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The Environmental Occurrence, Fate, and Behavior of Airborne Organic Contaminants of Emerging Concern in Norwegian Terrestrial Ecosystems

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Abstract

Airborne organic contaminants of emerging concern (AOCs) are a large assembly of organic compound groups. AOCs consist of legacy persistent organic pollutants (POPs) and new POP-like compounds. These compound groups are of emerging concern for ecosystems' health because they are, or are suspected to be persistent, toxic, bioaccumulative, and able to undergo long-range atmospheric transport (LRAT). Soil environments play an important role in the fate of AOCs because they have the ability to sorb and store large amounts of these contaminants. This study evaluated AOCs' occurrence in top soils from 45 remote background sites well distributed throughout Norway, and their environmental fate and behavior (e.g. association with soil organic matter, spatial distribution, environmental processes, and air-to-soil exchange). The soils were analyzed for the following AOC-groups: polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides, old and novel brominated flame retardants (BFRs), dechlorane plus (DPs), and chlorinated paraffins (CPs). In addition, 10 urban (Oslo area) top soils were sampled and analyzed equally in order to assess the anticipated effect highly populated areas can have on AOC-burdens in soils.

The assessment of the AOCs' occurrence in Norwegian background soils showed that all compound groups included in this study are present at concentrations varying from <1 to >100 ng/g dry weight. CPs, a new POP-compound group, were found at highest concentrations, followed by the legacy-POPs: PCBs and DDTs. This rating does not consider their compound-specific toxicity and the potential adverse effects that may occur in these ecosystems due to their presence. In the top soils investigated, the AOCs were found to be associated with the soil organic matter (SOM) fraction. The AOCs deposit from the atmosphere to vegetation and soil surfaces, and are further sorbed to and stored in the SOM fraction because of AOCs' hydrophobic, semi-volatile, and low water-soluble properties. From the air-to-soil exchange assessment it was found that the AOCs' were far from reaching equilibrium between air and soil, which indicates that these soils are likely to continue to take up and store AOCs from the atmosphere. Based on this, the Norwegian soils will most likely not act as sources of AOCs, but rather as storage compartments.

The AOC-concentrations in the urban soils were found to be significantly higher than in the remote, background soils. Local sources from the highly populated Oslo area seemed to cause this difference. The background soils did however not appear to be related to population density and thus; the background soils can be considered truly "background" i.e. not significantly affected by local sources but rather by LRAT of the AOCs in question. This was also supported by the AOCs' spatial distribution, where they were distributed with generally decreasing concentration levels from the south to the north in Norway. Consequently, the further away from large-scale source areas, such as central- and western Europe, and possibly also the largest Norwegian cities including Oslo, the lower were in general the AOC-burdens found in the background soils. Climatic factors, such as temperature and precipitation, also vary in this direction and their contribution to the trend observed along the latitudinal gradient has been emphasized.

Comparison with earlier studies showed that the background soil concentrations of legacy-POPs have decreased slightly over the last two decades. Norway's cold climate, the soils' large storage capacity, and the persistency of these compounds limits further transport and degradation of the legacy-POPs. As a result of this, they will most probably be present over several decades and their concentrations are not expected to drop significantly in the coming years. However, this does not imply that regulation of these compounds has no effect, but rather that soil and AOC-properties result in efficient storage of these contaminants in such environments. New POP-like compounds, such as CPs, NBFRs, and DPs, may on the other hand potentially increase in the near future due to their current (2019) and/or recent production and usage.

Norsk sammendrag

Luftbårne organiske forurensninger av fremvoksende bekymring (AOC-er) er en stor sammensetting av ulike grupper organiske forurensninger. AOC-er består av eldre persistente organiske forurensninger (POPs) og nye POP-lignende forbindelser. Disse sammensatte gruppene er av fremvoksende bekymring for økosystemers helse fordi de er, eller antas å være, vedvarende i miljøet, giftige, bioakkumulerende og i stand til å gjennomgå langdistanse atmosfærisk transport (LRAT). Jordmiljøer spiller en viktig rolle i AOC-ers skjebne fordi jord har evnen til å adsorbere og lagre disse forurensningene. Denne masteroppgaven evaluerte AOC-ers forekomst i toppjord fra 45 avsidesliggende bakgrunnsområder godt distribuert over hele Norge, og deres skjebne og oppførsel i miljøet (for eksempel assosiasjon til organisk materiale, romlig fordeling, miljøprosesser og luft-til-jord-utveksling). Jordprøvene ble analysert for følgende AOC-grupper: polyklorerte bifenyler (PCB), klororganiske (OC) plantevernmidler, gamle og nye bromerte flammehemmere (BFR), dekloran plus (DPs) og klorerte parafiner (CPs). I tillegg ble 10 urbane (Oslo-området) toppjord prøvetatt og analysert i likhet med bakgrunnsprøvene for å vurdere effekten svært befolkede områder kan ha på AOC-forekomster i jord.

Vurderingen av AOC-forekomsten i norsk bakgrunnsjord viste at alle gruppene av organiske forurensninger er tilstede. Konsentrasjonene varierte fra <1 til> 100 ng / g tørrvekt. CPs, en ny POP-gruppe, ble funnet i høyest konsentrasjoner, etterfulgt av de eldre-POP-ene: PCB-er og DDT-er. Denne vurderingen bedømmer ikke deres sammensetningsspesifikke toksisitet og de potensielle negative effektene som kan oppstå i disse økosystemene på grunn av deres tilstedeværelse. I de undersøkte toppjordene ble AOC-ene funnet å være assosiert med den organisk materiale (OM) fraksjon. AOC-ene avsettes på vegetasjon og jordoverflater fra atmosfæren, og videre adsorberes de til og lagres i OM-fraksjonen på grunn av AOCs hydrofobiske-, halv-volatile- og lite vannløselig egenskaper. Fra luft-til-jordutvekslingsvurderingen ble det funnet at AOC-ene er langt fra å være i likevekt mellom luft og jord. Dette indikerer at jorda sannsynligvis vil fortsette å ta opp og lagre AOC-er fra atmosfæren. På grunnlag av dette vil de norske jordene sannsynligvis ikke fungere som kilder av AOC-er, men heller som lagringsplass.

AOC-konsentrasjonene i de urbane jordprøvene var betydelig høyere enn i bakgrunnsprøvene. Lokale kilder fra det svært befolkede Oslo-området har sannsynligvis forårsaket denne forskjellen. Bakgrunnsjorda forekommer imidlertid ikke å være relatert til befolkningstetthet, og derfor kan disse jordprøvene betraktes som virkelig "bakgrunn", dvs. ikke betydelig påvirket av lokale kilder, men heller av LRAT av de aktuelle AOC-ene. Dette ble også støttet av AOC-ers romlige fordeling, hvor de ble fordelt med generelt reduserende konsentrasjonsnivåer fra sør til nord i Norge. Følgelig, jo lenger bort fra store kilder, som sentral- og vest-Europa, og muligens de største norske byene, inkludert Oslo, jo lavere var generelt AOC-forekomsten som ble funnet i bakgrunnsjorda analysert. Klimaforhold, slik som temperatur og nedbør, endres også i denne retningen, og deres bidrag til trenden observert langs breddegradgradienten har blitt diskutert.

I sammenligning med tidligere studier viste det seg at bakgrunnsjordkonsentrasjonene av eldre-POP-er har blitt redusert noe de siste to tiårene. Norges kalde klima, jordens store lagringskapasitet og persistensen til disse forbindelsene begrenser videre transport og nedbrytning. Som et resultat av dette er de tilstede i flere tiår, og konsentrasjonene forventes ikke å falle betydelig i de kommende årene. Dette innebærer imidlertid ikke at regulering av disse forbindelsene ikke har noen virkning, men at jord- og AOC-egenskaper resulterer i effektiv lagring av disse forurensningene i slike miljøer. Nye POP-lignende forbindelser, som CPs, NBFRs og DPs, kan derimot potensielt øke i nær fremtid på grunn av deres nåværende (2019) og / eller nyere produksjon og bruk.

Acronyms

AOC = Airborne Organic Contaminants of Emerging Concern

AMAP = The Arctic Monitoring and Assessment Program

ASE = Accelerated Solvent Extraction

BDE = Brominated diphenyl ethers

BFRs = Brominated Flame Retardants

BTBPE = Bis(2,4,6-tribromophenoxy) ethane

CLRTAP = Geneva Convention on Long-range Transboundary Air Pollution

CP = Chlorinated Paraffins

DBDPE = Decabromodiphenyl ethane

DDD = Dichlorodiphenyldichloroethane

DDE = Dichlorodiphenyldichloroethylene

DDT = Dichloro-diphenyl-trichloroethane

DL-PCBs = Dioxin-like polychlorinated biphenyls

DPs = Dechlorane plus (isomers anti and syn)

EMEP = The European Monitoring and Evaluation Program

f_S = Soil fugacity

f_A = Air fugacity

ff = Fugacity fraction

GC = Gas Chromatography

GMP = Global Monitoring Program

HBCD = Hexa-/heptabromobiphenyl

HCH = hexachlorocyclohexane

HCB = Hexachlorobenzene

K = Partitioning coefficient

K_{AW} = Air-water partitioning coefficient

K_{OW} = Octanol-water partitioning coefficient

K_{OA} = Octanol-air partitioning coefficient

K_{SA} = Soil-air partitioning coefficient

LCCP = Long-Chained Chlorinated Paraffins

LOI = Loss on Ignition

LRAT = Long-Range Atmospheric Transport

LRT = Long-Range Transport

MCCP = Medium-Chained Chlorinated Paraffins

MS = Mass Spectrometer

NBFRs = Novel Brominated Flame Retardants

ND-PCBs = Non-Dioxin like Polychlorinated biphenyls

NFR = Norwegian Research Council

NILU = Norwegian Institute for Air Research

OC = Organochlorine

PBDE = Polybrominated diphenyl ethers

PBT = Persistent, Toxic, and Bioaccumulative

PCBs = Polychlorinated biphenyls

PeCB = Pentachloro benzene

PFK = Perfluorokerosene

POPs = Persistent Organic Pollutants

PVC = Polyvinylchloride

Q = Quadrupole

SC = Stockholm Convention

SCCP = Short-Chained Chlorinated Paraffins

SERA = Source-Exposure Relationships for Airborne Organic Contaminant of Emerging Concern in Northern Terrestrial and Freshwater Ecosystems

SPE = Solid-Phase Extraction

TCDD = Tetrachlorodibenzo-p-dioxin

TCN = Tetrachloronaphthalene

TOF = Time of Flight

UAE = Ultrasound Assisted Extraction

Table of Content

1. Motivation and objectives

Throughout human history, anthropogenic pollution has caused harmful effects to ecosystems. In the mid- to late twentieth century, acidic precipitation (e.g. sulphur oxides and nitrogen oxides) was of high concern in Nordic regions. Consequently, air monitoring programs were implemented to assess this issue (Ottar 1976). From this, transboundary air pollution was confirmed. During the same period, large amounts of organic compounds for industrial and commercial use were produced and released to the environment. In 1962, the alarming effects of these organic pollutants', notably dichloro-diphenyl-trichloroethanes (DDTs), on ecosystems' health were revealed in Carson's book, *Silent Spring* (Carson 1962). The "oil-disease" Yusho, reported in Japan in 1968, was found to be caused by the exposure to the dioxin-like polychlorinated biphenyls (PCBs) (Yoshimura 2003). The industrial accident in Seveso, Italy (1976) exposed a large population to tetrachlorodibenzo-p-dioxin (TCDD) (Bertazzi et al. 1998). These cases of human- and ecosystem exposures to toxic organic pollutants caused harmful effects, such as increased cancer occurrence, skin diseases, and altered ecology. Therefore, in the decades to come, national and international regulatory measures where implemented to protect human health and our environment from hazardous organic compounds. However, today (2019) high-volume production and usage of many organic compounds with known harmful properties is still ongoing. Concern emerges also over more recently introduced organic compounds, such as chlorinated paraffins (CPs) and novel brominated flame retardants (NBFRs), and their potential adverse effects on ecosystems when released to the environment.

Within the research project "Source-Exposure Relationships for Airborne Organic Contaminant of Emerging Concern (AOCs) in Northern Terrestrial and Freshwater Ecosystems" (SERA), legacy persistent organic pollutants (POPs) and suspected POP-like compounds are studied to increase knowledge on these organic compounds' sources, their environmental fate and behavior, and their adverse effects on ecosystems. The responsible institution for this research project is the Norwegian Institute for Air Research (NILU). Participating institutions are Akvaplan-Norwegian Institute for Water Research (NIVA), Environment Canada- Division of Air Quality Research, the Research Council of Norway (NFR), and the University of Toronto (Canada).

The SERA-project targets primarily AOCs which may undergo atmospheric transport from industrialized- and urban source regions to remote areas, where they may accumulate in terrestrial ecosystem and persist over several decades. Some of the organic compounds included in this project have been studied for decades and are regulated because of their persistency in the environment, transboundary atmospheric transport, toxicity and ability to bioaccumulate. However, knowledge on POP-like compounds with suspected similar behavior, environmental transport, and toxicity as legacy POPs is far sparser. Therefore, the compounds in this project are referred to as airborne organic contaminants of emerging concern (AOCs), which include both legacy- and new POPs, and suspected POP-like compounds.

The objectives of this master thesis have been to study the occurrence, and the environmental fate and behavior, of AOCs in soil environments from the south to the north of Norway by analyzing these compounds in topsoil samples. The spatial distribution of AOCs in the study area will be used to assess the long-range atmospheric transport (LRAT) potential of these compounds. It will also provide information of the role of soils in northern ecosystems for storing these contaminants. This is important for predicting whether soils are likely to act as sources of AOCs to the air, now or in the future. This master thesis will also investigate whether concentrations have changed over time compared to previous studies, i.e. decreased for compounds that have been regulated, or if newer compounds can be found. This was achieved by discussing soil concentrations in the light of air concentrations for selected AOCs at equal study sites, and other data available from the literature, such as the Norwegian-United Kingdom transect from 1998 and 2008. These objectives aim to obtain a greater knowledge and understanding of the contaminants' sources, and their environmental fate and behavior, in northern terrestrial ecosystems.

2. Background

Persistent Organic Pollutants (POPs) is a generic term covering numerous organic compound groups with similar environmental fates (Stockholm Convention 2018b). Some POPs, such as dioxins, furans, and polyaromatic hydrocarbons (PAHs) are formed unintentionally during incomplete combustion. Other POPs, such as organochlorine (OC) pesticides (e.g aldrin, dichlorodiphenyltrichloroethane (DDT)), brominated flame retardants (BFRs), and polychlorinated biphenyls (PCBs), are produced intentionally. There are also compound groups with suspected POP-like behavior, such as novel brominated flame retardants (NBFRs), dechloranes, and medium- and long chained chlorinated paraffins (M/ LCCP). In this study, the POPs and the new POP-like compounds are referred to as airborne organic contaminants of emerging concern (AOCs).

