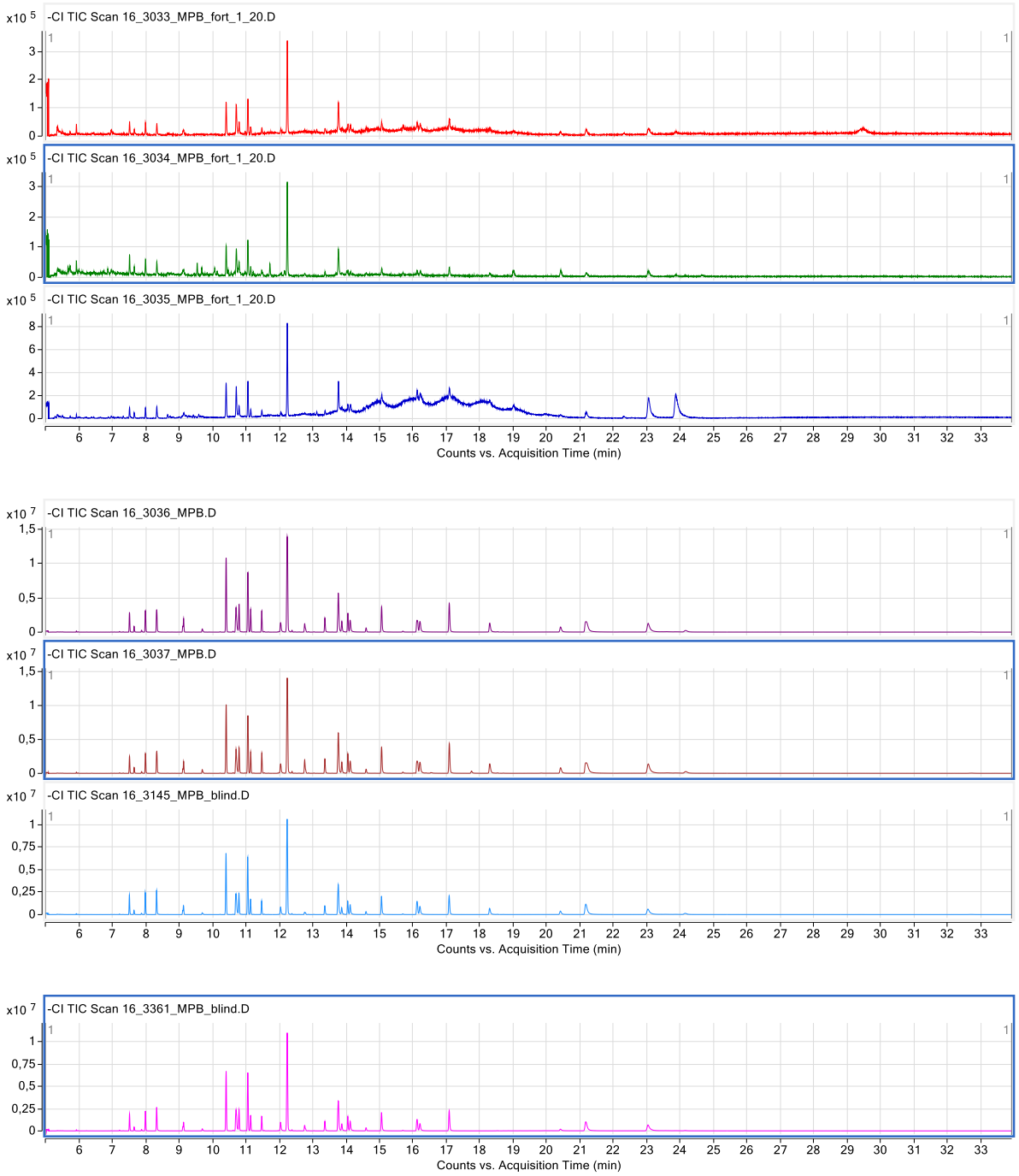


Figure A2: Chromatograms from dust/organic film samples

Table A9: Homologue groups of SCCPs included in the analytical process, type of fragment used, accurate mass of fragment and natural abundance.

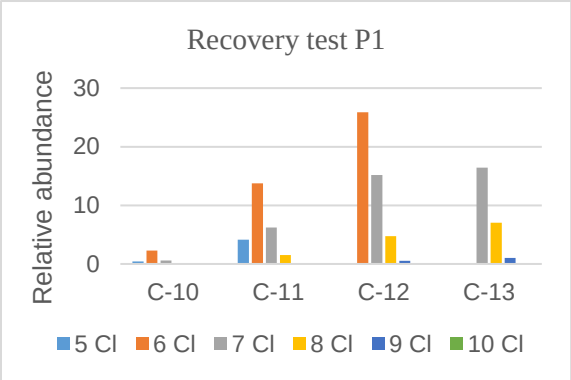
Homologue group	Fragment	m/z	Natural abundance (%)	Retention time (min)	Integration interval (min)
$C_{10}H_{17}Cl_5$	[M-HCl]-	277.9970	29	10.000	8.0-11.5
$C_{10}H_{16}Cl_6$	[M-HCl]-	311.9580	23.2	11.500	8.5-13.5
$C_{10}H_{15}Cl_7$	[M-Cl]-	346.9275	32.3	13.000	10.0-13.5
$C_{10}H_{14}Cl_8$	[M-Cl]-	380.8883	28.5	13.000	10.0-14.5
$C_{10}H_{13}Cl_9$	[M-Cl]-	416.8462	27.9	14.200	13.0-18.0
$C_{10}H_{12}Cl_{10}$	[M-Cl]-	450.8077	27.1	15.300	14.0-19.0
$C_{11}H_{19}Cl_5$	[M-HCl]-	292.0134	28.7	10.500	8.5-14.0
$C_{11}H_{18}Cl_6$	[M-HCl]-	325.9740	35.3	12.000	9.5-14.5
$C_{11}H_{17}Cl_7$	[M-Cl]-	360.9432	32	13.000	10.5-15.0
$C_{11}H_{16}Cl_8$	[M-Cl]-	394.9046	28.1	14.000	11.5-16.5
$C_{11}H_{15}Cl_9$	[M-Cl]-	430.8617	27.6	15.000	13.0-16.5
$C_{11}H_{14}Cl_{10}$	[M-Cl]-	464.8242	26.8	16.500	14.0-20.0
$C_{12}H_{20}Cl_6$	[M-HCl]-	339.9906	34.9	12.400	10.5-16.0
$C_{12}H_{19}Cl_7$	[M-Cl]-	374.9588	31.6	14.000	11.5-16.5
$C_{12}H_{18}Cl_8$	[M-Cl]-	408.9207	27.8	15.000	12.5-17.5
$C_{12}H_{17}Cl_9$	[M-Cl]-	444.8792	27.4	16.000	13.5-18.0
$C_{12}H_{16}Cl_{10}$	[M-Cl]-	478.8405	20.4	17.000	15.5-18.5
$C_{13}H_{21}Cl_7$	[M-Cl]-	388.9731	31.3	15.000	12.0-18.0
$C_{13}H_{20}Cl_8$	[M-Cl]-	422.9350	27.5	16.000	13.3-19.0
$C_{13}H_{19}Cl_9$	[M-Cl]-	458.8940	27.1	17.000	14.5-19.0
$^{13}C_{10}H_{16}Cl_6$	[M-Cl]-	323.0006		11.650	
TCN	M^-			9.680	

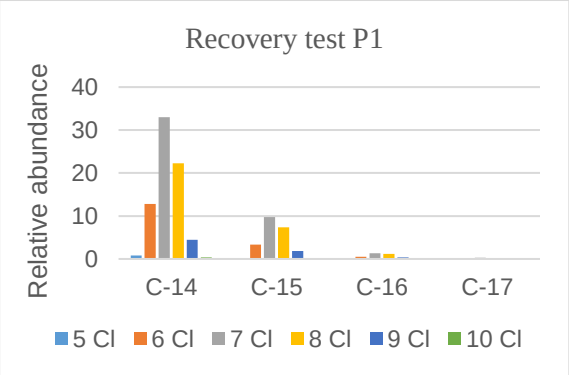
Table A10: Homologue groups of MCCPs included in the analytical process, type of fragment used, accurate mass of fragment and natural abundance.

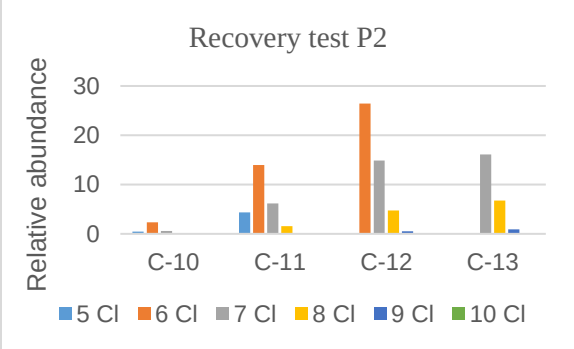
Homologue group	Fragment	m/z	Natural abundance (%)	Retention time (min)	Integration interval (min)
$C_{14}H_{25}Cl_5$	[M-Cl]-	355.0296	36.2	12.900	11.5-18.5
$C_{14}H_{24}Cl_6$	[M-Cl]-	369.0296	34.1	14.170	12.0-20.0
$C_{14}H_{23}Cl_7$	[M-Cl]-	402.9906	31	15.200	13.0-20.0
$C_{14}H_{22}Cl_8$	[M-Cl]-	436.9517	27.2	17.000	14.0-21.0
$C_{14}H_{21}Cl_9$	[M-Cl]-	472.9097	26.7	18.250	15.0-21.0
$C_{14}H_{20}Cl_{10}$	[M-Cl]-	506.8708	25.9	19.300	15.0-22.0
$C_{15}H_{27}Cl_5$	[M-Cl]-	349.0843	35.8	13.950	12.0-20.0
$C_{15}H_{26}Cl_6$	[M-Cl]-	383.0453	33.7	15.100	12.5-22.5
$C_{15}H_{25}Cl_7$	[M-Cl]-	417.0063	30.7	16.480	14.0-22.0
$C_{15}H_{24}Cl_8$	[M-Cl]-	450.9673	26.9	18.000	15.0-23.0
$C_{15}H_{23}Cl_9$	[M-Cl]-	486.9254	26.4	19.000	16.0-23.0
$C_{15}H_{22}Cl_{10}$	[M-Cl]-	520.8864	25.6	20.470	16.5-25.0
$C_{16}H_{29}Cl_5$	[M-Cl]-	363.1000	35.4	13.000	14.0-20.0
$C_{16}H_{28}Cl_6$	[M-Cl]-	397.0610	33.4	17.000	13.0-22.0
$C_{16}H_{27}Cl_7$	[M-Cl]-	431.0220	30.3	18.000	14.0-25.0
$C_{16}H_{26}Cl_8$	[M-Cl]-	464.9830	26.6	19.000	15.5-24.0
$C_{16}H_{25}Cl_9$	[M-Cl]-	500.9412	26.1	20.000	16.0-26.0
$C_{16}H_{24}Cl_{10}$	[M-Cl]-	534.9022	25.3	21.500	18.0-26.0
$C_{17}H_{29}Cl_7$	[M-Cl]-	445.0377	30	19.000	14.0-25.0
$^{13}C_{10}H_{16}Cl_6$	[M-Cl]-	323.0006		11.650	

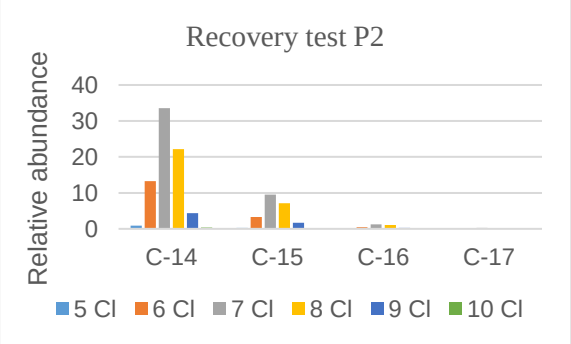
Table A11: SCCP and MCCP data from recovery tests. Alt. quant values are quantified using technical standard 55 % Cl by weight.

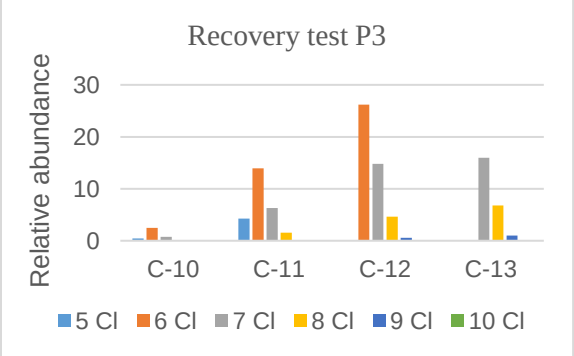
	SCCP (ng/sample)	MCCP (ng/sample)	Recovery (%)	SCCP alt. quant. (ng/sample)
Recovery test P1	10520	11338	81	4149
Recovery test P2	9969	9517	103	3931
Recovery test P3	10430	10265	108	4113
Recovery test P4	10718	12100	73	4227
Recovery test P5	10026	9826	95	3954
Recovery test P6	10067	10184	99	3970

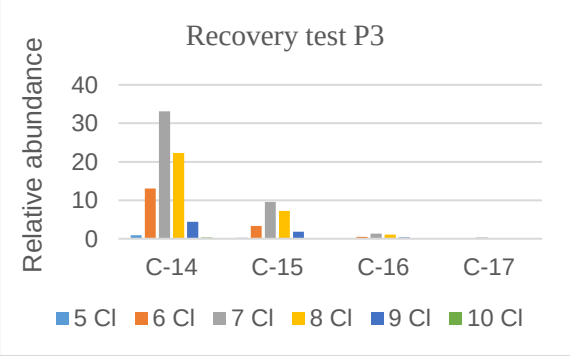

Recovery test P1
Relative abundance
30
20
10
0
C-10
C-11
C-12
C-13
5 Cl
6 Cl
7 Cl
8 Cl
9 Cl
10 Cl

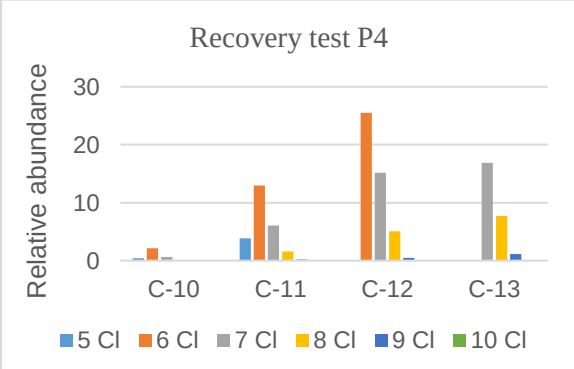

Recovery test P1
Relative abundance
40
30
20
10
0
C-14
C-15
C-16
C-17
5 Cl
6 Cl
7 Cl
8 Cl
9 Cl
10 Cl

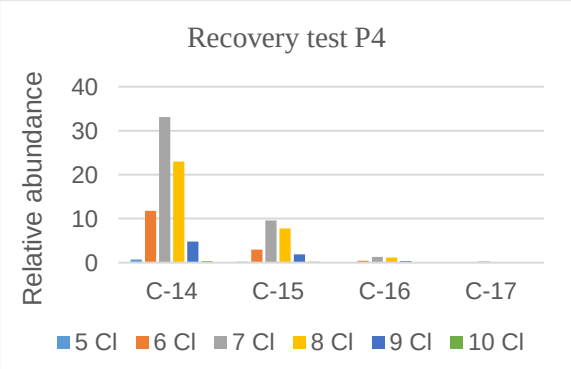

Recovery test P2
Relative abundance
30
20
10
0
C-10
C-11
C-12
C-13
5 Cl
6 Cl
7 Cl
8 Cl
9 Cl
10 Cl


Recovery test P2
Relative abundance
40
30
20
10
0
C-14
C-15
C-16
C-17
5 Cl
6 Cl
7 Cl
8 Cl
9 Cl
10 Cl


Recovery test P3
Relative abundance
30
20
10
0
C-10
C-11
C-12
C-13
5 Cl
6 Cl
7 Cl
8 Cl
9 Cl
10 Cl


Recovery test P3
Relative abundance
40
30
20
10
0
C-14
C-15
C-16
C-17
5 Cl
6 Cl
7 Cl
8 Cl
9 Cl
10 Cl


Recovery test P4
Relative abundance
30
20
10
0
C-10
C-11
C-12
C-13
5 Cl
6 Cl
7 Cl
8 Cl
9 Cl
10 Cl


Recovery test P4
Relative abundance
40
30
20
10
0
C-14
C-15
C-16
C-17
5 Cl
6 Cl
7 Cl
8 Cl
9 Cl
10 Cl