The compounds must have certain properties to be classified as POPs. They must be persistent, bioaccumulative, toxic (PBT), and long-range transportable (LRT) (Stockholm Convention 2018b). Persistent refers to the compounds' resistance to degradation and their ability to remain intact for years to decades in the environment. Bioaccumulation is the phenomenon where the compound's concentration increases with trophic level because of their lipophilic "fat loving" nature. This happens in the food chain, where compounds accumulate from primary producers to consumers, such as from fish to birds, and further to mammals. The toxicity of POPs to ecosystems' living organisms includes a wide range of potential adverse outcomes, such as growth inhibition, endocrine disruption, and carcinogenicity. To be classified as POPs, the compounds must be widely distributed in the environment through natural processes in soil, water, and most notably, air. These chemical properties depend on POPs' chemical structure and their resulting physicochemical properties, such as aqueous solubility, affinity to lipids and organic matter, and volatility. These properties vary between and within the numerous POP-groups. Consequently, the generic term POPs include a wide assembly of PBT compounds.

Globally, intentionally produced POPs, and also other AOCs (e.g. M/LCCPs, NBFRs), are used in several industrial and commercial applications, such as pest- and disease control, increased agricultural crop production, and safer homes (EPA 2009). However, several of these compounds have, or are believed to have, adverse effects on human health and the environment. The rising attention and concern of POPs' environmental presence began in the 1970s, when POP-pesticides where found in Arctic biota far away from any sources (Canadian Wildlife 1973; El-Shahawi et al. 2010). This highlighted their transboundary nature and potential risk to ecosystems living organisms. Consequently, restrictions and regulations on POPs' production and usage was prioritized within environmental sciences to protect ecosystems and human health from these compounds.

Because of POPs' transportation across international boundaries, one government alone cannot protect ecosystems from such compounds. Thus, to solve this global problem, international agreements must be developed. Two international agreements have been signed: i) in 1998, the Aarhus Protocol on Persistent Organic Pollutants under the 1979 Geneva Convention on Long-range Transboundary Air Pollution (CLRTAP) (UNECE 2003), and ii) in 2001, the Stockholm Convention on POPs (UNEP 2010).

The Stockholm Convention (SC) on POPs was adopted on May 22nd 2001, and put into force on May 17th 2004. It aims to protect the environment and human health from potential adverse effects of POPs (Table 1). This is accomplished by restricting and regulating their production, usage, release and disposal. The 182 participating countries (2019) have decreased legacy POPs' usage, production, and environmental concentrations globally. Legacy POPs refer to compounds produced and/or used in the twentieth century for pest control in agriculture, industrial- and unintentionally produced chemicals (UNEP/AMAP 2011). However, restrictions and regulations of legacy POPs have resulted in the development of new POP-like compounds to substitute the old ones. These compounds have chemical characteristics similar to legacy POPs, where some are listed on the SC on POPs (e.g. BFRs, SCCPs) and others might be classified as so in the future.

Table 1. Compounds listed on the SC on POPs (Stockholm Convention 2018a)

Compounds included in SC (2019)	Usage
Aldrin	*Agriculture, insecticide*
Chlordane	*Agriculture, insecticide*
Chlordecone	*Agriculture, pesticide*
Decabromodiphenyl ether (commercial mixture)	*Industrial, flame retardant*
Dichloro-diphenyl-trichloroethane (DDT) (incl. DDT group)	*Agriculture, insecticide*
Dieldrin	*Agriculture, pesticide*
Dioxins	*Unintentionally produced by-products*
Endosulfan and its related isomers (alpha and beta)	*Agriculture, insecticide*
Endrin	*Agriculture, insecticide*
Furans	*Unintentionally produced by-products*
Heptachlor	*Agriculture, insecticide*
Hexa-/heptabromobiphenyl (HBCD)	*Industrial, flame retardant*
Hexabromocyclododecane (HBCDD)	*Industrial, flame retardant*
Hexachlorobenzene (HCB)	*Unintentionally produced by-products and pesticide*
Hexachlorobutadiene (HCBD)	*Unintentionally produced by-product*
Hexachlorocyclohexane (alpha-, beta- and gamma-HCH (lindane))	*Unintentionally produced by-products and agricultural insecticide*
Mirex	*Agriculture, insecticide*
Octabromodiphenyl ether	*Industrial, flame retardant*
Perfluorooctane sulfonic acid (PFOS)	*Industrial*
Pentachlorophenol and its salts and esters	*Agriculture, pesticide*
Pentabromodiphenyl ether	*Industrial, flame retardant*
Polychlorinated biphenyls (PCBs)	*Industrial and unintentionally produced by-products*
Polychlorinated naphthalenes	*Industrial and unintentionally produced by-products*
Short chain chlorinated paraffins (SCCPs)	*Industrial*
Tetrabromodiphenyl ether	*Industrial*
Toxaphene	*Agriculture, insecticide*

In this study, the main compound groups included from the SC on POPs are PCBs, OC pesticides (DDTs, HCHs, HCB), BFRs, and SCCPs. These are highlighted in green in Table 1 above. Compound groups included that are not listed under the SC on POPs are dechlorane plus (DPs), MCCPs, and some NBFRs. To meet the SC's aim on POPs, it is central to know legacy POPs, and also other AOCs' usage, emissions, and spatial distribution in ecosystems. The section below introduces these compounds in order to assess the AOCs' occurrence, their environmental fate and behavior, and air to soil exchange, in northern terrestrial ecosystems.

2.1 Airborne Organic Contaminants – chemical structure, usage and regulation

2.1.1 Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are a group of well-studied, synthetic chlorinated compounds consisting of a biphenyl body with one to ten chlorine substituents (Lein 2017). PCBs meets the criteria for POP classification PBT, and they are long-range transportable due to their semi-volatile property. Therefore, PCBs were listed under the SC on POPs in 2004 as one of the initial POPs, and through the international POP protocol under the Convention on Long-range Transboundary Air Pollution (LRTAP) to protect ecosystems form potential harm. The PCBs' resistance to degradation has caused a global distribution of these compounds in several environmental compartments, such as water, air, soil, and biota. PCBs are toxic to aquatic life, are linked to reproduction disruption, and suppression of the immune system.

There are in total 209 PCB compounds, referred to as congeners, where the number and position of chlorine substituents on the biphenyl vary (Figure 1). Based on the congeners structure, PCBs are divided into dioxin-like (DL-PCBs) with a coplanar structure, and non-dioxin like with a non-coplanar structure, PCBs (NDL-PCBs). These chemical structure differences influence their toxicity, where the DL-PCBs are found to be more toxic to living organisms than NDL-PCB, and encompass similar toxicity profiles as dioxins.

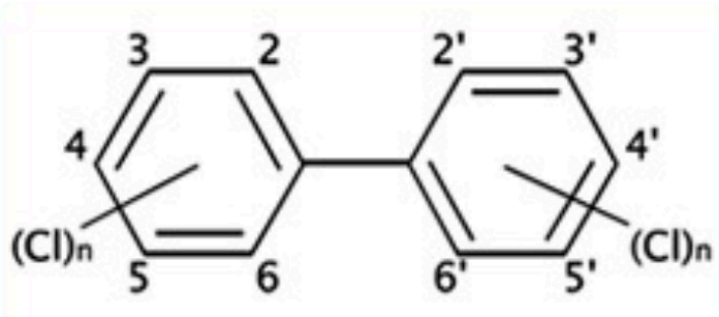

Figure 1: General PCB structure. The numbers indicates possible chlorine atom positions on each carbon atoms in the benzene rings (Lein 2017).

From the 1930s until they were banned in the 1970s, PCBs were extensively used in industrial applications as technical mixtures, such as Aroclors and Clophens. The technical mixtures contained typically between 50 to 100 individual PCB-congeners, and a varying degree of chlorination. The applications were for instance in electronic equipment (e.g. transformers, heat exchange fluids) and construction materials. This was because of the PCBs' high chemical and thermal stability, and electrical resistivity (Voogt & Brinkman 1989).

2.1.2 Organochlorine (OC) pesticides

Organochlorine (OC) pesticides are chlorinated hydrocarbon derivatives, and these are commonly used in agriculture and chemical industries (Jayaraj et al. 2016). Several OC pesticides, such as the well-studied dichloro-diphenyl-trichloroethane (DDT), hexachlorocyclohexane (HCH), and hexachlorobenzene (HCB), meets the PBT criteria for POPs and are consequently classified as such. During their lifecycles, these compounds enter the environment from several sources, for instance from industrial discharges, from pesticide application, and from polluted landfill residues.

DDT is an insecticide widely used during and after World War II to control insect-transmitted human diseases, such as malaria and typhus, and as agricultural pest control. DDT's excessive use and its physicochemical properties (e.g. toxicity, resistance to degradation, lipophilicity, and low water solubility) led to a worldwide DDT dispersion and concern for ecosystems health. In the environment, DDT is degraded to the metabolites dichlorodiphenyldichloroethane (DDD) and to the highly persistent dichlorodiphenyldichloroethylene (DDE) through dechlorination (Figure 2) (Sudharshan et al. 2012). These metabolites caused a decrease in bird populations, for instance in bald eagles and brown pelicans, due to eggshell thinning (Harada et al. 2016; Lundholm 1997). Consequently, because of DDT and its metabolites harm to ecosystems, its production and usage was regulated and restricted in the 1970s. In 2004, DDT was also listed as one of the initial legacy POPs under the SC on POPs.

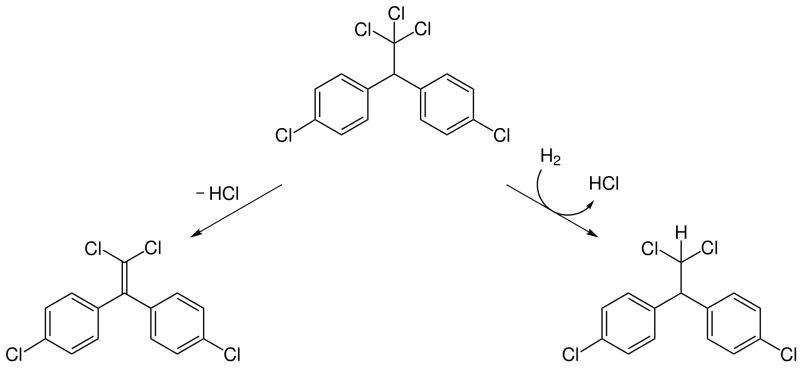

Figure 2: Structures of DDT (top) and its metabolites, DDE (left) and DDD (right) (Sudharshan et al. 2012).

HCHs was, next to DDT, extensively used as insecticides after World War II, and consequently, this compound group is present in environments worldwide (Vijgen et al. 2010). To protect the environment and human health from these compounds, the SC on POPs listed the HCH-isomers α, β, and γ (Lindane) in 2009 with the purpose to eliminate usage and production, and address HCH wastes. HCH insecticide comprises two main groups: i) technical mixture with the whole isomer mixture (α-θ), and ii) Lindane containing the isomer γ-HCH (Figure 3). Agricultural applications of technical HCH mixtures resulted in inedible crops, and it was found in the late 1950s that only γ-HCH possessed insecticidal properties. Therefore, γ-HCH isolation was developed and this created the insecticide Lindane. Lindane production produces waste containing other HCH-isomers and if not treated correctly, hazardous HCH waste can constitute a risk to ecosystems.

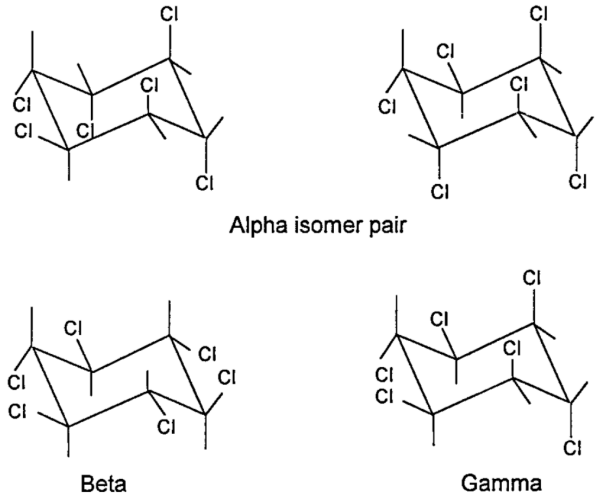

Figure 3: Structures of HCH-isomers, with two α-enantiomers. These structures shows the chlorine atoms spatial placement (Willett et al. 1998).

HCB (Figure 4) was introduced in the 1940s as a fungicide, and reached a peak usage time in the 1950-60s (Barber et al. 2005). Later, 1970-80s, HCB was used as a wood-preserving agent and in industrial applications. HCB was listed on the SC on POPs as one of the initial POPs in 2004, and meets therefore the criteria for being classified as a POP. The production and usage of HCB has therefore ceased, but unintentionally HCB is produced as a by-product in industrial processes (e.g. manufacture of chlorinated solvents and pesticides). The volatility of HCB is greater than for other legacy POPs (e.g. PCBs, DDTs). This results in a stronger LRAT potential, and therefore HCB is well distributed in the global environment and is detected in Antarctica and Artic environments.

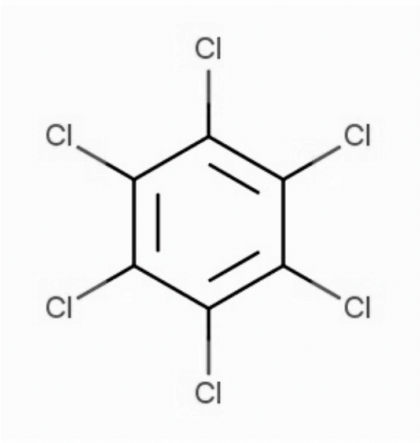

Figure 4: Chemical structure of HCB (ECHA 2019). The molecular formula for HCB is C_6Cl_6.

2.1.3 Brominated flame retardants (BFRs)

Brominated flame retardants (BFRs) are a large group of chemicals used extensively as fire inhibitors in household and commercial products since the 1970s (Jans 2016). Some BFRs, such as penta-, and deca- brominated diphenyl ether (BDE), and hexa-/heptabromobiphenyl (HBCD), was regulated in the SC on POPs in 2005, and subsequently, these compounds meet the POP criteria PBT and LRT. BFRs are organic compounds with bromine substituents, which is the fire inhibiting component. BFRs are used as i) additives: not chemically bond to the material, or ii) reactive: chemically bond. This affects their emissions to the environment, where additive BFRs leach out or evaporate more easily than reactive due to the lack of chemical bonds.

Conventional polybrominated diphenyl ether (PBDE) formulas, such as pent-, octa-, and deca-BDE, are one of the additive flame retardants groups that have received most scientific and public attention. This is because of their abundant use, persistence, semi-volatile- and lipophilic properties, and toxicity (Wang et al. 2015). The chemical structure and properties of PBDEs are similar to PCBs, including their spatial position and number of bromine atoms on the two phenyl rings (Figure 5). This gives a total of 209 PBDE congeners. In this study, the BFRs included were PBDE-congeners.