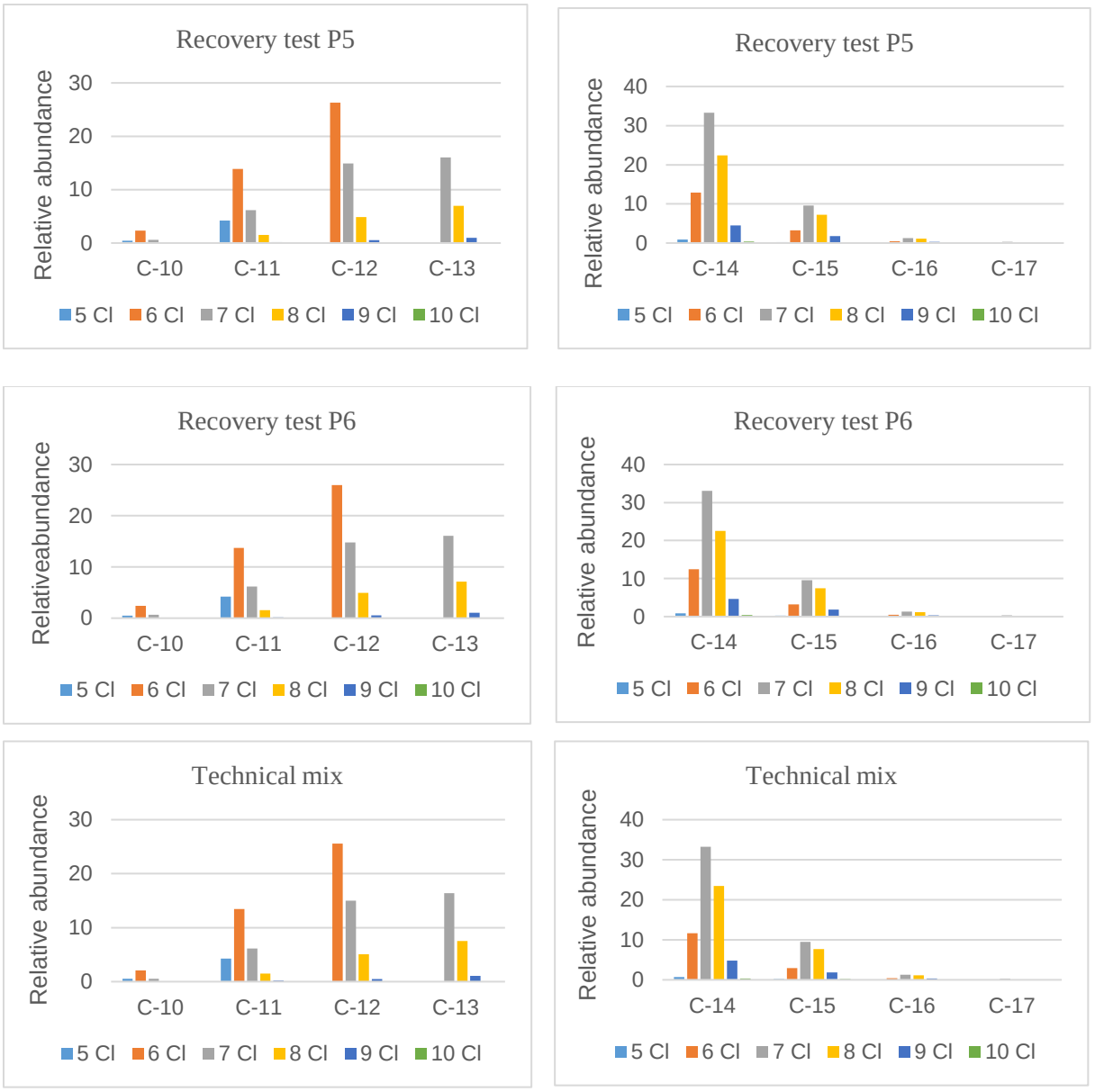


Figure A3: Homologue group distribution in six parallels of recovery test, and mixture of technical standards used for comparison and quantification of recovery tests.

Table A12: Sample characteristics for AAS samples.

	Sampled from (date)	Sampled to (date)	Sample volume (m3)
Andøya 1	24.10.2016	26.10.2016	1349,89
Andøya 2	31.10.2016	02.11.2016	1350,58
Birkenes 1	20.10.2016	22.10.2016	1368,68
Birkenes 2	22.10.2016	24.10.2016	1333,02
Zeppelin 1	19.10.2016	21.10.2016	1212,71
Zeppelin 2	26.10.2016	28.10.2016	1204,28
Lab blank (PUF)			1
Lab blank (no PUF)			1

Table A13: SCCP and MCCP data from AAS samples.

	SCCP (ng/sample)	MCCP (ng/sample)	SCCP ($pg/m^{3)}$	MCCP ($pg/m^{3)}$	Sum CP (pg/m^3)	Recovery (%)
Andøya 1	149	3.8*	110	2,8*	113	84
Andøya 2	336	2.3*	249	1,7*	251	78
Birkenes 1	63.5	0.6*	46,4	0,4*	46,8	105
Birkenes 2	56.3	7.2*	42,3	5,4*	47,7	83
Zeppelin 1	186	48.5	153	40.0	193	112
Zeppelin 2	293	342	243	284	527	106
Lab blank (PUF)	4,5*	0,1*				101
Lab blank (no PUF)	0,9*	0,1*				87

**Below method detection limit*

APPENDIX B

B.1 Chemical analysis

B.1.1 SOLVENTS, REAGENTS AND MATERIALS

All materials used in the sampling, laboratory work and analysis is listed in Table B1. Standards, and content of standard solutions POP I, PBDE I, new bromine, dechlorane, pesticide, PCB and DDT is listed in Tables B2 to B9.

Table B1: Solvents, reagents and materials used for sampling, laboratory work and analysis

	Producer/origin	Size	Purity grade	Use
AAS sampling unit	Digitel (Hegenau, CH)			Active air sampling
Acetone Pestinorm	VWR Chemicals	2.5 L	99.70 %	Cleaning of PUF material, Turbovap system
Agilent MassHunter qual B 07.00	Agilent (Santa Clara, USA)			Inspection of chromatograms, MS spectra
Agilent MassHunter quant B. 06.00	Agilent (Santa Clara, USA			Quantification process
Alkaline soap (Extrane)	Merck (Darmstadt, D)	1 L		Cleaning of glassware
Aluminium foil	Caterwrap	450mx150mm		Storage of PUF sampling material
Aluminium foil sheets	Korff	100x100 mm		Cover for Turbovap glasses
Auto sampler Agilent 7693	Agilent (Santa Clara, USA			For GC
Brown glass vials	Supelco	40 mL		Ultrasound extraction
Caps for GC vials incl. Septum				For GC
Column for GC HP 5ms Ultra Inert	Agilent (Santa Clara, USA	15+15 m		For GC
Cotton wool	Vernon Carus	500 g		Stopper in chromatography column used in silica clean-up
Diethyl ether SupraSolv	Merck (Darmstadt, D)	1 L		Extractions
Filter holder	Digitel (Hegenau, CH)			Holder for GFF sampling material

Fume hood cover Versi-Dry	Thermo Scientific	508x91500 mm		Plastic backed paper fume hood cover
GC- Agilent 7890B	Agilent (Santa Clara, USA			Separation of components in samples
GC vials	Chromacol (USA)	300 µL		For GC
Glass centrifuge tubes	Schott Duran (D)	10 mL		Acid clean-up
Glass chromatography columns	Schott Duran (D)	15 mm i.d.		Clean-up of samples using silica
Glass fibre filter	Whatman	150 mm		Sampling material
Glass housing for AAS sampling	Digitel (Hegenau, CH)			Holder for PUF sampling material
Glass vial	Chromacol (USA)	2 mL		Preparation of internal standards
Glass vial (pointed bottom)	Chromacol (USA)	1 mL		Storage of sample
Glass water cooled condensation tubes	Schott Duran (D)			Extractions
Glassware (Erlenmeyer, beakers, measuring cylinders)	Schott Duran (D)			General laboratory work
Heat mantles	VWR			Soxhlet extractions
Hypodermic needles Microlance	Becton Dickinson Medical			Volume reduction using N^2 gas
iso-Octane Emsure	Merck (Darmstadt, D)	1 L	99.50 %	Solvent used for samples during analysis on GC
iso-Propanol	Kemetyl (SE)			Wetting of wipes used for dust/organic film collection
Latex tops for Pasteur pipettes	Svenska latex AB (SE)			General laboratory work
Methane	Paraxair (NO)			Gas used in CI source for creation of thermal electrons
Micropipettes	Blaubrand (D)	20, 50, 100 µL		Transfer of standards to samples, transfer of samples to GC vials
MS office Excel	Microsoft (USA)			Final steps of quantification procedure
N^2	Paraxair (NO)			Volume reduction of samples
N^2 evaporation system				Volume reduction of samples
n-Hexane Pestinorm	VWR Chemicals	2.5 L	95.00 %	Extractions, rinsing of glassware
Nitrile gloves	Ansell			General laboratory work
Ovens				Cleaning of glassware, heating of silica, sodium sulphate
PAS sampling system	RECETOX (CZ)			Passive air sampling
Pasteur pipettes	Scherf prazision GMBH			General laboratory work
PTV inlet	Agilent (Santa Clara, USA			Sample introduction onto the GC column

PUF disks	Sunde Søm & Skumplast A/S (NO)	14x1.35 mm		Sampling material
PUF plugs	Digitel (Hegenau, CH)	75x45mm		Sampling material
Q-TOF- Agilent 7200	Agilent (Santa Clara, USA)			Compound identification/quantification
R studio	R			Statistical analysis
Round bottom flasks	Schott Duran (D)	500 mL		Extractions
Silica gel 60Å	Merck (Darmstadt, D)	1 kg		Clean-up of samples
Sodium sulphate	Merck (Darmstadt, D)	1 kg		Removes traces of water from sample during silica clean-up
Soxhlet extractor	Schott Duran (D)	100 mL		Extraction of GFFs
Soxhlet extractor	Schott Duran (D)	200 mL		Extraction of PUF disks
Soxhlet extractor	Schott Duran (D)	300 mL		Extraction of PUF plugs
Sulfuric acid Emsure (glass bottle)	Merck (Darmstadt, D)	1 L	95-97 %	Clean-up of samples
Sulfuric acid Emsure (plastic bottle)	Merck (Darmstadt, D)	1 L	95-97 %	Clean-up of samples
Toluene Pestinorm	VWR Chemicals	2.5 L	99.70 %	Cleaning of PUF material
Tongs				Removal of metal ring from GFF holders
Turbovap	Zymark			Volume reduction of samples
Turbovap glasses	Biotage	200 mL		Volume reduction of samples on Turbovap system
Tweezers (flat front)				Removal of GFFs from holder
Tweezers (long)				Placing of PUF disks in soxhlet extractors
Ultrasonic bath	VWR			Extractions
Vial caps Teflon liner	Supelco			
Whirl mixer	VWR			Mixing during acid clean-up, homogenization of samples
Ziploc bags	Polynova			Storage of sampling material