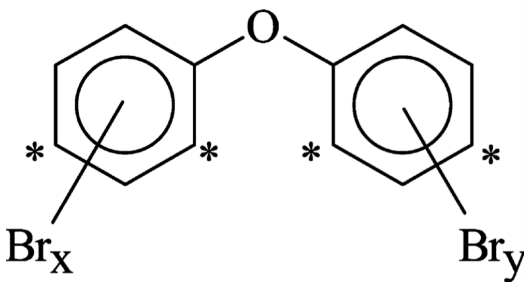

*Figure 5: General chemical structure for PBDEs, where * signifies most active sites of substitution, and x and y is the number of bromine atoms (Rahman et al. 2001).*

Today, in 2019, several emerging novel BFRs (NBFRs) have replaced conventional BFRs. Because conventional BFRs were restricted under the SC on POPs and CLRTAP, NBFRs have been developed to substitute historical BFRs. For example, decabromodiphenyl ethane (DBDPE) replaces deca-BDE, and bis (2,4,6-tribromophenoxy) ethane (BTBPE) are commonly used to substitute octa-BDE. The new generation of BFRs, NBFRs, are indicated to be generally analogous to conventional BFRs with respect to their environmental behavior and toxicity (McGrath et al. 2017).

BFRs and NBFRs are released to the environment from diverse sources (Hassanin et al. 2004). Examples of such sources are manufacturing, industrial processes, during the use of products containing them (e.g furniture, construction materials), and electronic waste- and recycling facilities. Since these compounds are volatile enough to be transported with air, and because of their lipophilic property, BFRs may accumulate in northern latitudes and sorb to organic material in terrestrial ecosystems. Therefore, a shift from conventional- to NBFRs in industrial and commercial products may not benefit the environment and ecosystems health because of their predicted similar physicochemical properties, emissions and environmental behaviors. Consequently, NBFRs are of interest when studying the occurrence of AOCs in terrestrial ecosystems.

2.1.4 Dechlorane plus (DPs)

Dechlorane plus (DPs) is a group of new highly chlorinated flame-retardant chemicals used in industrial and house hold products (Wang et al. 2016). DPs are not yet listed on the SC on POPs, but they are however listed on the European candidate list under REACH. This imply that usage and production of DPs must be approved by the European Commission (Environmental Agency Norway 2019). Regulation and restrictions on the BFRs (e.g. deca- and octa-PBDEs), created a demand for new, non-brominated, chemicals that can act as flame retardants. Therefore, DPs stepped in as a replacer for PBDEs in several products, such as plastics used in electrical and electronic equipment. DPs were additionally developed as a substitute for the pesticide and flame retardant dechlorane, also called Mirex, because of its ban in the 1970s.

DP-formulations contains two stereoisomers, syn and anti (Figure 6), in the ratio of 1:3, respectively. DPs was first detected in the environment in 2006 close to the production facilities of DPs (OxyChem, North America), and has later been found in Artic regions, indicating their LRAT potential (Möller et al. 2010). Since its first detection in 2006, DPs have gained scientific attention, and in 2017, DPs was included in several of the Norwegian Environmental Agency's monitoring programs. This is because DPs is found to bioaccumulate and -magnify, and to have potential toxic effects on ecosystems. DPs is further characterized as persistent, to have low volatility, high K_{OA} (log11-12), and consequently low water solubility.

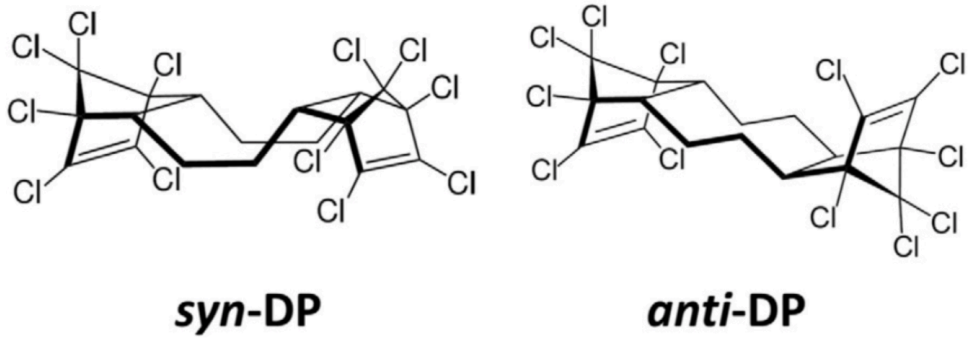

Figure 6: Chemical structure of dechlorane plus stereoisomers, syn (left) and anti (right) (Wang et al. 2016). The chemical formula for DP is $C_{18}H_{12}Cl_{12}$. This figure gives a good indication of the high chlorination degree for DPs.

2.1.5 Chlorinated paraffins (CPs)

Chlorinated paraffins (CPs) are a large group of polychlorinated n-alkanes produced in large volumes as industrial chemicals (van Mourik et al. 2016). CPs are divided into three subgroups based on their carbon chain lengths: short- (SCCPs; $C_{10\text{-}13}$), medium- (MCCPs; $C_{14\text{-}17}$), and long- (LCCPs; $C_{\geq 18}$) chained. The subgroup SCCPs became a part of the SC on POPs in 2018, where the purpose is to eliminate its global production and usage. M/LCCPs are not regulated under the SC on POPs but may in the future be so due to their similar properties as SCCPs. Within CP-subgroups, there are thousands of congeners with varying carbon chain lengths and chlorine numbers and positions. This gives varying physicochemical properties and environmental fates, but generally, CPs have a high chemical stability, low vapor pressure, and are flame-resistant. Because of these properties, and their low production cost, CPs are used in a wide range of industrial applications for different purposes, such as metal working fluids, plasticizers in plastics and rubbers, and as additives in paints. This has resulted in an abundance of CPs in the environment.

In environmental sciences, SCCPs have received more attention than M/LCCPs due to their predicted higher toxicity, simpler analytical quantification, and global distribution in environmental compartments. Consequently, there is a need to fill knowledge gaps on M- and LCCPs, and also SCCPs, to protect ecosystems health.

SCCPs are primarily used as softener and flame retardants in plastic, paint, leather materials, and as lubricants in metalworking- and shipping industry (Figure 7). SCCPs are released into the environment during all life stages, from production, storage and transport to usage, and finally disposal (UNEP 2016). This compound group bioaccumulates and persists in the environment, in addition to toxify ecosystems. It also undergoes long-range atmospheric- and oceanic transportation (van Mourik et al. 2016). Consequently, SCCPs meet the PBT and LRT POP-criterias.

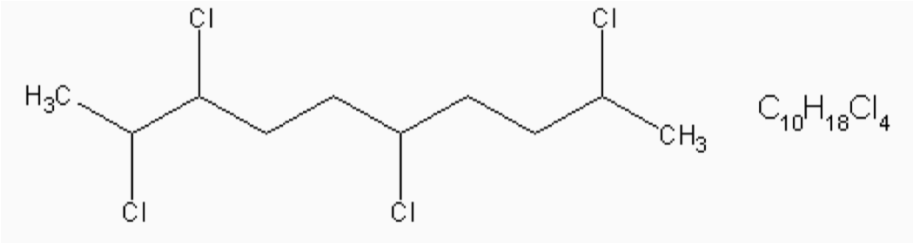

Figure 7: Chemical structure for the SCCP $C_{10}H_{18}Cl_4$ (UNEP 2016). For longer chains, the number of carbon atoms on the chain will increase, and for higher chlorination, the number of chlorine atoms on the chain will increase. Spatial position and number of chlorine atoms, and the length of the carbon chain, gives different congeners of CPs.

MCCPs, a less studied CP-group, is suspected to also be PBT, and the global production volume is expected to be higher than for SCCPs (Glüge et al. 2018). In the environment, MCCP concentration have been found to surpasses those of SCCP. Global treaties on SCCPs production and usage (e.g. the SC on POPs) have caused an increase in the MCCP-production, and MCCPs were also listed as an alternative chemical to replace SCCPs. MCCPs are used in plasticizers in polyvinylchloride (PVC) plastics, additives to polymeric materials, and as extreme pressure additives in metal working fluids. Because of its uncertain chemical properties, production volumes, and application areas, it is challenging to predict the concentration and potential harm to the environment.

2.2 Sources and emission of AOCs to the environment

AOCs are emitted to the environment from old and new sources and they are dispersed to air, soil, and water (UNEP/AMAP 2011). Industrialized and urban areas emit most AOCs, such as the central-western Europe, with its large industrial and agricultural activity, and populated cities (Figure 8). From these source regions, AOC-emissions occur mainly because of the AOCs' semi-volatile property, and these compounds volatilize to the ambient environment. This property, and because they are resistant to degradation, makes them globally dispersed. They are mainly dispersed through long-range transportation (LRT) after being volatilized, deposited, re-emitted, eroded, and from terrestrial runoffs to aquatic environments.

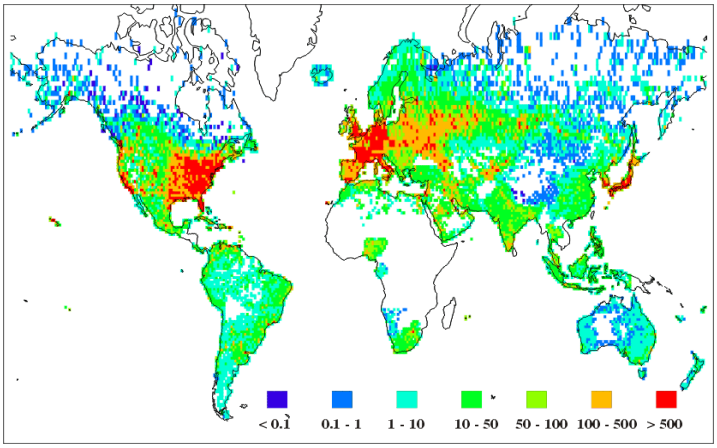

Figure 8: Global emission patterns of total PCBs in kg tons from 1930 to 2000. Modelled by Dr. Knut Breivik.

AOC-emissions can be divided into two main categories: (i) primary emissions and (ii) secondary emissions (Halse 2015). Primary emissions comprise of intentionally emissions, and is a result of production, use, and disposal of intentionally produced AOCs, whereas unintentionally emissions are AOC-by-products formed unintentionally from combustion-, chemical- or industrial processes. Secondary emissions refer to AOC-re-emissions from previous AOC-deposition and reservoirs. This can occur in environments with AOC-accumulation capacity, such as soil and vegetation surfaces, oceans, and snow/ ice. Consequently, AOC-emissions to environmental compartments are diverse and it is challenging to distinguish their origin. However, their environmental fate and behavior must be examined to understand AOCs migration globally from these sources and their emission pathways.

2.3 AOCs' environmental fate and behavior

AOCs' environmental fate and behavior is strongly influenced by their distribution between various environmental phases. The environmental distribution of AOCs is determined by individual AOCs' physicochemical properties (Halse 2015). Relevant properties for determining their environmental fate and behavior are their semi-volatility, low aqueous- and high lipid solubility, and persistency. These properties affect their partitioning between different environmental compartments, such as air, water, and organic surfaces (e.g. vegetation, soil). In environmental sciences, octanol is often used as a surrogate for organic environmental matrices that are non-polar or contain non-polar fractions, such as fats, waxes, and soil organic matter. The AOCs' partitioning behavior between these compartments is described using partitioning coefficient (K). A compound's K is calculated as the ratio between the concentrations (mol m^{-3}) in two phases, X and Y, when equilibrium is established. This is expressed as $Kx/y = \frac{Cx}{Cy}$, where K is unitless (Wania et al. 2015). Partitioning coefficient are often reported on a logarithmic basis when the concentration between the two phases differ strongly. For example, the logarithmic octanol-water partition coefficients ($\log K_{OW}$) of *p,p'* DDT and PCB 77 are 6,39 and 6,70, respectively. This implies that under equilibrium conditions the ratio between organic environmental matrices and water is approximately 1 million to 1 ratio, respectively.

Determining AOCs' partition coefficients (K) (e.g. octanol and water (K_{OW}), octanol and air (K_{OA}), or air and water (K_{AW})) provides valuable information for explaining or predicting the environmental fate and behavior of the organic pollutant. Soil to air equilibrium partition coefficient (K_{SA}) is highly relevant when assessing air to soil exchange of AOCs (Hippelein & McLachlan 2000). This exchange is driven by the gradient in chemical potential between the two phases. A high K_{SA} imply that the soil is far from being saturated with a chemical and therefore, air can "feed" the soil with chemicals without being depleted. Accurate data on AOCs' partitioning between environmental compartments and their physicochemical properties are therefore essential in assessing AOCs' environmental fate and behavior.

AOC chemical partitioning space maps can be used to predict and estimate AOCs' behavior and fate in the environment (Figure 9). The chemical partitioning space map for the AOCs included in this study distinguishes between i) volatile in the top left corner, ii) hydrophobic ("water fearing") in the top right corner, and water-soluble in the bottom left corner. The closer the compound reaches a corner, the stronger is the respective property. The placement of the compounds in the chemical space-map is based on their partitioning coefficient, K_{OA} and K_{AW} (air-water partition coefficient).

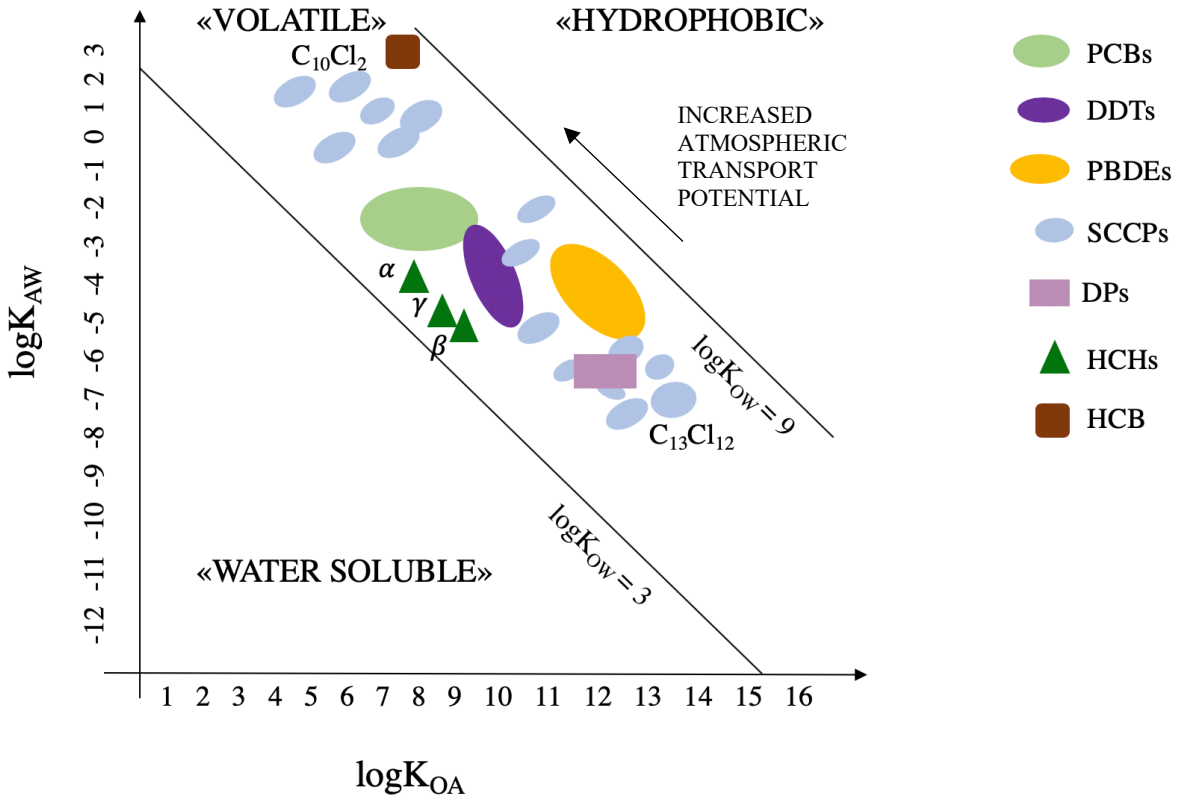

Figure 9: Chemical partitioning space map, based on (Halse 2015; Wania et al. 2015), where the equilibrium phase distribution for the major AOC-groups included in this study are shown. The x-axis is the partitioning coefficient between octanol and air, and y-axis is the partitioning coefficient between air and water.