Table B2: Single component standards and technical grade CP standards used in the analytical procedure

Component	Name	Producer	Concentration
Technical SCCP 51.5% Cl		Dr. Ehrenstofer, Germany	100 µg/mL
Technical SCCP 55.5% Cl		Dr. Ehrenstofer, Germany	100 µg/mL
Technical SCCP 63% Cl		Dr. Ehrenstofer, Germany	100 µg/mL
Technical MCCP 52% Cl		Dr. Ehrenstofer, Germany	100 µg/mL
Technical MCCP 57% Cl		Dr. Ehrenstofer, Germany	100 µg/mL
1,5,5,6,6,10 hexachlorodecane (^{13}C labelled)	CP I	Cambridge Isotope Laboratories	100 µg/mL
1,2,3,4 Tetrachloronaphthalene	TCN		3.5 µg/mL

Table B3: Components present in the POP I standard mixture

Component	Concentration (pg/µL)
^{13}C PCB- 28	242
^{13}C PCB- 52	243
^{13}C PCB- 101	244
^{13}C PCB- 105	243
^{13}C PCB- 114	244
^{13}C PCB- 118	244
^{13}C PCB- 123	241
^{13}C PCB- 138	245
^{13}C PCB- 153	245
^{13}C PCB- 156	241
^{13}C PCB- 157	245
^{13}C PCB- 167	242
^{13}C PCB- 180	243
^{13}C PCB- 189	243
^{13}C PCB- 209	243
^{13}C α-Hexachlorocyclohexane (HCH)	996
^{13}C β-HCH	203
^{13}C γ-HCH	1006
^{13}C δ-HCH	1010
^{13}C *p.p.*Dichlorodiphenyldichloroethylene (DDE)	330
^{13}C *o.p.*Dichlorodiphenyldichloroethane (DDD)	327
^{13}C *p.p.*DDT	334
^{13}C Pentachlorbenzene (PeCB)	101
^{13}C HCB	93,0
^{13}C *trans*-Nonachlor	314
^{13}C *cis*-Nonachlor	2535
^{13}C *trans*-Chlordane	510

^{13}C *cis*-Chlordane	2540
^{13}C Oxychlordane	2499
^{13}C Heptachlor epoxide	1005
^{13}C Heptachlor	2530
^{13}C Dieldrin	2536
^{13}C Mirex	532
^{13}C Dechlorane plus syn	532
^{13}C Endosulfan I	2532
^{13}C Endosulfan II	2532
^{13}C Endosulfan Sulfate	2552
d14 Trifluralin (di-n-propyl)	2559
^{13}C Endrin	2531
^{13}C Aldrin	2524
^{13}C Isodrin	2535

Table B4: Components present in the PBDE I standard mixture

Component	Concentration (pg/µL)
^{13}C PBDE-28	260
^{13}C PBDE-47	263
^{13}C PBDE-99	263
^{13}C PBDE-153	265
^{13}C PBDE-183	265
^{13}C PBDE-197	261
^{13}C PBDE-206	262
^{13}C PBDE-209	589

Table B5: Content of new-bromine standard.

Component	Concentration (pg/µL)
^{13}C 1,2-Bis(2,4,6-tribromphenoxy)ethane (BTBPE)	1009
^{13}C Hexabromobenzene (HBB)	963
^{13}C d17 2-ethyl-1-hexyl 2,3,4,5-tetrabromobenzoate (EHTBB)	987
^{13}C Decabromodiphenyl ether (DBDPE)	995
^{13}C 1,2,3,4,5-pentabromobenzene (PBBz)	1027

Table B6: Components present in Dechlorane ^{13}C and ^{12}C standard mix used for assessing potential interferences

Component	Concentration (pg/ µL)
^{13}C10 Dechlorane Plus syn	49
Dechlorane Plus Syn	99
Dechlorane Plus Anti	96
Dechlorane 601	89
Dechlorane 602	91
Dechlorane 603	91
Dechlorane 604	96
Dibromaldrin	93
1,2,3,4 TCN	26

Table B7: Components present in pesticide ^{13}C and ^{12}C standard mix used for assessing potential interferences

Component	Concentration (pg/ µL)
^{13}C PCB- 28	20
^{13}C PCB- 52	20
^{13}C PCB- 101	20
^{13}C PCB- 105	20
^{13}C PCB- 114	20
^{13}C PCB- 118	20
^{13}C PCB- 123	20
^{13}C PCB- 138	20
^{13}C PCB- 153	20
^{13}C PCB- 156	20
^{13}C PCB- 157	20
^{13}C PCB- 167	20
^{13}C PCB- 180	20
^{13}C PCB- 189	20
^{13}C PCB- 209	20
^{13}C α-HCH	82
^{13}C β-HCH	17
^{13}C γ-HCH	82
^{13}C δ-HCH	82
^{13}C *p.p.*DDE	27
^{13}C *o.p.*DDD	27
^{13}C *p.p.*DDT	27

^{13}C PeCB	8
^{13}C HCB	8
^{13}C *trans*-Nonachlor	26
^{13}C *cis*-Nonachlor	207
^{13}C *trans*-Chlordane	42
^{13}C *cis*-Chlordane	207
^{13}C Oxychlordane	204
^{13}C Heptachlor epoxide	82
^{13}C Heptachlor	206
^{13}C Dieldrin	207
^{13}C Mirex	43
^{13}C Dechlorane plus syn	43
^{13}C Endosulfan I	207
^{13}C Endosulfan II	207
^{13}C Endosulfan Sulfate	208
d14 Trifluralin (di-n-propyl)	208
^{13}C Endrin	206
^{13}C Aldrin	206
^{13}C Isodrin	207
^{12}C α-HCH	435
^{12}C β-HCH	116
^{12}C γ-HCH	290
^{12}C Dieldrin	435
^{12}C Aldrin	435
^{12}C Endrin	290
^{12}C Mirex	290
^{12}C Isodrin	174
^{12}C Trifluralin	174
^{12}C *trans*-Chlordane	435
^{12}C α-Chlordane	116
^{12}C γ-Chlordane	116
^{12}C Oxychlordane	174
^{12}C *trans*-Nonachlor	116
^{12}C *cis*-Nonachlor	116
^{12}C Heptachlor	174
^{12}C Heptachlor epoxide	290
^{12}C Heptachlorendoepxide	290
^{12}C Endosulfan I	40
^{12}C Endosulfan II	22
^{12}C Endosulfan sulphate	116
^{12}C Hexachlorobenzene	15
^{12}C Pentachlorbenzene	15
^{12}C *o.p.*DDE	145
^{12}C *p.p.*DDE	145
^{12}C *o.p.*DDD	145

^{12}C *p.p.*DDD	145
^{12}C *o.p.*DDT	145
^{12}C *p.p.*DDT	145
Dechlorane Plus Anti	295
Dechlorane Plus Syn	328
1,2,3,4 TCN	74

Table B8: Components present in PCB ^{13}C and ^{12}C standard mix used for assessing potential interferences

Component	Concentration (pg/µL)
^{13}C PCB- 28	20
^{13}C PCB- 52	20
^{13}C PCB- 101	21
^{13}C PCB- 105	20
^{13}C PCB- 114	20
^{13}C PCB- 118	20
^{13}C PCB- 123	20
^{13}C PCB- 138	21
^{13}C PCB- 153	21
^{13}C PCB- 156	20
^{13}C PCB- 157	21
^{13}C PCB- 167	20
^{13}C PCB- 180	20
^{13}C PCB- 189	20
^{13}C PCB- 209	20
^{13}C α-HCH	84
^{13}C β-HCH	17
^{13}C γ-HCH	85
^{13}C δ-HCH	85
^{13}C *p.p.*DDE	28
^{13}C *o.p.*DDD	27
^{13}C *p.p.* DDT	28
^{13}C PeCB	9
^{13}C HCB	8
^{13}C *trans*-Nonachlor	26
^{13}C *cis*-Nonachlor	213
^{13}C *trans*-Chlordane	43
^{13}C *cis*-Chlordane	214
^{13}C Oxychlordane	210
^{13}C Heptachlor epoxide	85
^{13}C Heptachlor	213
^{13}C Dieldrin	213

^{13}C Mirex	45
^{13}C Dechlorane plus syn	45
^{13}C Endosulfan I	213
^{13}C Endosulfan II	213
^{13}C Endosulfan Sulfate	215
d14 Trifluralin (di-n-propyl)	215
^{13}C Endrin	213
^{13}C Aldrin	212
^{13}C Isodrin	213
^{12}C PCB-18	22
^{12}C PCB-28	22
^{12}C PCB-31	22
^{12}C PCB-33	22
^{12}C PCB-37	22
^{12}C PCB-47	22
^{12}C PCB-52	22
^{12}C PCB-66	22
^{12}C PCB-74	22
^{12}C PCB-99	22
^{12}C PCB-101	22
^{12}C PCB-105	22
^{12}C PCB-114	22
^{12}C PCB-118	22
^{12}C PCB-122	22
^{12}C PCB-123	22
^{12}C PCB-128	22
^{12}C PCB-138	22
^{12}C PCB-141	22
^{12}C PCB-149	22
^{12}C PCB-153	22
^{12}C PCB-156	22
^{12}C PCB-157	22
^{12}C PCB-167	22
^{12}C PCB-170	22
^{12}C PCB-180	22
^{12}C PCB-183	22
^{12}C PCB-187	22
^{12}C PCB-189	22
^{12}C PCB-194	22
^{12}C PCB-206	22
^{12}C PCB-209	22
^{12}C HCB	19
^{12}C PeCB	19
1,2,3,4 TCN	70

Table B9: Components present in DDT ^{13}C and ^{12}C standard mix used for assessing potential interferences

Components	Concentration (pg/µL)
^{13}C α-HCH	20
^{13}C β-HCH	4
^{13}C γ-HCH	20
^{13}C δ-HCH	9
^{13}C *p.p.*DDE	6
^{13}C *o.p.*DDD	6
^{13}C *p.p.*DDT	7
^{12}C α-HCH	14
^{12}C β-HCH	4
^{12}C γ-HCH	10
^{12}C Dieldrin	14
^{12}C Aldrin	14
^{12}C Endrin	10
^{12}C Mirex	10
^{12}C Isodrin	6
^{12}C Trifluralin	6
^{12}C *trans*-Chlordene	14
^{12}C α-Chlordane	4
^{12}C γ-Chlordane	4
^{12}C Oxychlordane	6
^{12}C *trans*-Nonachlor	4
^{12}C *cis*-Nonachlor	4
^{12}C Heptachlor	6
^{12}C Heptachlor epoxide	10
^{12}C Heptachlorendoepxide	10
^{12}C Endosulfan I	4
^{12}C Endosulfan II	7
^{12}C Endosulfan sulphate	4
^{12}C HCB	0.5
^{12}C PeCB	0.5
^{12}C *o.p.*DDE	5
^{12}C *p.p.*DDE	5
^{12}C o.p.DDD	5
^{12}C *p.p.*DDD	5
^{12}C *o.p.*DDT	5
^{12}C *p.p.*DDT	5
Delta-HCH	15
1,2,3,4 TCN	71

B.1.2 QUALITY ASSURANCE

All solvents used in the study were from batches controlled and approved by NILU, according to accredited routines. Standard solutions used (with the exception of CP technical standards) were prepared and controlled for accuracy in concentration and purity in accordance with NILU's accredited routines. In addition, the laboratory procedure described is based on NILU's accredited method for analysis of POPs in air samples. This method is however not accredited or fully validated for CPs.

Pre-cleaning of the PUF plugs was done with soxhlet extraction using toluene (24 hours, new plugs only), acetone (8 hours) and n-hexane (8 hours) followed by drying in vacuum according to NILU's accredited routines. Dry and clean PUFs were subsequently wrapped in aluminum foil and Ziploc bags. The glass housings (Digitel) for the PUFs were soaked overnight in tap water and alkaline soap, rinsed thoroughly in tap water, heat-treated at 400℃ before further cleaning in acetone and n-hexane. Prior to use, the GFFs were heat treated at 400℃. The GFF holders were soaked overnight in tap water and alkaline soap before thorough rinsing with tap water, and further cleaning in acetone and n-hexane. In addition, all glassware used in the laboratory procedure was heat treated at 400°C, and rinsed with n-hexane, or other suitable solvent prior to use.

Silica and sodium sulfate was activated by heat treating at 550℃. After activation, the silica and sodium sulfate was given an expiry date of four weeks.

Blank samples are an important aspect of quality assurance. This is covered extensively in the Materials and methods, and Results and discussion sections of this paper.

B.1.3 EXTRACTION

B.1.3.1 Soxhlet extraction

For samples collected from active samplers, the GFF and the PUF plugs were extracted separately, using the same portion of solvent for both extractions. The GFF holders were unwrapped, and the metal ring holding the GFF in place was removed using a tong pre-cleaned in n-hexane. The plastic ring protecting the GFF was removed using tweezers pre-cleaned in n-hexane. The GFF was folded twice, and transferred to a 100 mL soxhlet extractor. 50 µL CP I internal standard was added to the GFF prior to extraction. This was done by adding the exact volume of internal standard using a micropipette, to a vial containing approximately 0.5 mL n-

hexane. This solution was transferred to the GFF in the soxhlet using a Pasteur pipette. The GFFs were extracted for eight hours using 10% diethyl ether in n-hexane.

The PUFs were transferred from the packing material to a 300 mL soxhlet extractor, and a metal rod pre-cleaned with n-hexane was used to position the PUFs correctly in the soxhlet. The PUFs were subsequently extracted for eight hours using the same portion of 10% diethyl ether in n-hexane that were used in the GFF extraction. After extraction, the glassware and extract was cooled down to room temperature, and the remaining solvent in the PUFs was removed using a pre-cleaned metal rod to squeeze the PUFs. The extracts were subsequently volume reduced using the Turbovap system as described in section B.1.6.

For samples collected using passive sampling the laboratory procedure was similar, with the exception of the GFF step, and the use of 200 mL soxhlet. In addition, the transfer of the PUF disc to the soxhlet was done by rolling the disc up using pre-cleaned metal tweezers, and inserting into the soxhlet using the same tweezers. The internal standard was added to the PUF disk, using the same method as above.

B.1.3.2 Ultrasonic extraction

The ultrasonic extraction process was done by placing the sample material in 50 mL sample vials, which were pre-cleaned in n-hexane. Internal standard addition was done by adding the exact volume (50 µL) of CP I internal standard using a micropipette, to a vial containing approximately 0.5 mL n-hexane. This solution was transferred to the vials using Pasteur pipettes. The vials were filled with 10% diethyl ether in n-hexane solvent to cover the material, corked, and placed in an ultrasonic bath for a set time. When repetition was required, the extract from the vial was transferred to a TurboVap glass pre-cleaned with n-hexane. The TurboVap glass was covered in aluminum foil, while the vial was filled with new solvent to cover the material inside. The vial was placed in the ultrasonic bath again, and the collected extracts pooled in the corresponding TurboVap glass for volume reduction (see section B.1.6).

B.1.4 ACID CLEANUP

After extraction, all samples were volume reduced as described in section B.1.6, and transferred to glass centrifuge tubes. To remove matrix related and acid labile potential interferences, 2 mL concentrated sulfuric acid was added to the samples in the centrifuge tubes using Pasteur pipettes, and the content was mixed using a whirl mixer, and left overnight. The acid treated extracts were transferred to clean centrifuge tubes, and the acid procedure was repeated until

the acid was without any color. The samples were subsequently transferred to pre-cleaned TurboVap glasses for volume reduction before silica cleanup.

B.1.5 SILICA CLEANUP

After acid cleanup, samples were cleaned further using activated silica. Glass columns (15 mm inner diameter) with pre-cleaned cotton stoppers fitted at the base, were dry packed with 4 g activated silica, topped with a 1 cm layer of sodium sulfate. The packed columns were washed through using 30 mL of 10% diethyl ether in n-hexane, while making sure the columns did not run dry. The samples were applied to the columns, and eluted with 30 mL of 10% diethyl ether in n-hexane. The extracts was collected in Turbovap glasses for volume reduction (see section B.1.6).

B.1.6 VOLUME REDUCTION USING TURBOVAP

All volume reduction after extraction, acid cleanup and silica cleanup of the samples and tests was performed on a TurboVap 500 from Zymark. The TurboVap glassware was rinsed prior to use using n-hexane, and the samples transferred. The volume of all samples were reduced to 0.5 mL, using the optical sensor endpoint function on the instrument. Prior to use, the TurboVap system is cleaned by reducing approximately 10 mL of acetone to 0.5 in each of the two compartments.

B.1.7 FINISHING

During the last volume reduction in the laboratory procedure, the solvent was changed to iso-octane using the TurboVap, and following this, the samples were transferred to sample vials with a tapered bottom. The volume was reduced further to 100 µL using a gentle stream of N_2 gas directed through surgical needles. The needles were changed between each sample. As the final step, 20 µL TCN was added as a recovery standard, and the samples were mixed well using a whirl mixer. 20 µL of the samples were transferred to pre-cleaned GC vials using micropipettes, and analyzed using a GC/Q-TOF instrument.