Volatile AOCs with low K_{OA} and high K_{AW} are found in the upper left region of the map (Figure 9). These AOCs (e.g. HCB, SCCPs) have a large evaporation potential from sources or environmental surfaces, such as soil and vegetation. Hydrophobic AOCs with high K_{OA} in the upper right region (e.g. PBDEs, DPs) have a strong affinity for octanol and are therefore expected to sorb to organic matter (e.g. carbon and lipids). If present in the atmosphere, these compounds will sorb strongly to particles and are consequently prone to deposition to, and retention on, vegetation and soil surfaces rather than evaporation and leaching. In the Norwegian background soils investigated in this study, AOC-compound groups with such behavior are expected to be found. Finally, AOCs in the chemical space map lower left region have low K_{OA} and K_{AW} partitioning coefficients and are therefore water-soluble. In the environment, these compounds can be found in dissolved state in water phases and are prone to leaching.

In the chemical space map (Figure 9), the space indicated by the two lines is of importance in terms of LRAT and bioaccumulation assessment. These compounds are volatile enough to stay in air for a while, and involatile enough to deposit and accumulate on surfaces. They are water-soluble enough to allow water-uptake, and water-insoluble enough to prefer accumulation to fatty tissues, and have further molecules of a size that is small enough to pass through biological membranes. This AOC-chemical space map is consequently useful to predict the behavior and fate of AOCs in the environment, and it can further be exploited to discuss AOC-groups migration processes in the global environment, such as long-range transport (LRT).

AOC migration processes distribute AOCs globally and to regions far away from sources as a result of general atmospheric- and oceanic circulation (Wania & Mackay 1996). As early as in 1974 (Rappe et al. 1974), global AOC-distribution and accumulation in high latitude regions have been discussed in environmental sciences. Since then, the underlying migration processes in the atmosphere and ocean causing this global distribution has been assessed and recognized as long-range transportation (LRT), global fractionation, and grasshopping (Figure 10) (Wania & Mackay 1997).

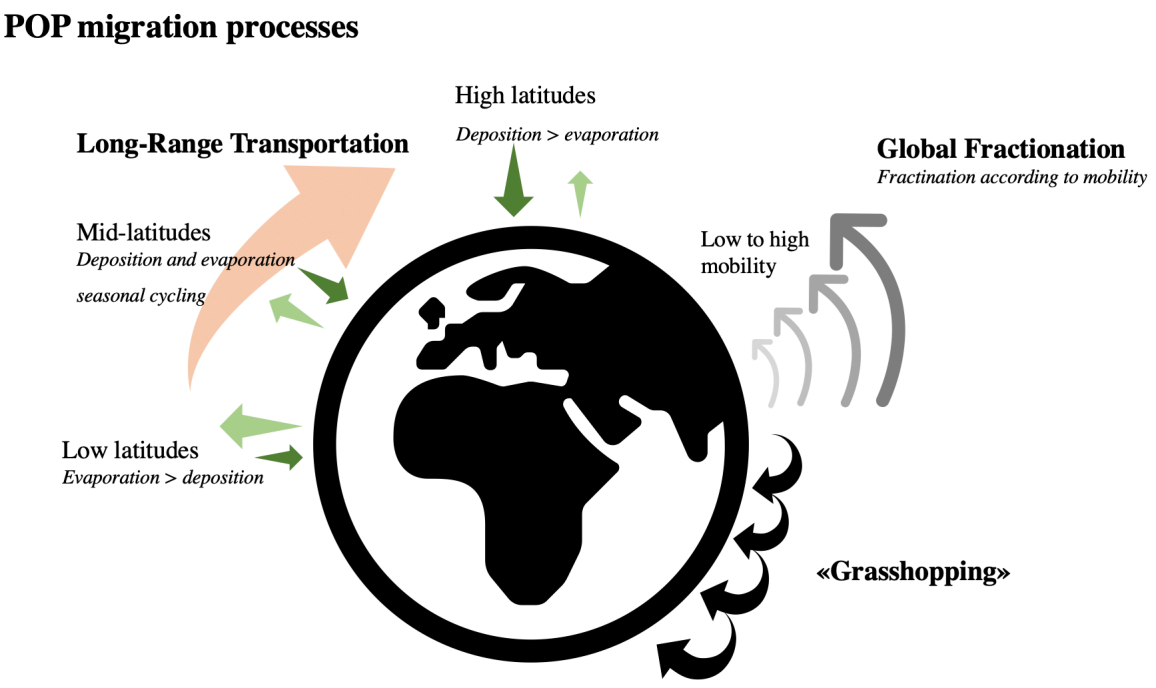

Figure 10: AOCs migration processes, based on (Wania & Mackay 1997).

LRT occurs in the atmosphere and oceans with general circulation, and through migrating species, with varying transportation velocities between these environmental compartments (upper left corner, Figure 10). In the atmosphere (i.e. LRAT), AOCs undergo fast and far-reaching transportation with moving air masses as gasses or aerosols. Because of AOCs semi-volatile property, they can remain in the atmosphere after emission or evaporate from surfaces, where higher temperatures result in a stronger evaporation. AOCs favoring deposition to surfaces, such as less-volatile compounds with a higher molecular weight and high K_{OA}, are thus more likely to be transported with ocean currents and/ or deposit to surfaces, which limits their LRAT. Ocean circulation is slower than atmospheric (years to decades), but a substantial amount of AOCs can be transported since water itself and organic components suspended in the water (e.g plankton and dissolved organic material) have a high capacity to store AOCs despite their low water-solubility. Consequently, air and ocean are efficient AOC-distributors in the global environment and central medias for AOCs' migration processes.

Global fractionation is a process that fractionates AOCs according to their mobility in air and water with increasing latitude (upper right corner, Figure 10) (Wania & Mackay 1997). Global fractionation is a temperature-dependent process, where high temperatures at low latitudes favor evaporation, and lower temperature at higher latitudes favor deposition from the atmosphere. This is because decreasing temperature results in reduced vapor pressure and degradation, causing i) a shift towards higher partitioning to surfaces than to the atmosphere, ii) reduced evaporation, and iii) increased persistency because decreased temperatures results in reduced degradation. Additionally, AOCs with high mobility will deposit further away from sources than AOCs with low mobility. Deposited AOCs can be re-emitted after deposition and undergo further transportation to higher latitudes, causing AOC re-cycling in the environment (Ockenden et al. 2003). This stepwise process is referred to as the "grasshopper effect". From the chemical space map (Figure 9) compounds in the low part within the two lines (e.g SCCPs) are expected to have a high mobility in air and low interaction with surfaces until cold regions are reached. Compounds in the upper region (e.g PCBs) can potentially undergo grasshopping due to their less volatile nature, and even less volatile AOCs are deposited close to their sources and re-emission is limited.

The grasshopper effect refers to AOCs' accumulation at higher latitudes as a consequence of temperature differences affecting AOCs volatility and repeated deposition and (re)-volatilization (lower right region, Figure 10). In warm, equatorial regions, high temperatures favor evaporation of AOCs and consequently, moving air masses to the north and south transport these compounds with atmospheric circulation. With a latitudinal gradient, temperature decreases, and AOCs volatility decreases and deposition with atmospheric aerosols and surface interaction increases. This can occur in a series of steps with a latitudinal gradient, where deposition and re-emission as a result of varying seasonal temperatures gives a "hopping" effect. Subsequently, an AOC-concentration gradient with increasing latitude is observed, where accumulation occurs in colder, polar regions. As a consequence of AOCs' global fractionation and/or grasshopping, the Northern Hemisphere and Arctic regions have received high loads of pollution. Therefore, these regions are of special interest for research into the distribution of AOCs.

2.4 Environmental monitoring of AOCs

Identification and assessment of AOCs in the global environment requires international and national monitoring programs. Monitoring of AOCs provides information on concentration changes and trends over time, which can be related to their source regions, usage- and production pattern, and their distribution, transportation and degradation in the environment. In 2007 the Stockholm Convention on POPs established a Global Monitoring Plan (GMP), which provides a harmonized global framework for POPs in air, human milk, and water (Magulova & Priceputu 2016). There are further three main international monitoring programs: i) The European Monitoring and Evaluation Program (EMEP), ii) The Arctic Monitoring and Assessment Program (AMAP), and The Global Atmospheric Passive Sampling network (GAPS). Through these programs, including the GMP, AOCs can be globally identified and assessed.

Air, water, soil, and biota are fundamental media included in AOC-monitoring. Air is a key monitoring medium because of the AOCs' semi-volatile property and their fast and far-reaching transport potential. Water, both oceanic and fresh water, is also of relevance in distributing and storing AOCs. AOC-concentrations observed in water provide information on migration processes, retention and storage, as well as AOCs leaching from terrestrial to aquatic ecosystems. Concentrations in biota allow to assess the uptake of AOCs by living organisms, bioaccumulation, and further their ecotoxicity.

Soils, and most notably background soils, are of particular interest in AOC-monitoring because of their large storage- and retention capacities for these compounds. The capacities are mainly explained by AOCs strong tendency to partition to soil organic matter because of their low water solubility and fat-loving nature. Background soils are remotely located from potential sources, and therefore, the mechanism for AOC-inputs at these locations is primarily caused by atmospheric deposition (Hassanin et al. 2004; Meijer et al. 2002). The input and distribution of AOCs in these soils is a composite function of proximity to sources and LRAT, and deposition processes will vary depending on vegetation, soil properties and environmental variables (e.g. temperature, precipitation) (Nam et al. 2008). Loss mechanisms occurring in soil environments includes retention in soil organic matter, biodegradation, burial in deep soil layers and volatilization (e.g. air-soil exchange). Monitoring of AOCs in soil environments is consequently essential to identify fluxes between the atmosphere and soil surfaces, re-cycling, and to assess storage-, retention, and degradation capacities (Moeckel et al. 2008; Ockenden et al. 2003).

Assessments of latitudinal gradients of pollutant concentrations in background soil are useful to increase the understanding of AOCs behavior in soil and their flux between air and soil. Additionally, in the global AOC-inventory and migration processes, boreal background soils are important due to their relatively long distance from source regions, high global carbon stock proportion, cold climate resulting in slow degradation and cold condensation, and vegetation canopies that scavenge for airborne AOCs (Moeckel et al. 2008). Consequently, the background soils from Norway included in this study is of high relevance when assessing AOCs environmental distribution and behavior, storage capacities, and their air to soil exchange.

2.5 Analysis of Airborne Organic Contaminants

Sensitive, specific, and comprehensive analytical methods are required to measure AOC-concentrations in complex matrices in order to evaluate sources, distribution patterns, and environmental fate of AOCs. AOC-analysis in environmental samples is often challenging due to the compounds' physicochemical properties, such as hydrophobic and lipophilic, resulting in "trapping" of AOCs within lipophilic environmental matrices. To extract the target compounds from such materials requires methods that tend to co-extraction substantial amounts of the sample matrix. These co-extracted substances can cause interferences during the instrumental analysis, making it necessary to remove them before extracts can be analyzed for target compounds. Therefore, the analytical procedures required to enable qualitative and quantitative AOC-determination in environmental samples, such as soil, are: i) extraction, ii) an often comprehensive clean-up, and iii) instrumental analyses. This step-wise procedure is needed to isolate bound AOCs from the sample matrix, and further separate them from interfering substances, and finally determine them in the purified extracts.

2.5.1 Sample preparation

Sample extraction

Extraction of organic pollutants from soil aims to obtain compounds in solution to enable qualitative and quantitative analysis. There are various commonly used extraction methods for organic pollutants, such as: Soxhlet extraction, Accelerated Solvent Extraction (ASE) and Ultrasound Assisted Extraction (UAE) (Jans 2016; Zuloaga et al. 2012). The Soxhlet method is an old, time-consuming (~8h) technology, and it requires relatively large amounts of solvents (150-400mL of e.g. hexane/acetone) to extract one sample. ASE, a newer, "greener", extraction technology, requires less solvents (20-40mL) and time (<1h) then Soxhlet (Wang et al. 2010). This is because the apparatus used for extraction is pressurized, which allows extraction at temperatures exceeding the organic solvents boiling point under atmospheric pressure (Giergielewicz-Możajska et al. 2001). In 1996, the first scientific paper on ASE was published (Richter et al. 1996), and since then, ASE has been recognized as an acceptable and recommendable extraction method for AOCs in complex environmental samples, such as organic matter rich soils (Wang et al. 2010).

Accelerated Solvent Extraction (ASE) was applied as extraction method for all soil samples from the Norwegian latitudinal gradient. The extraction process is step-wise, where the analytes first are desorbed from a solid particle, then diffuse to pores with solvent, and finally transferred to the solvent bulk (Giergielewicz-Możajska et al. 2001). The elevated pressure (>10MPa) and temperature (100°C) increase the movement of molecules and a higher kinetic energy within ASE cells is generated. The effect of this is increased analyte solubility, weakening and disruption of bonds between analytes and matrix components, decreased viscosity, and surface tension, which enables the solvent to penetrate more readily into pores and between matrix components. Consequently, AOCs bound to the soil matrix can be desorbed from soil particles efficiently and therefore, extraction time and solvent volume decreases.

Extracting compounds of interest from environmental samples leads to an extraction of matrix compounds. In environmental samples, such as soil, not only analytes can be solubilized. Matrix components, such as humic acids, lipids, and waxes, will be co-extracted under the extraction process. (Giergielewicz-Możajska et al. 2001). These co-extracted compounds can interfere with the AOCs' instrumental analyses. Therefore, clean-up procedures are needed before instrumental analysis to remove these potential interferences.