B.2 Instrumental analysis

B.2.1 INSTRUMENTAL PARAMETERS

The gas chromatographic separation was done using a two-part column, HP-5ms Ultra Inert stationary phase, length 15 + 15 meters, with flow rates of 1.2 mL min^{-1} on the first section of the column, and 1.4 mL min^{-1} on the second section. Inner diameter of the column was 250 µm,

and the film thickness was 0.25 µm. Samples were introduced using a programmed temperature vaporization (PTV) inlet in solvent vent mode, starting at 50 ℃, holding for 0.35 min, increasing by 500 ℃/min to 320 ℃, holding for 3 minutes, before changing by 10 ℃/min to 290 ℃, and holding for 5 min.

The GC oven temperature program was as follows: initial temperature 45 ℃, hold time 2 min. Change rate 70 ℃/min to 180 ℃, hold for 1 min. Change rate 10 ℃/min to 280 ℃, hold for 1 min, then change rate 10 ℃/min to 310 ℃ and hold for 15 min.

The Q-TOF MS was fitted with a chemical ionization ion source run in ECNI mode using methane gas to create thermal electrons. The ion source was kept at 120 ℃ to optimize the formation of the $[M-Cl]^-$ ion. 250 electron volts in the source, and an emission current of 5 µA.

B.3 Quantification

The quantification of CP content in samples and blank samples was based on the work of Tomy et al. (1997). The quantification was performed against a quantification standard with known content of CP technical mixture and known content of internal standard, which was included in the same sample run on the instrument as the sample in question. Equation 1 was used:

Equation 1:

$$\text{Sample (ng)} = \frac{\text{Total HG area smple}}{\text{Total HG area std}} \times \frac{\text{Rel. ab. std}}{\text{Rel. ab. smple}} \times \frac{\text{Avrg. Mm smple}}{\text{Avrg. Mm std}} \times \frac{\text{Amount ISTD smple}}{\text{Amount ISTD std}} \times \frac{\text{Area ISTD std}}{\text{Area ISTD smple}} \times \text{Consentration std (ng/µL)} \times \text{Amount std (µL)}$$

Where Total HG area represents the integrated signal of the ion from the most abundant homologue group present, divided by the natural abundance of the isotopic combination of this ion, Rel. ab. represents abundance of the most abundant homologue group relative to the total CP content weighted by the chlorine content of the homologue group, and Avrg. Mm represents the average molar mass of the CPs present. For air samples, the result is converted to relevant units by dividing the equation result by the sampled air volume. The weighting of the relative

abundance of the homologue groups by chlorine content is done in order to correct for the variation in ionization degree in the ion source, as mentioned in section 1.3.3.

Recovery of internal standard in samples was calculated using a relative response factor (RRF_g) from a quantification standard analyzed on the GC/Q-TOF during the same sample run (Equation 2), and subsequently calculated using the relative response factor in Equation 3.

Equation 2:

$$\text{RRFg} = \frac{\text{Amount TCN x Area ISTD}}{\text{Amount ISTD x Area TCN}}$$

Equation 3:

$$\text{Recovery ISTD(\%)} = \frac{\text{Amount TCN x Area ISTD x 100}}{\text{RRFg x Amount ISTD x Area TCN}}$$

Figures B1 and B2 show the spreadsheets used to quantify SCCP and MCCP content respectively. Integrated areas obtained from the MassHunter software were exported as excel files, and pasted into the spreadsheets. Prior to export, the integration of all m/z values was controlled, and where necessary, re-integrated manually.

The column of the spreadsheets containing response proportional to number of Cl, is the basis for graphs showing homologue group distribution.

Spreadsheet for determining the formula group abundance profiles of short chain PCAs in environmental samples							
							Factor ng til pg
Sample:	17/0317_Zeppelin2				***Sample amount:***	1204,28	1000
Homologue group	***Area***	***Total HG area***	***Adj. resp. normalized***	***Homologue Total***	***Norm area / Cl #***	***Response prop. to Cl #***	***Prop response x molar mass***
10,5	3654,387047	12601,335	1,1		0,23	1,55	4,88
10,6	21619,79495	93188,771	8,3		1,39	9,57	33,39
10,7	14942,69522	46262,214	4,1	***15,0***	0,59	4,07	15,61
10,8	4229,17068	14839,195	1,3		0,17	1,14	4,78
10,9	223,8763895	802,424	0,1		0,01	0,05	0,25
10,10	0	0,000	0,0		0,00	0,00	0,00
11,5	9142,382583	31854,992	2,9		0,57	3,93	12,90
11,6	30781,14915	87198,723	7,8		1,30	8,95	32,50
11,7	16458,43894	51432,622	4,6	***16,4***	0,66	4,53	17,99
11,8	2943,265425	10474,254	0,9		0,12	0,81	3,48
11,9	425,5134	1541,715	0,1		0,02	0,11	0,49
11,10	49,10378985	183,223	0,0		0,00	0,01	0,06
12,6	28307,47824	81110,253	7,3		1,21	8,33	31,40
12,7	12946,21476	40969,034	3,7		0,52	3,61	14,84
12,8	4093,460951	14724,680	1,3	***12,6***	0,16	1,13	5,06
12,9	740,7026674	2703,294	0,2		0,03	0,19	0,89
12,10	135,9263469	666,306	0,1		0,01	0,04	0,21
13,7	117683,0397	375984,152	33,7		4,81	33,10	140,81
13,8	57467,6925	208973,427	18,7	***56,1***	2,34	16,10	74,02
13,9	11045,6598	40758,892	3,7		0,41	2,79	13,79
Max prop respons						33,10	
Totals		***1116269,507***			***14,54***	***100,00***	***407,37***
	Sample		***Standard (51)***				
	Area:	***Amount:***	***Area:***	***Amount:***			
TCN	49597,9229	20	221603,4778	40			
ISTD	100241,273	50	28115,05158	50			
12C SCCP				100			
Total HG area most abundant ion:			***Total HG area most abundant ion:***				
	375984,1523		3619421,95				
Response prop. to Cl # :			***Response prop. to Cl # :***				
	33,10		31,65				
Average molar mass:			***Average molar mass:***				
	407		387,06				
			RRFg:				
			0,073007795				
Amount SCCP (ng):		293					
Amount SCCP(pg/m3		243					
Recovery ISTD (%):		106,3					

Figure B1: Spreadsheet used for the quantification of SCCPs in all samples and blanks in the study. Example showing spreadsheet from air sample Zeppelin 2. Modified after Tomy (Tomy et al. 1997).

Spreadsheet for determining the formula group abundance profiles of medium chain PCAs environmental samples							
							Factor ng to pg
Sample:	17/0317_Zeppelin2				*Sample amount:*	1204,28	1000
Homologue group	*Area*	*Total HG area*	*Adj. resp. normalized*	*Homologue Total*	*Norm. area/Cl #*	*Response prop. to Cl #*	*Prop. Resp. x molar mass*
14,5	142762,837	394372,5	0,9		1,243944641	1,34	4,93
14,6	1897695,443	5565089,3	13,2		14,62801322	15,74	63,27
14,7	3563406,827	14253627,3	33,8	***75,5***	32,11380883	34,55	150,63
14,8	1108233,955	9235283,0	21,9		18,20642506	19,59	92,05
14,9	369848,2901	2125564,9	5,0		3,72474303	4,01	20,19
14,10	68674,56699	265152,8	0,6		0,418177464	0,45	2,42
15,5	37893,1312	105846,7	0,3		0,33386579	0,36	1,37
15,6	483262,4392	1434013,2	3,4		3,76934899	4,06	16,87
15,7	1195824,356	3895193,3	9,2	***21,6***	8,775976222	9,44	42,49
15,8	752705,3024	2798161,0	6,6		5,516290984	5,94	28,72
15,9	202886,8546	768510,8	1,8		1,346703323	1,45	7,50
15,10	26217,91217	102413,7	0,2			0,17	0,96
16,5	2474,909421	6991,3	0,0		0,022052128	0,02	0,09
16,6	63990,77568	191589,1	0,5		0,503598138	0,54	2,33
16,7	143073,6804	472190,4	1,1		1,063857695	1,14	5,31
16,8	98941,75487	371961,5	0,9	***2,8***	0,733284397	0,79	3,93
16,9	34464,58972	132048,2	0,3			0,25	1,32
16,10	1556,039023	6150,4	0,0		0,009699837	0,01	0,06
17,7	18791,53489	62638,4	0,1	***0,1***		0,15	0,73
						34,55	
	Totals	***42186797,737***				***100,00***	***445,18***
	Sample		***Standard 57%***				
	Area:	***Amount:***	***Area:***	***Amount:***			
ISTD	100241,273	20	19469,68743	20			
12C MCCP				100			
	Total HG areamost abundant ion:		***Total HG area most abundant ion:***				
	14253627,31		41243511,3				
	Response prop. to Cl # :		***Response prop. to Cl # :***				
	34,55		18,84				
	Average molar mass:		***Average molar mass:***				
	445		476,69				
	Amount MCCP (ng):	342					
	Amount MCCP(pg/m^3)	283,9					

Figure B2: Spreadsheet used for the quantification of MCCPs in all samples and blanks from the study. Example showing spreadsheet from air sample Zeppelin 2. Modified after Tomy (Tomy et al. 1997).