Sample clean-up

Clean-up of the sample extracts is needed to remove interfering compounds, such as lipids, humic substances, and polar components. Within analytical chemistry, one of the biggest challenges are compounds of interest that are contained in a complex matrix. This creates interfering constituents and makes analysis extremely difficult. In the literature, a large number of different clean-up methods have been reported (Zuloaga et al. 2012). The method chosen for a specific project depends on target compounds properties and on the nature of the sample matrix. For organic analysis in biological environmental samples, such as oil, vegetation, and soil, acid clean-up followed by a solid-phase extraction (SPE) is a recommended approach to remove co-extracted matrix compounds. In this project, concentrated sulfuric acid and a silica-based SPE were applied as acceptable clean-up methods prior to instrumental analyses.

Acid clean-up removes matrix and acid labile matrix components in sample extracts. Sulfuric acid is a strong oxidizing agent and it has a strong affinity for water, as well as hydrogen and oxygen inside molecules (ChemicalBook 2017). When the acid is added to the solvent-based soil extracts, it reacts with many organic compounds including those extracted from soils, resulting in oxidation and charring. The products of these reactions usually dissolve better in acid than in non-polar solvents, such as hexane. This allows for a separation of matrix components from the acid-stable analytes, which partition to the non-polar solvent. Consequently, sulfuric acid removes co-extracted interfering compounds and therefore cleans the extract. This method is restricted to acid-stable target compounds because acid-labile compounds would be destroyed by reaction with the sulfuric acid.

Solid-Phase Extraction (SPE) clean-up and can selectively remove interferences. SPE is a chromatographic method that separates compounds based on their physicochemical properties to selectively remove interferences (Arsenault 2012). Silica-based SPE is a liquid-solid phase extraction chromatography method that separates compounds according to their polarity. The stationary phase are polar silica particles (SiO_2), packed into a glass column, and the mobile phase is a non-polar solvent. The extract is added to the top of the column and the target compounds are eluted by the mobile phase. Silica is a polar molecule because of its active, hydrophilic polar surfaces containing acidic silonal functional groups (Si-O-H). The silica particles act as a sorbent for polar non-analytes present in the sample solution because of their large surface area and functional groups. (Telepchak et al. 2004). Apart from polar compounds originating directly from the soil, these can also be breakdown products from acid labile co-extracted compounds. Consequently, silica is performed to remove polar impurities, and thus reduces the amount of interfering co-extracted compounds in the sample.

Soil organic matter

The soils sampled were characterized by determining soil organic matter (SOM) by the loss-on-ignition method (LOI). SOM is an important parameter in assessing the distribution of AOCs in soil due to their affinity to SOM resulting from their hydrophobic nature. LOI is a widely used method to determine organic content in environmental samples, such as soil and sediments (Heiri et al. 2001). The principle of this method is that the organic fraction of the soil is oxidized to carbon dioxide (CO_2) under elevated temperature, 500 to 600°C. At higher temperatures, 900-1000°C, the carbonate content, such as calcium oxides (CaO), are removed. LOI for SOM content at such temperatures would give an overestimated SOM in the soil samples. Therefore, the temperature for SOM determination needs to be well below the one of carbonate burning. The weight loss from the LOI method principle equals the amount of SOM that was present in the sample, and hence, SOM content can be determined.

2.5.2 Instrumental analysis of Airborne Organic Contaminants

Gas chromatography (GC) and Mass spectrometry (MS) analytical techniques are used in environmental sciences to detect and quantify the presence of trace organic pollutants in environmental samples (Hernández et al. 2012). GC techniques separate compounds of interest from each other and from interfering co-extracted compounds in order to determine their concentrations. Coupling of GC to a MS as the detector allows for the analysis, and later quantification, of a broad range of organic compounds. This was the principle instrumental setup used for the quantitative analysis of AOCs in this study (Figure 11).

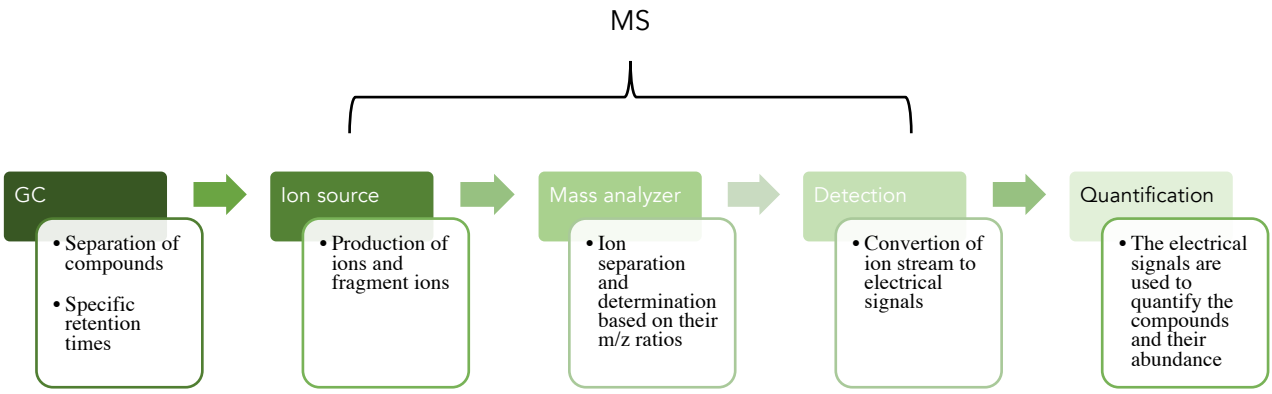

Figure 11: Extracted summary of the GC/MS system principles for AOCs instrumental analysis. More information on this system is described below.

Gas chromatography

The principle of chromatography encompasses the exploitation of organic compounds' dissimilar volatility and to a lesser extent polarity to separate compounds in a solution to enable quantitate determination. For this purpose, the most common system is gas chromatography (GC). In a GC instrument the separation is achieved in a long (typically 15-60 m, and for some applications up to 120 m), narrow (typically 0,20-0,32 mm internal diameter) column. The GC column consists of a fused silica tube coated with a thin polymer film on the inner wall, which acts as the stationary phase. The outside is coated with polyimide, a synthetic resin that greatly increases the robustness of the column, preventing it from breaking easily. In the GC system used in this study, the sample extract is injected into a glass tube (referred to as "liner") where it is vaporized in an inert helium atmosphere at temperatures that do not degrade the analytes. Thereafter, the vaporized sample is carried through the GC column by a gas (typically helium), which acts as the mobile phase. A separation is achieved in this system because the analytes present in the sample interact differently with the stationary phase and move faster or slower through the column, eluting from it after different times (retention times).

The interaction is dependent on the compounds' physicochemical properties, such as their vapor pressure and polarity. In GC's based on vapor pressure, the separation is optimized with the use of a temperature program, where the temperature is increased with time. In this way, readily vaporized compounds, such as solvents, are eluted first, then eventually all analytes will follow with increasing temperature. For polarity dependent separation, the stationary phase column is coated with polar to highly unpolar material to enable separation. Generally, the stronger the interaction with the column, the slower the compounds will be carried through with the mobile phase, and consequently, a separation is created. These separated compounds are then transferred to a detector, such as a mass spectrometer, where they are identified.

Mass spectrometry

Mass spectrometry (MS) determine analytes quantitatively and qualitatively based on their compounds of interest mass to charge (m/z) ratio and signal intensity (Hernández et al. 2012). From the GC, the gaseous compounds enter the mass spectrometer, where they are converted to ions by an ion source (Skoog & Leary 1992). To achieve a strong signal for AOCs in the MS, also at trace amounts, it is important to minimize the influence of interfering compounds. The ion formation can be suppressed by the presence of large amounts of sample compounds, resulting in a low signal and hence a low sensitivity of the analytical method. Therefore, the extracts' clean-up methods prior to instrumental analysis is highly important for a successful analysis and further quantification

In the system used for analysis of PCBs, PBDEs, NBFRs, and OC pesticides in this study, the ion formation in MS is obtained by bombarding the uncharged compounds present in the sample with high energetic electrons. Which ionization mode is most efficient in ionizing the analytes depends on their properties. Positive or negative ions are produced, usually of ±1 charge, depending on the instrument used and the analytes' properties. For example, CPs and current used pesticides were ionized by electron ionization which produces negative ions.

During the ionization process, the compounds can also be fragmented into fragment ions. Specific masses and relative abundance of these fragment ions are characteristics for each compound and its molecular structure. The output of this process is a stream of ions that are accelerated into the mass analyzer by applying suitable voltages. In this process, mass analyzers (e.g. quadrupole, time of flight, magnetic sectors) are used to separates the compounds based on their m/z ratio. Thereafter, this stream is guided through the detector by electrical or magnetic fields. The MS converts the beam of ions from the mass analyzer into electrical signals, and from these electrical signals the analytes are quantified based on their m/z ratio. The signal intensity produced is a measure of the compounds' abundance. Therefore, the results from these analyses can then be interpreted to evaluate AOCs' occurrence, and their environmental fate and behavior.

3. Materials and methods

3.1 Study area

Within the SERA project, the terrestrial ecosystem is included as one of the environmental compartments involved in the source-exposure relationships for AOCs. On the background of this, Norwegian soils were sampled to gain knowledge on the AOCs occurrence, and their environmental fate and behavior nationally, and to assess their air to soil exchange by considering both the soil and air concentrations.

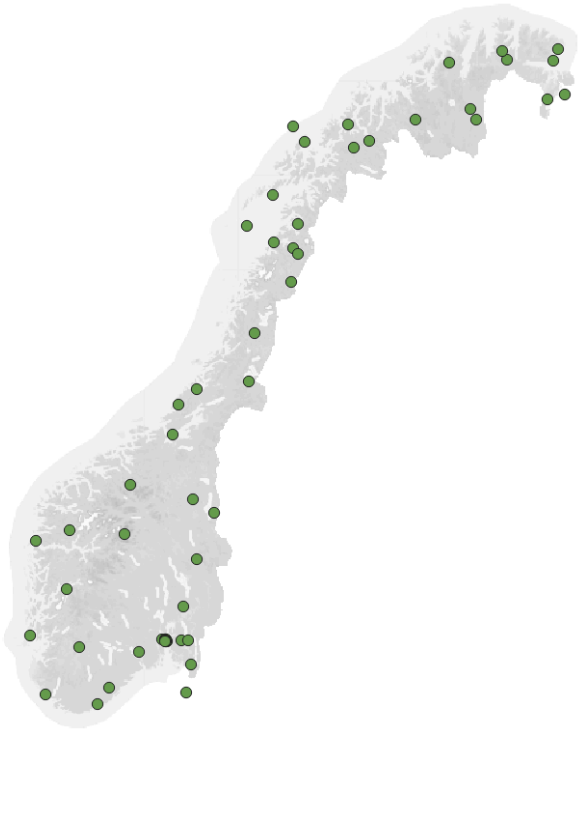

Figure 12: Sample sites included in this study. The map presents all 55 sampling sites. The name of each site with their respective coordinates are given in Appendix B.1.

To meet the SERA-project's, and this study's objectives, 10 urban- and 45 remote sites well distributed throughout Norway were chosen (Figure 12). The sample sites were selected based on the Nordic Exposure Model (NEM) resolution, in where Norway is divided into 15 grid cells (3.75° by 3.75°). Three sampling sites with a maximum distribution in each grid were selected to assess the variability within each cell. More detailed location information is given in Appendix B.1. Additionally, at each site, passive air samples were taken in 2016.

3.2 Sampling

Background and urban soils (n=55) from the Norwegian latitudinal gradient were sampled by Helene Lunder Halvorsen and colleagues in the summer 2016. Top-soils (0-5cm) were sampled and analyzed to obtain knowledge of the AOCs occurrence in Norway. Top-soils have a high soil organic matter (SOM) content originating from the vegetation (Ockenden et al. 2003). Above ground vegetation is in direct contact with the air. The large surface area of leaves and needles compared to the ground surface results in deposition, scavenging, and adsorption of AOC-compounds to the vegetation canopies. As a result of plant senescence, old leaves and needles drop to the ground, where the organic material accumulates and decomposes over time and becomes a part of the soil. This organic-rich soil part is referred to as the organic O-horizon. Below the O-horizon is often an A-horizon still rich in organic material, but with some mineral material present. These horizons' properties (e.g. degree of degradation, and amount of mineral soil in the A-horizon) vary with site parameters (e.g. vegetation, geology, and climate). In this project's study area, soil formation processes are relatively slow as degradation and bioturbation are limited due to boreal climatic- and environmental factors, such as low temperatures, varying vegetation quality, and fauna. As a result of AOCs interaction with vegetation, and consequently the soil organic material, the organic horizons (O- and A-horizon) were sampled to assess AOCs' terrestrial occurrence, behavior, and their air to soil exchange.

The soil sampling was performed by first removing the fresh litter layer, and then a bulb planter with 5 cm in diameter was used to extract 5 soil cores from the O- and A-horizon over a several square meter area at each sampling site. This was done to obtain a representative sample from each site. All the 5 cores form each site were assembled to obtain a composite sample and packed in two to three layers of aluminum foil and placed in two zip-locked bags. All soil samples were placed in a freezer and stored at NILU Kjeller until sample preparation. The soils were characterized by determining the soil organic matter (SOM) content by the loss-of-ignition method (Appendix A.2.3).

3.3 Sample preparation

Soil sample preparation for organic analysis aims at extracting analytes from sample matrix, and thereafter obtain a purified sample free from interfering matrix compounds. Sample preparation is required for a successful instrumental analysis, and thereafter quantification of the analytes. AOC analysis in soil requires an extraction method, followed by several step-wise clean-up procedures (Figure 13). In this study, the samples were extracted with accelerated solvent extraction (ASE), and cleaned with acid, powdered copper, silica-based solid-phase extraction (SPE), and removal of acid-stabile, non-polar, matrix compounds by centrifugation. These methods were performed after NILU's laboratory practices for analyses of organic contaminants in soil (NILU 2018c).

3.3.1 Accelerated solvent extraction (ASE)

Accelerated solvent extraction (ASE) extracts compounds of interest from the soil matrix. Prior to extraction, the composite soil sample consisting of 5 cores from each site was homogenized to attain a representative sample. Thereafter, a subsample of 5-15g (wet weight) from the field-moist homogenized soil was chemically dried with anhydrous sodium sulfate (Na_2SO_4) and ground in a mortar until a free-flowing powder was achieved. This soil sample was then packed in ASE cells for extraction, and further spiked with labeled internal standards. The cells were run on ASE Dionex 200 apparatus for extraction with acetone: hexane (1:1 v/v) solvent, 100^0C and 1500Psi. As a result, extracted soil samples in acetone: hexane (40mL) were obtained, and these were ready for sample clean-up. Information on this method is given in Appendix A.2.1.