The technical standard chosen for quantification standard for SCCPs in air samples was the standard with the lowest chlorination degree of the ones available, 51% Cl by weight. This is due to higher degree of similarity between the air samples and this technical mixture than to the other available technical mixtures. Figure B3 shows the homologue group distribution in four air samples from AMAP, while Figure B4 shows homologue group distribution in three

technical mixtures with varying degree of chlorination. By visual inspection of these distributions, it is clear that the 51% technical mixture is the closest fit. It is however not a perfect fit, as there seems to be higher content of the shorter chain SCCPs in the air samples than in the technical mixture, which has highest content of the C_{12} group. The similarity of quantification standard and sample is important for the validity of the results, as described in section 1.3.3.

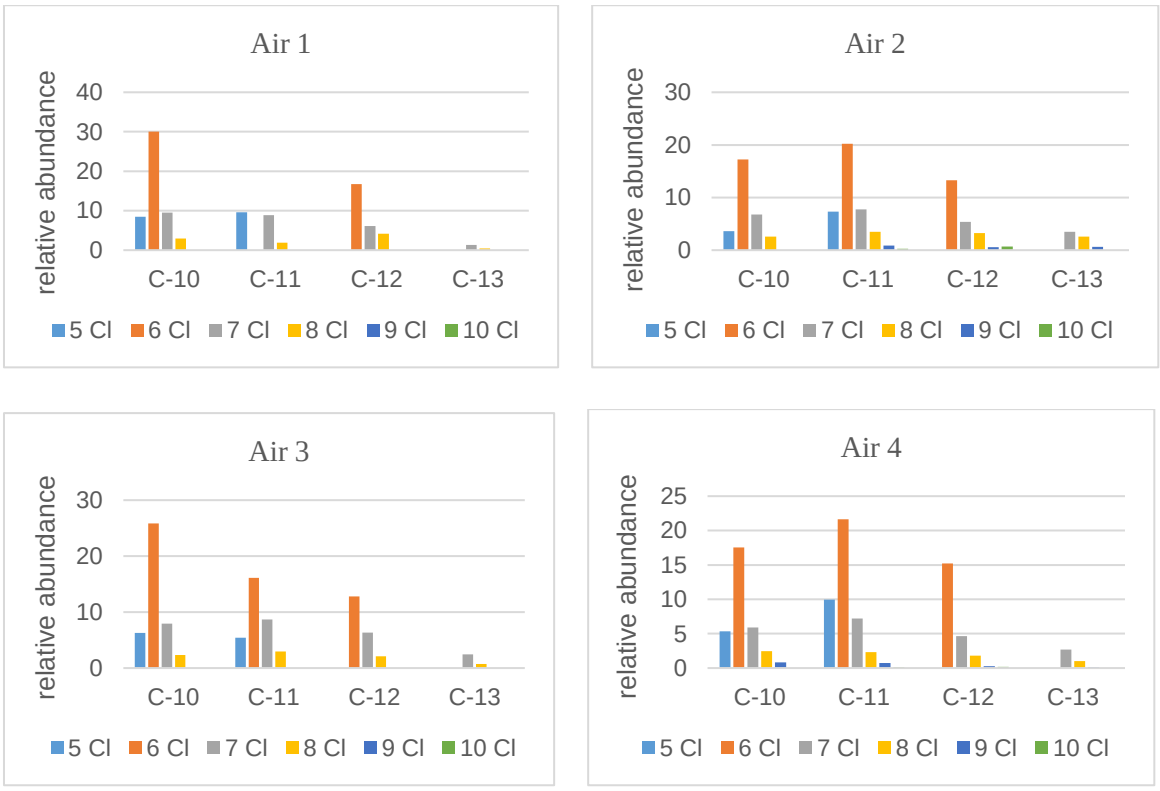


Figure B3: Homologue group distribution in air samples from AMAP (SCCPs).

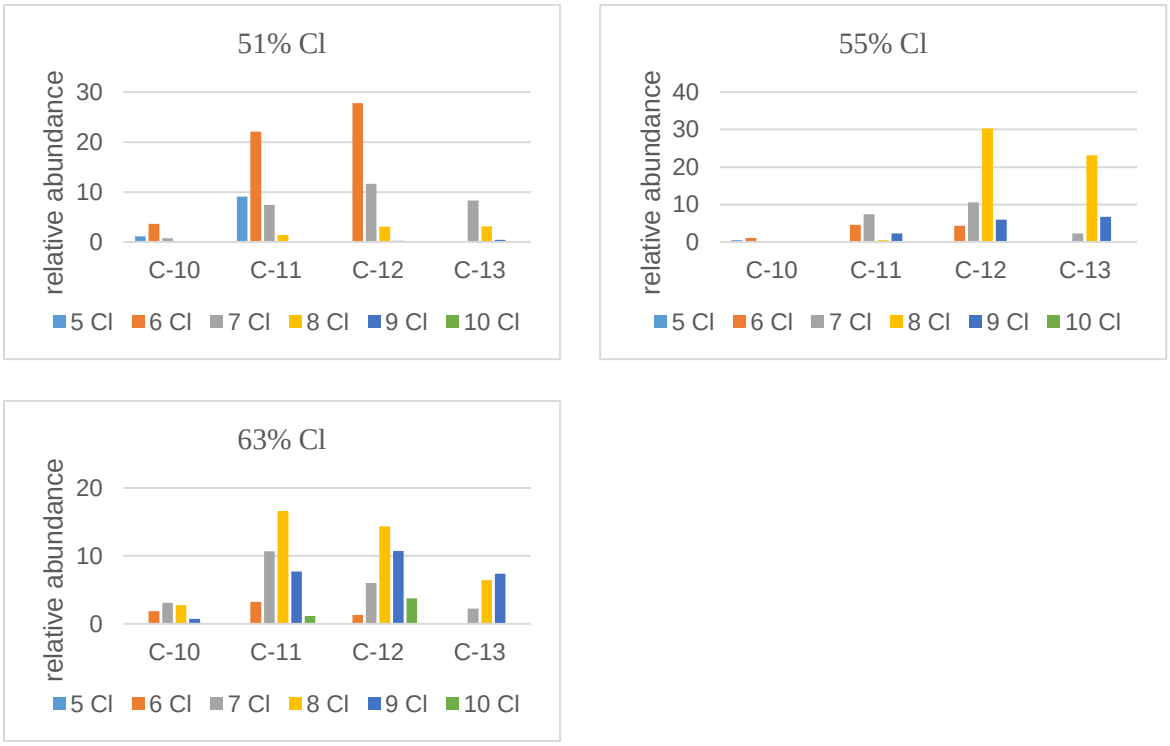


Figure B4: Distribution of homologue groups in technical standards (SCCPs)

APPENDIX C

This appendix contains information on statistical procedures.

Calculations of averages, means and standard deviations in this study has been performed using Excel 2013 or 2016 from the MS Office package. The construction of homologue group distribution figures and histograms displaying results has also been done using Excel. Statistical procedures (ANOVA and hierarchical clustering) and the construction of box and whisker plots and outlier detection has been done using R studio.

C.1 STORAGE BLANKS:

A printout of the estimates and p-values associated with the ANOVA model from the storage test from R studio can be found in Figure C1, in addition, an effects plot can be found in Figure C2. No significant factor was found.

```
> summary(smod2)$coefficients[,c(1:2)]
                    Estimate Std. Error
(Intercept)         18.487901   13.78915
STfreezer           -9.674702   19.50080
tmeshort           -14.946551   19.50080
STfreezer:tmeshort  39.871881   27.57830


Anova Table (Type III tests)

Response: CP
            Sum Sq Df F value Pr(>F)
(Intercept) 1025.4  1  1.7976 0.2168
ST           140.4  1  0.2461 0.6332
tme          335.1  1  0.5875 0.4654
ST:tme      1192.3  1  2.0903 0.1863
Residuals   4563.4  8
```

Figure C1: R studio printout showing the estimated parameters associated with a two-factor ANOVA model on the storage blanks.

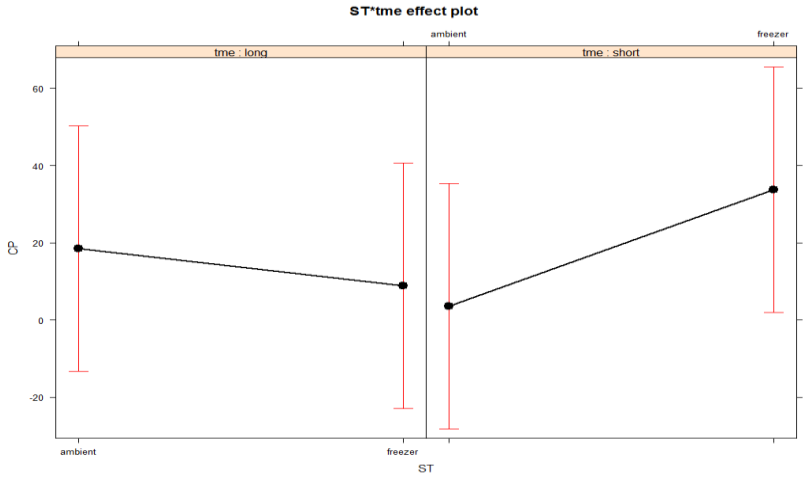


Figure C2: Effect plot from two factor ANOVA model applied to storage tests.