3.3.2 Sample clean-up

The extracted soil samples were cleaned with i) acid, to remove acid-labile matrix components, ii) activated copper, to avoid chromatogram interferences by sulfur, iii) silica-based solid-phase extraction (SPE), to remove polar components, and finally iv) centrifuged at low temperature (-9ºC) to remove acid-stabile, non-polar matrix compounds (e.g. waxes from soil organic matter). Prior to clean-up, the extracts obtained by ASE (40mL) where solvent-exchanged to hexane and concentrated (0.5mL) with the use of an evaporation system (Turbovap 500). These clean-up method procedures are briefly summarized in a flowsheet below (Figure 13), and a detailed description is given in Appendix A.2.2.

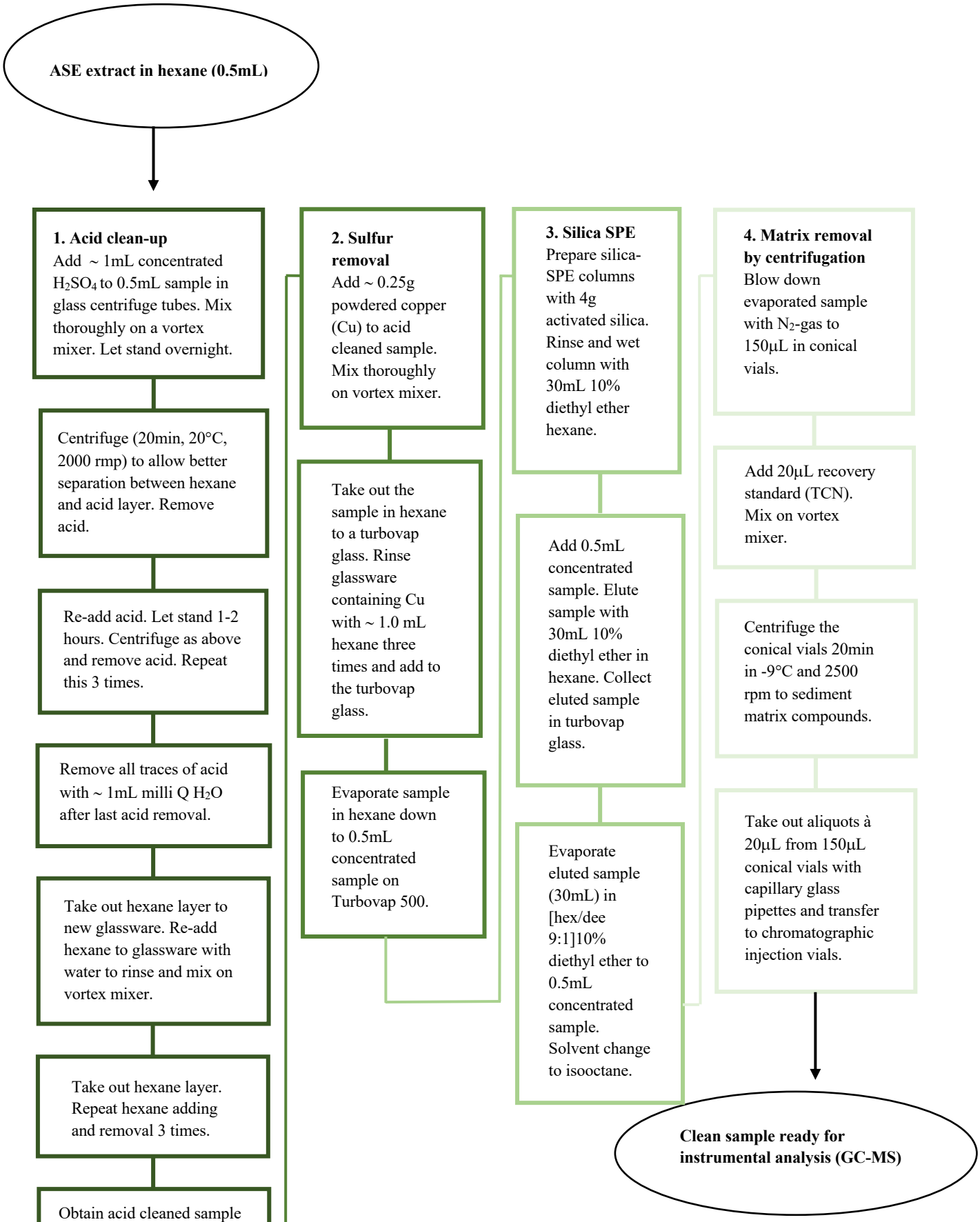

Figure 13: Comprised summery of sample extract clean-up. The numbers indicated in the first row boxes (1-4) signifies the order in which the step-wise clean-up procedures were performed. To complement this figure, detailed information for all steps in the sample clean-up is given in Appendix A.2.2.

3.3.3 Quality assurance and control

All solvents and standard solutions used in the sample preparation were from controlled and approved NILU-batches according to accredited routines (NILU 2018b). Sample preparation quality assurance and control were ensured with blank samples at the rate of one for every eight soils extracted. The blanks were prepared in the same way as the soil samples and analyzed in parallel with them to evaluate possible contamination during the sample preparation and analysis. All samples were spiked with isotopic labeled internal standards prior to extraction, and added a recovery standard just before instrumental analysis (Appendix A.1.1, Table 2-8).

3.4 Instrumental analyses

The instrumental techniques used for quantitative and qualitative AOC determination in the soil samples were chosen based on the chemical nature of the compound groups of interest. For all AOC compound groups assessed in this study, gas chromatography coupled to a mass spectrometry (GC/MS) technique was applied (see Background 2.5.2) (NILU 2018a). Two GC/MS instrumental techniques were used, where information on these is given below with their respective compound groups. Detailed GC/MS instrumental parameters are given in Appendix A.3.

3.4.1 Instrumental analysis of chlorinated paraffins (CPs) and dechlorane plus (DPs)

The instrumental analysis for chlorinated paraffins (CPs) and dechlorane plus (DPs) was done by the use of an Agilent high-resolution capillary GC coupled to a Quadrupole-Time of Flight (Q-TOF) MS. This detector produces mass spectra with relative high resolution of approximately 15 000 FWHM (full with half measure: $m/w_{0,5h}$ were m is the mass, and $w_{0,5h}$ is the width of the peak at half maximum height).

The most suitable ionization technique for CPs and DPs analysis in GC/Q-TOFMS is electron capture negative ionization (ECNI) mode. The ECNI source applies a buffer gas, methane (CH_4), to create thermal electrons. These electrons combine with substituents with high electron affinity, in this case the chlorine atoms, on the molecules present in the ion source. Consequently, negatively charged ions are created in the source and these are guided to the mass analyzers.

The ions produced in the ion source can be characterized by the ratio between their mass and their charge. In Q-TOF-MS this mass-to-charge (m/z) ratio is found by the use of Quadrupole (Q) and Time-Of-Flight (TOF) mass analyzers. A Q mass analyzer consist of four parallel metal rods connected electrically. The beam of ions travels through the rods with different interaction based on their m/z ratios. This allows for ion separation and selection because the interfering ions will collide with the rods and consequently, not be guided to the TOF mass analyzer. The TOF mass analyzer principle is that the ions are separated based on m/z ratios in a field free region after acceleration through a fixed accelerating potential. Ions of the same initial translational energy and different m/z require different times to traverse a given distance in the field-free region. As a result of this, the ions' masses, structure, elemental- and isotopic composition present in the sample can be identified and further quantified.

3.4.2 Instrumental analysis of PCBs, PBDEs, DDT-group, and some OC pesticides

The instrument applied for PCBs, PBDEs, and NBFRs analyses was the GC/HRMS Agilent 6890 GC and Ultima Autospec Micromass. In this system, the MS mode is electron ionization (EI), where highly energetic electrons collide with the analyte molecules and create positively charged molecular ions (+1) and fragment ions. The relative intensity of different fragment ions, called mass spectrum, is characteristic for each substance. This depends mainly on the energy of the electrons used for ionization and can be catalogued in mass spectra libraries. The mass analyzer used to enable ion separation is a magnetic sector. The beam of ions is accelerated through the magnetic sector by applying suitable voltage. Thereafter, the ions are deflected according to their m/z ratios. As a result of this, the mass analyzer separates ions and thereafter, the identity of compounds present in the sample can be concluded from the mass spectra obtained while the intensity of the signal is related to the concentration of the respective compound in the sample.

To ensure the high mass resolution, this mass spectra uses a lock-mass signal to continually correct for small changes in mass readings caused by the sample. Lock-mass ions with exact known fragment masses are generated from a standard that is infused constantly directly into the MS. Here, perfluorokerosene (PFK) was applied as a suitable lock-mass standard. The infusion of PFK gives a high signal throughout the sample series. This is done by "locking" one of the fragments ions' masses in each retention window. During analysis, the instrument cycles through the ions present in the sample, including the chosen lock-masses from PFK, and corrects itself constantly for small variations to match the observed lock-mass with the expected one. The correction also applies to the masses monitored for measuring the target compound masses. The intensity of the lock-mass signal over time can be used to assess variations in the detector's sensitivity over time.

3.5 Quantification

Quantification of compounds was performed by using quantification standards with known contents of target compounds, internal standards (ISTD), and recovery standard (tetrachloronaphthalene (TCN)) (NILU 2018a). The internal standards added to the samples prior to extraction followed the analytes through sample preparation and instrumental analysis. The recovery standard TCN was added right before instrumental analysis (Figure 13). The recovery standard corrects for variations of the injection volumes and variations of the detector's sensitivity during the GC-MS analysis. To measure how much of the internal standard was lost during samples preparation, the isotopically labeled internal standard recoveries are determined relative to the recovery standard TCN before analyte quantification. It is then assumed that the loss of each target compound equals that of a chosen internal standard. A calibration is obtained by plotting the ratio of the peak intensity of the analyte compounds to that of the internal standard as a function of the analyte concentration. MassHunter/Lynx was the software used as quantification tool. The program was set up in a way that it quantifies the compounds of interest present in the sample from the GC-MS output and automatically corrects for internal standard recoveries. The equations applied for quantification are given in Appendix A.4 (eq. A.4 2-5).

3.5.1 Quantification evaluation and limitations

Identification of uncertainties in the quantification of PBDEs, the DDT-group, PCBs, and some OC pesticides (e.g. α-, β-, γ-HCH, HCB) was accomplished by evaluating the lock-mass signal intensities within the retention time range of the target compounds and their respective internal standards. The lock-mass signal may indicate whether matrix components caused temporary variations in detector sensitivity. Ideally, the intensity of the lock-mass signal is constant over time. If interfering matrix components reaches the detector, they can cause a temporarily "drop" or "hop" in the lock-mass signal intensity. This indicates temporarily lower or higher instrument sensitivity which consequently affects the quantification accuracy for the compounds of interest. This is of risk if the "drop/hop" is at the same time as when the compounds of interest or their internal standards are eluted. Therefore, evaluating the lock-mass signals are useful when assessing uncertainties in the quantification.

CPs' structural complexity gives consequences for the quantification. Industrially produced CP mixtures contain a vast number of structurally similar CPs with thousands of possible isomers. For example, for CPs with C_{17} carbon chain and 5 to 17 chlorine there are around 53 000 possible theoretical isomers. Therefore, quantification of all individual CPs in environmental samples is not achievable with current technology. From mass spectra obtained from MS detection, CPs appear as broad heaps rather than well-defined peaks. This is because the various compounds have varying retention times but identical mass to charge ratio. As a result of these limitations, CPs are quantified as homologue groups, not individual congeners (Tomy et al. 1997) (Gao et al. 2016). A further complication is related to the fact that chemical standards available for CPs do not necessarily show the same congeneric composition as present in the samples. Since the sensitivity of the detector used depends on the chlorine content this can create additional uncertainty (Reth et al. 2005).

3.6 Data processing

3.6.1 Correction for recovery of internal standards

Blank and soil samples were corrected for recoveries of the internal standards that were added prior to extraction. There was assumed that the target compounds experience the same losses as the chosen internal standards during sample processing. This recovery correction is built into the MassHunter/Lynx quantification. The equations the software uses are given in Appendix A.4.

3.6.2 Blank sample correction and raw data processing

Concentrations of individual target compounds measured in the samples were corrected for average concentrations of the respective compounds detected in the blank samples. The variability of the blank concentrations was also used to derive method detection limits (MDL) for individual compounds. The MDL indicates the lowest measurable concentration that can be distinguished from zero with a given certainty (ca. 99% in this study). MDLs for each individual compound was calculated as the average blank concentration plus three times the standard deviation (STD) of the blanks (equation (Eq).1):

Eq.1

$$MDL = mean_{blank} + (3 * STD_{blank})$$

An instrumental detection limit was used when a target compound was not detected in the blank samples. This limit is based on the background noise created by the instrument. Soil sample concentrations below MDL values were not included for further processing in this study. All soil samples were blank corrected by subtracting mean blank concentration (pg/sample) for each individual compound from the soil concentrations after the evaluation of soil samples below MDL.

Blank corrected results were processed by converting the quantified concentrations to mass unit per dry weight (pg/g dw) and soil organic matter (pg/g SOM) (Eq.2-3):

Eq.2

$$\frac{pg}{dw} = \frac{\left(\frac{pg}{sample}\right)}{dw}$$

Eq.3

$$\frac{pg}{SOM} = \frac{\left(\frac{pg}{dw}\right)}{SOM\ fraction}$$

Where pg/sample was obtained from the quantification and dry weight was the weight of the soil extracted in the ASE cells and corrected for its moisture content. For the conversion to pg/g SOM, the fraction of SOM in the dry soils (0 to 1) was obtained from soil characterization by loss-on-ignition (Appendix A.2.3, Eq.1).

3.6.3 Statistical analysis

In this study, statistical analyses were performed in the R Statistics and Microsoft Office Excel 2018. Box and density plots were produced in R to visualize the dataset (Appendix B.2.1). These plots were applied to assess the normal distribution of the data set and to identify potential outliers. A non-parametric paired-sample Wilcoxon test was run in R to test if there was a significant difference between the background and urban soils. This test was run with the use of average concentrations for the different compound groups. A Wilcoxon test was chosen because the data used was not log-transformed, and consequently, not normally distributed. The hypothesis tested was H_0: background = urban, and the alternative hypothesis, H_1: urban > background. If the p-value was found to be <0.05, H_0 was rejected and it was established that urban concentrations was significantly different from background concentrations.

Evaluation of the AOCs spatial distribution and environmental behavior was achieved by use of a correlation test in R (Pearson's correlation), where a correlation coefficient was obtained (r) with its p-value. The correlation coefficient (r) measures the strength of linear relationship between the two variables, such as SOM content and latitude with concentration levels. A correlation between the two variables tested was defined as statistically significant when $p<0.05$. Prior to this correlation test, the concentrations were converted to $\log_{10}$ to meet the criteria for normal distribution.

To test if there was a significant difference between the concentration levels in the south and north of Norway, a two-sample t-test with 95% confidence interval was performed in R. Prior to this test, the concentrations were converted to $\log_{10}$ to meet the t-test criteria for normal distribution. The hypothesis applied for this test was, H_0: south = north, and alternative hypothesis, H_1: south > north. H_0 was rejected if $p<0.05$. This rejection would imply that south of Norway is ascertained to have higher concentration levels than the north.

3.6.4 Geographic Information System (GIS)

Q-Geographic Information System (GIS) 3.4 was the program applied for all map representations in this thesis.

3.6.5 Assessment of air to soil exchange

The air to soil exchange of PCBs was investigated by determining soil to air equilibrium partition coefficient K_{SA} (Eq. 4-7) and by quantifying the soil to air fugacity ratios. These ratios are used to evaluate the exchange direction (Eq. 8-10) (Li et al. 2010).

A fugacity capacity (Z value, mol/(m^{3}Pa)) is calculated to describe the potential of a material (e.g. soil, water, air) to retain a chemical. This capacity, Z_A and Z_S, is calculated for both air and soil:

Eq.4

$$Z_A = \frac{1}{RT}$$

Where R is the gas constant, and T is the average temperature (K) during the sampling period (June to August 2016) for each site. This temperature is applied for all air to soil exchange equations.

Eq.5

$$Z_S = \frac{\varphi'_{SOM} log K_{OA}}{RT}$$

Where φ'_{SOM} is the mass fraction of SOM, and K_{OA} is the octanol-air partitioning coefficient. K_{OA} is highly temperature dependent and spans over several ranges of magnitude. Therefore, K_{OA} was calculated based on the approach by Li et al. 2003 (Li et al. 2003), where the temperature (K) was the average temperature for the sampling period. Equation below was used for the calculation of adjusted K_{OA} (T) values:

Eq.6

$$K_{OA}(T) = K_{OA} - \left(\left(\frac{\Delta U_{OA}}{R * 2.303}\right) * \left(\frac{1}{T}\right) - \left(\frac{1}{298.15}\right)\right)$$

Where K_{OA} refers to values at 25^{0}C, ΔU_{OA} internal energies of phase transfer (J/mol), R is the gas constant, and T is the average temperature (K).

To describe the partitioning between air and soil, a soil-air partition coefficient (K_{SA}) was calculated as the ratio of the Z-values above. This gives:

Eq.7

$$K_{SA} = \frac{Z_S}{Z_A} = \frac{\varphi'_{SOM}}{K_{OA}}$$

The greater the value of K_{SA} for a given chemical, the stronger is the retention in soil (Cabrerizo, A. et al. 2011).

The fugacity *f* expresses a chemical's tendency to escape from a given medium. Chemicals tend to escape from medias where they have a high fugacity to media where they have a low fugacity (Li et al. 2010). The fugacity is proportional to the concentration, and it is defined as C/Z (where C is the concentration in mol/m^3) and it is expressed as:

Eq.8

$$f_A = C_A RT$$

Eq.9

$$f_S = \frac{(C_S\, RT)}{K_{SA}}$$

Where C_A and C_S is concentration in air (pg/m^2) and soil (pg/g dw), respectively. The fugacity fraction (*ff*) is used to assess a chemical's equilibrium between the two interacting phases, air and soil, and gives an indication of the net direction of a chemicals air-soil exchange. This value is calculated as the fugacity in soil, divided by the sum of air and soil fugacities:

Eq.10

$$ff = \frac{f_S}{(f_S + f_A)}$$

When the *ff* value is ~0.5, this indicates chemical equilibrium between air and soil. If the value is >0.5, net volatilization from soil to air is occurring, and <0.5 indicates net deposition from air to soil. These calculations can therefore be used to assess the air to soil exchange of AOCs in terrestrial ecosystems and further evaluate the soils' role in the global burden of these compounds.

4. Results and discussions

This chapter presents initially results from the quality assurance and control measure used (4.1). Thereafter, a result overview is given for the pollutant concentrations' occurrence in the background and urban soils (4.2), followed by the discussion of these results in the light of the research questions this thesis is based on (4.3-4.7). The quality assurance and control section includes analyte concentrations in laboratory blank samples and recoveries, and sample matrix effects on the chromatographic results. Comments on potential field variability is presented in the quality assurance and control to assess the representability of the study design. The soil concentrations in the result overview are reported as mass unit per unit dry weight soil (ng/g dw).

The main objective of this thesis was to study the occurrence, environmental fate and behavior, and air to soil exchange of AOCs in Norwegian terrestrial ecosystems. To meet the aim of this study, evidence for these objectives were assessed by: i) investigating the association of AOCs to soil organic matter, ii) AOCs' spatial distribution from south to north in Norway, iii) associations within and between AOC-groups, iv) air to soil exchange, and v) temporal variations. This assessment is reported and interpreted in this section based on soil- and air concentrations, as well as site variables.

4.1 Quality assurance and control

Quality assurance and control is used to secure that the results are accurate and traceable. The analysis of organic contaminants in trace amounts has many potential error sources, such as loss or contamination during sample preparation, the analysis, and also the quantification. Therefore, blank sample levels and matrix effects which may have potentially affected the quantification are presented to assure true values and to secure traceability of the organic analysis in this study. The representability of the soil samples from each study site is further discussed to assess potential field variability.

4.1.1 Laboratory blank samples

Laboratory blank samples (n=8) were prepared and analyzed in parallel with the soil samples (Table 2). The results obtained were used for blank correction of the soil samples analysis, calculation of method detection limits, and identification of invalid results (see Materials and Methods 3.6.2).

Table 2. Summarized blank sample concentrations, MDL, and percent recoveries (Rec).

Compound*	**Mean ± SD pg/g dw**	**MDL pg/g dw**	**Rec%**
PeCB	42 ± 42	167	25
HCB	14 ± 6	32	30
Σ_{32}PCB	105 ± 23	175	76
Σ_{7}PCB	40 ± 9	66	69
Σ_{6}DDx	20 ± 11	54	81
Σ_{3}HCH	14 ± 4	26	62
$\Sigma_{syn\&anti}$DP	71 ± 100	375	102
Σ_{25}PBDE	318 ± 151	770	87
Σ_{5}PBDE	178 ± 98	540	95
Σ_{14}NBFRs	1,400 ± 400	4200	70
$\Sigma_{10,5\text{-}13,9}$SCCPs	21,000 ± 8,000	44,000	72
$\Sigma_{14,6\text{-}17,7}$MCCPs	18,000 ± 12,000	55,000	72

**Σ_{32}PCB is the sum of all PCB-congeners analyzed and Σ_{7}PCB is the sum of the indicator PCB-congeners: 28, 52, 101, 118, 138, 153, and 180. Σ_{6}DDx includes o,p' and p,p' DDT and their metabolites DDE and DDD. For the OC pesticide HCH, Σ_{3}HCH is the sum of the α-, β-, and γ-HCH isomers. $DP_{syn\&anti}$ are the two isomers of dechlorane plus. Σ_{25}PBDE is the sum of all PBDE-congeners analyzed (Appendix B.2), and Σ_{5}PBDE is the sum of indicator PBDE-congeners: 47, 99, 100, 153, and 154. Σ_{14}NBFRs represents all compounds analyzed for this group (e.g. DPTE, PBEB, EHTBB etc.). CPs are divided into the two sub-groups: SCCPs and MCCPs, based on their carbon chain length (10-13 and 14-17 C respectively) and with their chlorination degree (e.g. 10,5 signify C_{10} and Cl_5).*

The recovery of internal standard was found to vary from 25% to 95%. This imply that there was a spread in recoveries for the different compound groups analyzed. Therefore, from these blank recoveries, the laboratory procedures do not preserve the target compounds. However, when the analytes of interest where quantified in MassHunter/ Lynx, the results were recovery corrected with respect to the internal standard (see Materials and Methods 3.6.1), and thus, the losses during sample preparation was accounted for.

Evaluation of congener distributions for selected compound groups in blank samples can be used to discuss and reveal potential contamination sources. PCBs, and also PBDEs, showed a trend of decreasing concentration with increasing degree of chlorination/ bromine content (Figure 14). This is because less halogenated congeners are more volatile than those with higher halogenation degree. As a result of this, the lower halogenated congeners have a higher abundance in the gas phase, whereas a larger portion of the higher halogenated congeners is associated with particles. Consequently, we can assume that air is most likely to be the main contributor to blank contamination of PCBs and PBDEs in this study.

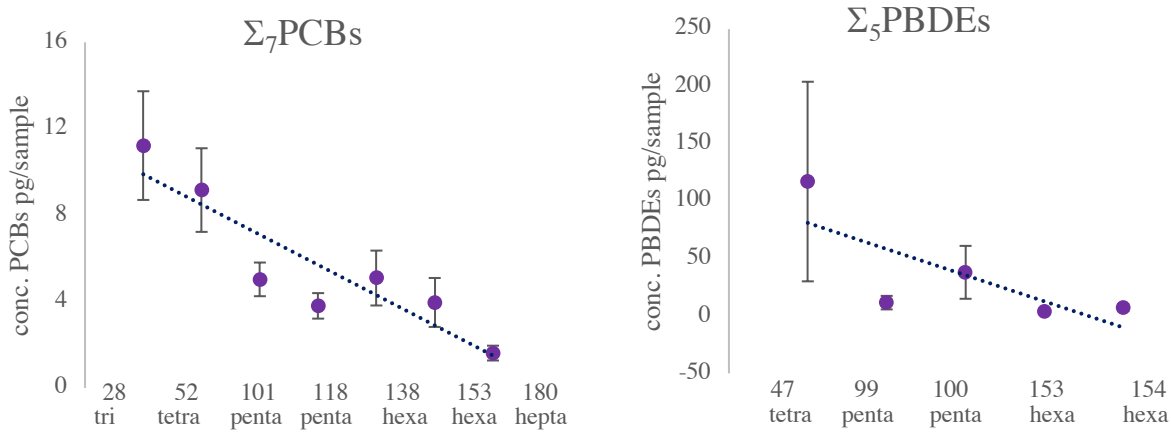

Figure 14: The distribution of Σ7PCB (left) and Σ5PBDEs (right) in blank samples (n=8), where x-axis is PCB/PBDE-congeners with increased halogenation degree (tri-hepta), and y-axis is mean concentration in pg/sample with standard deviation.

Chlorinated paraffins (CPs) was the compound group with highest concentration levels in the blank samples (Table 2), and this can be related to indoor sources. CPs are frequently measured in indoor house dust, where SCCPs are generally present at higher concentrations than MCCPs (Cequier et al. 2014). The concentration levels found in the blanks in the present study where about the same for SCCPs and MCCPs (Table 2). Indoor sources for CPs are multiple because of their abundant use in household and industrial products, such as softener in plastic products (e.g. PVC), flame retardants, and construction materials (e.g. isolation windows) (van Mourik et al. 2016). Consequently, their abundant use in indoor products results in high contamination of these compounds in the blank samples.

Indoor air is also likely to be the main contamination source for the other compound groups included in Table 2. The compound groups included are semi-volatile, and as a result of this, they can be present in the gas phase. However, because of their hydrophobic and low water-soluble nature, these compounds can sorb to dust particles. Thus, deposition of small dust particles on laboratory equipment can also be a source of contamination. In indoor environments, all compound groups assessed in this study have been detected in house dust, and therefore, this can be a possible explanation for the contamination levels (Kjærvik & Rostock 2018). However, the relatively low spread of the compound-specific blank concentrations suggest that the contribution of particle-associated contamination was low (Table 2, standard deviations). The amount of dust affecting each sample would vary much more than the volume of air (gas phase) getting in contact with each sample during the sample preparation. Consequently, air is likely to be the main source of contamination during sample preparation.

4.1.2 Sample matrix effects

Matrix effects are one of the main challenges when analyzing trace organic compounds in complex soil matrices by GC-MS (Zuloaga et al. 2012). Matrix components were still present in the sample extracts even after the comprehensive clean-up procedures (see Materials and Methods, Figure 13). In the soil samples from this study, the main problem was co-extracted long-chain alkanes (waxes) from SOM. However, an evaluation of lock-mass signals can identify these matrix effects, and this can be used to evaluate the reliability of quantified concentrations (see Materials and Methods 3.5.1).

Assessment of the lock-mass signals for PCBs, PBDEs, and the DDT-group, revealed that there was in general low signal suppression ("drops" and/or "hops") at the analytes elution times (Figure 15). The signal suppression was categorized based on the size of the drop/hop, from low/slightly to badly affected. Evaluation of the PCBs' lock-mass signals showed generally no significant signal suppression for all congeners analyzed, but three samples (14 Ekkerøy, 53 Aremark, and 46 Vatnedalen) may be slightly affected by matrix effects due to a drop in signal response at the analytes elution times.

For the PBDEs, BDE-17 and 154 was considered slightly affected by matrix components in about half of the soil samples, and these may therefore be interpreted with caution. Some samples were also badly affected (53 Aremark, 30 Øvrevatn, and 38 Hummelfjell). For the congeners eluting after BDE-154 (e.g. 184, 197, 209) there was a good signal response. Σ_3HCH had overall good signal responses and therefore, the sensitivity and accuracy in the analysis and quantification is reliable. For the DDT-group, the lock-masses showed that about one third of the samples might be slightly affected by matrix effects. This effect was however considered relatively low with a signal response drop of less than 50%. It should be noted that this uncertainty affected o,p' DDT and DDE because carbon labeled internal standard were available for the other isomers, p,p'- DDT/E, and for DDD, only the o,p' -DDD was available (Appendix Table A.1.3).

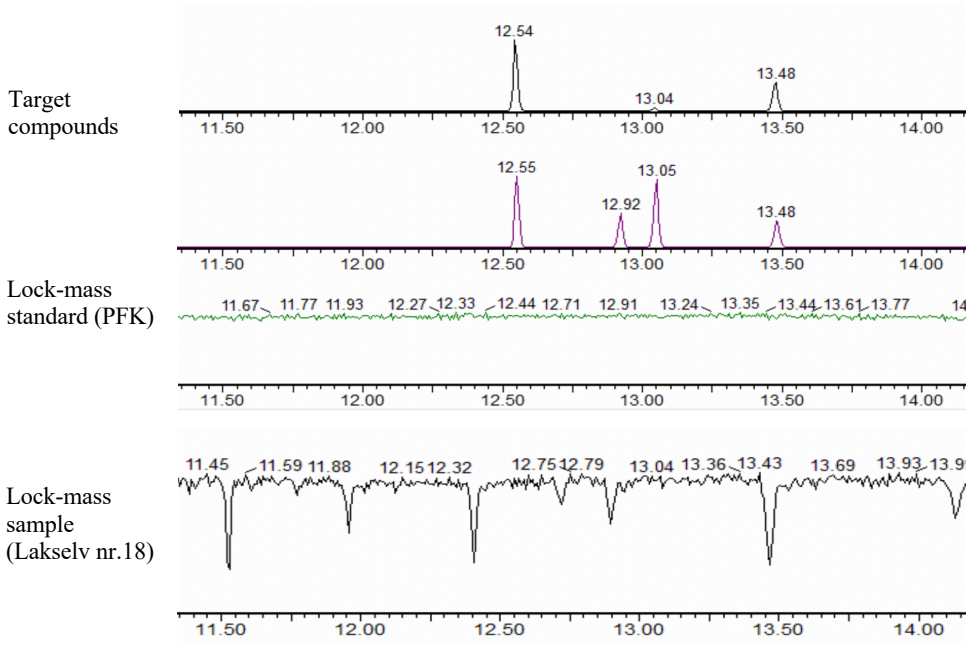

Figure 15: Example of drops in the lock-mass signal. This figure shows the constant, stable signal from the lock-mass standard (green), and the repetitive drops in the lock-mass signal from sample 18 Lakselv. These "pulses" of drops are caused by alkanes from the SOM. However, none of the drops are found at the elution times for the target compounds, and the quantification is consequently not affected in this sample.