C.2 FIELD BLANKS:

The field blanks were analyzed using ANOVA. A R studio printout of estimates associated with the ANOVA model can be found in Figure C3. A significant difference can be found between the ambient group and at least one of the others.

```
Call:
lm(formula = CP ~ category, data = fb2)

Residuals:
   Min     1Q Median     3Q    Max
-7.700 -5.225 -1.400  3.875  9.450

Coefficients:
             Estimate Std. Error t value Pr(>|t|)
(Intercept)    25.133      4.077   6.165 0.000166 ***
categoryBlank  -9.708      5.393  -1.800 0.105388
categoryCold  -11.083      5.766  -1.922 0.086745 .
categoryWorst  -9.433      5.766  -1.636 0.136254
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1

Residual standard error: 7.062 on 9 degrees of freedom
Multiple R-squared:  0.3459,   Adjusted R-squared:  0.1279
F-statistic: 1.587 on 3 and 9 DF,  p-value: 0.2597
```

Figure C3: R studio printout showing estimates associated with the ANOVA model applied to field blanks.

C.3 HIERARCHICAL CLUSTERING:

Hierarchical clustering was performed on all blanks (laboratory (PUF/no PUF), storage, field, reagent), TurboVap tests, materials test, indoor air samples, dust/organic film samples and air samples. The printout from R studio is shown in F

igure C4, and a list of the samples attached to the numbers in the figure can be found in Table C1. The clustering method used Euclidean distance and complete linkage.

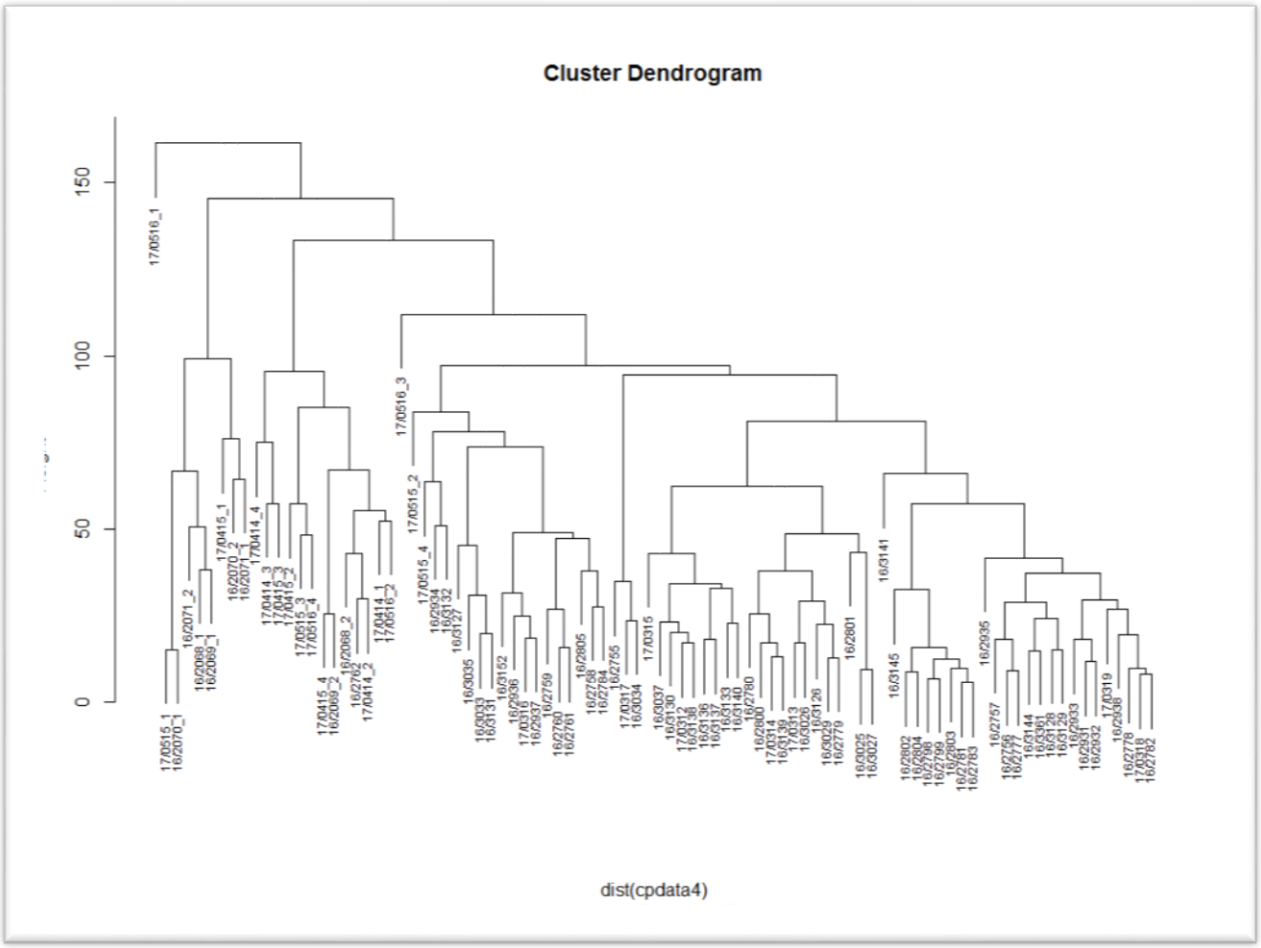


Figure C4: Cluster dendrogram Cluster dendrogram from hierarchical clustering of the homologue group data from all samples and blanks included in the study.

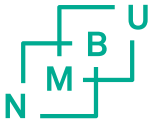
Table C1: Description of sample numbers used in the clustering analysis

	Description	**Sample no.**
Air samples	Andøya 1	17/0312
	Andøya 2	17/0313
	Birkenes 1	17/0314
	Birkenes 2	17/0315
	Zeppelin 1	17/0316
	Zeppelin 2	17/0317
	Lab blank (PUF)	17/0318
	Lab blank (no PUF)	17/0319
Indoor air	Lab (cleaning/storage)	16/3025
	Clean room	16/3026
	Lab (extraction)	16/3027
	Field blank	16/3029
	Lab blank (PUF)	16/3144
	Lab blank (no PUF)	16/3152
Dust/organic film	Lab (cleaning/storage)	16/3033
	Clean room	16/3034
	Lab (extraction)	16/3035
	Field blank	16/3037
	Lab blank P1	16/3145
	Lab blank P2	16/3361
Storage blanks	Freezer P1	16/2755
	Freezer P2	16/2756
	Freezer P3	16/2757
	Lab blank (no PUF) P1	16/2758
	Ambient	16/2759
	Ambient	16/2760
	Ambient	16/2761
	Lab blank (no PUF) P2	16/2762
	Freezer 2 P1	16/2931
	Freezer 2 P2	16/2932
	Freezer 2 P3	16/2933
	Lab blank (no PUF) P3	16/2934
	Ambient 2 P1	16/2935
	Ambient 2 P2	16/2936
	Ambient 2 P3	16/2937
	Lab blank (no PUF) P4	16/2938
Field blanks	cold P1	16/2777
	cold P2	16/2778
	cold P3	16/2779

	Lab blank (PUF) P1	16/2780
	worst case P1	16/2781
	worst case P2	16/2782
	worst case P3	16/2783
	Lab blank (no PUF) P1	16/2784
	Ambient P1	16/2798
	Ambient P2	16/2799
	Ambient P3	16/2800
	Air sample car	16/2801
	Lab blank (PUF) P2	16/2802
	Lab blank (PUF) P3	16/2803
	Lab blank (PUF) P4	16/2804
	Lab blank (no PUF) P2	16/2805
Materials test	Glove new	16/3126
	Glove lab	16/3127
	Bench cover lab	16/3128
	Bench cover new	16/3129
	Latex pipette top un-used	16/3130
	Latex pipette top used	16/3131
	Ziploc bag	16/3132
	Alu. foil	16/3133
	Vial cap new	16/3136
	Vial cap lab	16/3137
	Micropipette pack new	16/3138
	Micropipette pack lab	16/3139
	Lab blank P1	16/3140
	Lab blank P2	16/3141
Adsorbent test	Old P1	17/0414_1
	Old P2	17/0414_2
	Old P3	17/0414_3
	Old P4	17/0414_4
	New P1	17/0415_1
	New P2	17/0415_2
	New P3	17/0415_3
	New P4	17/0415_4
Turbovaptest	Cleaned P1	17/0515_1
	Cleaned P2	17/0515_2
	Cleaned P3	17/0515_3
	Cleaned P4	17/0515_4
	Uncleaned P1	17/0516_1
	Uncleaned P2	17/0516_2
	Uncleaned P3	17/0516_3

	Uncleaned P4	17/0516_4
Acid test	Glass bottle P1	16/2068_1
	Glass bottle P2	16/2068_2
	Plastic bottle P1	16/2069_1
	Plastic bottle P2	16/2069_2
	Flask P1	16/2070_1
	Flask P2	16/2070_2
	Lab blank P1	16/2071_1
	Lab blank P2	16/2071_2

Sometimes air sampling gives unexpected results. Photo: Helene Lunder Halvorsen



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