4.1.3 Comments on field variability

Soil cores from individual study sites can differ in soil properties and contamination level. Soil environments are found to vary with respect to soil properties, such as SOM quantity and quality, microbial community, nutrients, and degree of bioturbation. In the sampling campaign in 2016, soils from 55 locations in Norway were sampled, with 5 cores at each site (see Materials and Methods 3.2). These samples represent each study area, but the variability of AOCs at each site can be large due to varying soil properties. This variation may occur over distances of just meters horizontally and few centimeters in soil depth (Kurt-Karakus et al. 2007). However, since 5 cores were sampled and assembled to one sample, this variability was assessed to some extent.

The variability at each study site was also partly assessed by determining the SOM content. SOM content characterizes the soil samples. This soil property was applied to correct for variation between study sites when reporting concentrations based on unit target compound per gram SOM (ng/g SOM). As a result of this, one soil property (SOM content) is taken into account in order to assess the variability when analyzing for AOCs. An approach to further assess the variability could have been to analyze all the soil cores taken from one site, and thereafter evaluating the variability between these cores. However, this approach would have spanned over the objectives of this study. In earlier studies, equal sampling campaign methods (Halse et al. 2015; Meijer et al. 2003; Ockenden et al. 2003) have been used and consequently, the study design applied appears adequate for the intentions of this study.

4.2 Overview of the results

Table 3. presents an overview of the results obtained in this study for the Norwegian background (n=45) and urban (n=10) soils, expressed as ng/g dw. Results considered invalid, either because of matrix related disturbances, instrumental recovery of less than 10%, or values below MDL, were excluded from the results' statistical summaries and processing. The result overview gives the terrestrial occurrence of the AOCs included in this study (see also Appendix B.2 Raw data, Table B.2.1 to B.2.8).

Table 3. Result overview reported as ng/g dw, for background (green) and urban soils.

Compound*	**Mean ± SD**	**Min – max**	**MDL**	**% samples >MDL**
Σ_{32}PCBs	2.8 ± 4.0	<MDL – 22	0.2	91%
	6.7 ± 4.7	0.5 – 15	0.2	100%
Σ_{7}PCBs	1.5 ± 2.3	<MDL – 13	0.07	93%
	3.8 ± 2.5	0.3 – 8.0	0.07	100%
PeCB	0.2 ± 0.1	<MDL – 0.6	0.2	76%
	0.4 ± 0.4	<MDL – 1.2	0.2	80%
HCB	1.3 ± 2.0	<MDL – 1.8	0.03	98%
	2.8 ± 5.5	0.1 – 16	0.03	100%
Σ_{6}DDx	3.6 ± 7.5	<MDL – 37	0.05	91%
	4.4 ± 7	0.05 – 21	0.05	100%
Σ_{3}HCH	1.5 ± 2.5	<MDL – 13	0.03	91%
	0.05 ± 0.03	<MDL – 0.1	0.03	80%
Σ_{25}PBDE	1.2 ± 2.6	<MDL - 125	1.3	20%
	150 ± 460	<MDL - 1500	1.3	60%
Σ_{5} PBDE	0.4 ± 0.7	<MDL – 7.2	0.5	18%
	0.5 ± 0.4	<MDL – 1.2	0.5	40%
Σ_{15}NBFRs	0.9 ± 1.5	<MDL – 5.3	4.2	81%
	0.8 ± 0.6	<MDL – 1.7	4.2	100%
$\Sigma_{syn\&anti}$DP	2.4 ± 6.0	<MDL – 29	0.4	50%
	1.1 ± 1.2	<MDL - 3.6	0.4	70%

$\Sigma_{10.5\text{-}13.9}$SCCPs	15 ± 16	<MDL - 65	44	24%
	510 ± 1500	<MDL – 4,700	44	60%
$\Sigma_{14.5\text{-}17.7}$MCCPs	67 ± 47	<MDL – 167	55	47%
	87 ± 95	<MDL - 150	55	50%

* *see text under Table.2.*

The number of samples with values >MDL for the different AOCs varied (Table 3). MDL is calculated from the blank samples, and if there is a relatively high contamination in the blanks, the MDL will be larger (see Materials and Methods 3.6.2). Background sites have generally low concentration levels and are therefore sensitive to high blank levels. From Table 2, PBDEs, NBFRs, and CPs, are the compound groups with highest contamination. As an effect of this, the number of samples >MDL are found to be lowest for these groups. Consequently, samples >MDL vary between AOC-groups because of their concentration levels in the terrestrial environments and the blank sample levels.

From the result overview it can be seen that legacy POPs, such as PCBs and PBDEs, are present in Norwegian terrestrial ecosystems. The findings of regulated and restricted legacy POPs highlight their environmental persistency, and that today (2019), there might still be sources contributing to their appearance in the environment (e.g. construction materials with PCBs, household- and industrial products with PBDEs flame retardants, waste sites). Global values of PCBs in background soils are found to be about 5.4ng/g dw on average, with the highest levels in central Europe (France, Germany, Poland), and also with increased concentrations at higher latitudes (>50^0 N) and higher SOM content (Meijer et al. 2003) (Table 4). When comparing these values to the values obtained in this study, it is suggested that Norwegian background soils have a lower burden of PCBs than the global environment. From the same global study, the concentration of HCB was found to be 0.7 on average. This is below the level found in Norway. A possible explanation for this can be related to HCB's volatility and LRAT-potential, contributing to an accumulation at higher latitudes (see Background 2.1.2, and 2.3: Figure 8). In a study from UK and Norwegian background soils, PBDE levels were found to be generally higher in UK soils (Hassanin et al. 2004). These findings for PCBs and PBDEs can be linked to proximity to source regions and LRAT potential. Consequently, the legacy POPs included in this study are found in Norwegian terrestrial ecosystems, but with a lower occurrence than in

central Europe and the global environment, which most probably is due to distance from the sources (see also Background 2.2, Figure 8).

Newly and non-regulated AOCs are occurring in Norwegian terrestrial ecosystems. The detection of AOCs in background and urban soils indicates that these predicted hazardous chemicals are transported with air from source areas (e.g. urban and populated areas in Norway, and industrial areas in central Europe and beyond), and are thereafter deposited in terrestrial ecosystems. DPs, an AOC with increased scientific attention (see Background 2.1.4), was detected in relatively high amounts (2.4 ng/g dw in the background soils). This may be related to the replacement of PBDEs with $DP_{syn\&anti}$ as flame retardants in products, such as electronic equipment. The suggested justification for DP's presence in the Norwegian soils can also be applicable for NBFRs. Consequently, newly and non-regulated AOCs of emerging concern, and also legacy POPs, are present in Norwegian terrestrial ecosystems at varying concentration levels (Figure 16).

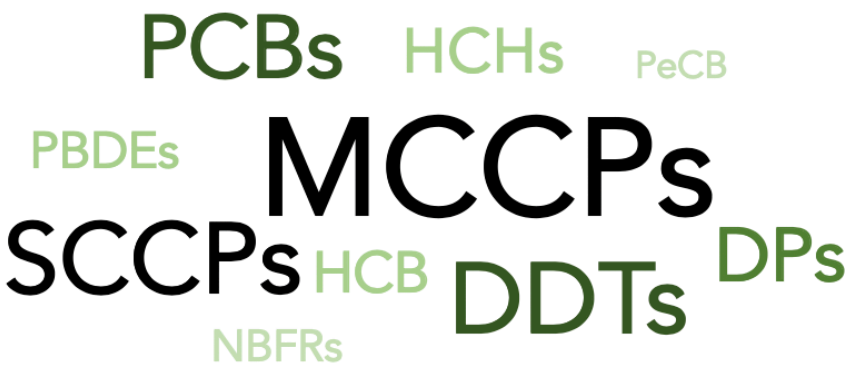

Figure 16: Illustration of the relative contribution of AOC-groups included in this study for the background soils. Size and color of the compound group name represent their contribution, where SCCPs are found in highest level, followed by DDTs, PCBs, and DPs. The remaining compound groups are found in lower amounts. Accurate concentration levels are reported in Table 3.

The newly regulated SCCPs (SC on POPs in 2018), as well as the non-regulated MCCPs, were found in high amounts relative to the other compound groups in the background and urban soils. The concentrations of MCCPs was further much higher than those of SCCPs (67 and 15 ng/g dw in background soils, respectively). This can be linked to their numerous application areas, and the replacement of SCCPs with MCCPs (see Background 2.1.5), and thus they are abundant in environments. In Chinese background soils, the average concentration of sum SCCPs and MCCPs was found to be 62 ng/g dw (min-max 0.42-420) (van Mourik et al. 2016). This value

is lower compared to the Norwegian background soils, ~80 ng/g dw (min-max <MDL – 170) $\Sigma_{10,5\text{-}17,7}$CPs, and this indicates that Norway have a relatively high burden of CPs compared to Chinese background soils. However, the range (min-max) for the Chinese soils is wider and it may indicate an even higher variability than the soils from Norway. In background soils from the UK, the level of SCCPs was found to be 50 ng SCCPs/g SOM (Halse et al. 2015), which is higher than the background soils assessed in this study (~25ng SCCPs /g SOM) (Table 4). This can be related to their proximity to sources, where many of the Norwegian sampling sites are situated relatively far away from heavily industrialized areas in central Europe, America, and Asia. Consequently, CPs are occurring in relatively high amounts in Norwegian terrestrial ecosystems compared to other AOCs studied, but still at lower concentrations than in background soils closer to European source areas (e.g. UK) (see also Background 2.2, Figure 8).

Table 4. Comparison of concentration levels for some of the assessed AOCs in this study. Reported as ng/g dw with mean ± standard deviation and range, where this information was available.

Compound	This study	Other studies*
PCBs	2.8 ± 4.0 <MDL – 22	5.4 0.02 – 96.9
HCB	1.3 ± 2.0 <MDL – 1.8	0.7 0.01 – 5.2
DDTs	3.7 ± 7.5 <MDL - 37	71 ± 160 0.9 - 700
HCHs	1.5 ± 2.5 <MDL - 13	9.5 ± 11 0.3 - 40
Σ_5PBDEs	0.4 ± 0.7 <MDL – 7.2	1.2 0.2 – 5.1
DPs	2.4 ± 6 <MDL - 29	>3,000
SCCPs**	25 ± 20 <MDL - 120	50 ± 115 <0.8 - 570

**PCBs and HCB: Global review (Meijer et al. 2003), DDTs and HCHs: China, surface soil in an agricultural area (Zhang et al. 2011), PBDEs: Wooded area in France (2008) (McGrath et al. 2017), DPs: e-waste sites in Asia (Wang et al. 2016), and SCCPs: UK background soils (Halse et al. 2015).*

*** ng/g SOM*

The occurrence of AOCs in Norwegian background and urban soils are up to 1,000 times lower than those found at dumping sites in Asia (Table 4) and Africa. In Asian developing countries (e.g. Cambodia, Vietnam) the average concentrations of PCBs and DDTs at dumping sites were found to be around 100 ng/g dw each (Minh et al. 2006). This is more than fifty times higher than the concentrations observed in the Norwegian background soils. Compared to the concentration levels for DPs found in Chinese electronic (e-) waste recycling site (>3,000 ng/g dw)(Wang et al. 2016), concentrations in the Norwegian background soils were roughly 1,000 times lower. From an e-waste recycling site in Africa, Ghana, the concentration of Σ_5PBDEs was found to be around 50 ng/g dw (Akortia et al. 2017), and even higher levels have been reported for similar sites in China (>1,000 ng/g dw) (McGrath et al. 2017). Differences may be expected due to differences in soil types but the influence on e-waste is likely to dominate in these examples. However, this highlights the variability of AOCs' occurrence in terrestrial environments, and that distance from sources and land use impacts on the overall burden of these contaminants.

According to the Norwegian guidelines on environmental quality classification for soil, the Norwegian background and urban soils assessed are of good quality and there are no human health risks expected at these levels (Environmental Agency Norway 2009). From Norwegian soil contamination state of condition classes, Σ_7PCBs <10 ng/g dw, <40 ng/g dw for DDT, <80 ng/g dw BDE-99 and <2 ng/g BDE-209$_7$ is referred to as a very good environmental status and represents the threshold for clean soil. For the non-regulated compound groups (e.g. DPs, NBFRs, MCCPs), such threshold values have not been established yet (2019). From the result overview (Table 3), the compound groups with established threshold values fell with large margin within the class of clean soil. The threshold for hazardous waste for PBDEs and CPs is 2 500,000 ng/g, and 50,000 ng/g for PCBs. The results found in the soils are expected to be far from hazardous for our health. However, it is important to have in mind that even though the Norwegian soils are of good environmental status for our health, other organisms (e.g. earthworms) may ingest much more soil than humans, and consequently be more exposed. Therefore, it is alarming that these compounds are present in terrestrial environments, and that they may accumulate over time and thus creating a possible vulnerable situation for terrestrial ecosystems because of their toxicity.

Where quantifiable, soils from background sites had close to one order of magnitude lower concentrations compared to the urban sites (Table 3). Urban and background concentration levels were found to be significantly different ($p<0.05$) from each other on average even when taking only samples >MDL into account. The compound groups' mean values with standard deviations, and ranges (min-max) reported gives an indication of the high variation in the data. Potential factors contributing to this variation, such as their association with site variables (e.g. SOM content and latitude), distance from source regions, and environmental factors (e.g. temperature, precipitation) are assessed in the following sections. This is done to provide potential explanations for the variation seen in the results and to discuss the environmental behavior of AOCs in terrestrial ecosystems. Prior to this assessment, the results were transformed to a logarithmic scale ($\log_{10}$) before further processing. This was done because of the high variation in AOCs' concentration levels and non-normally distributed, righted tailed data set (Appendix B.2.1).

4.3 Association of AOCs with soil organic matter (SOM)

In the type of environment assessed (i.e soils), most of the AOCs' concentrations have been found to be linked to the SOM (Meijer et al. 2002; Meijer et al. 2003). Apart from this association, other factors may affect the concentrations, and these might actually provide more information on the environmental fate and behavior. However, such factors may be difficult to investigate if they are covered by the SOM effect. Therefore, evidence for an influence of soil organic matter (SOM) content on AOCs was assessed to see if there actually is a relationship. If so, this will be accounted for by normalizing the concentrations based on SOM to identify other factors that may affect the AOCs' environmental fate and behavior.

The relationship was investigated between analyte concentrations and the fraction of SOM relative to the soil dry weight. This approach provides information on AOCs sorption and partitioning to SOM, which is linked to their physicochemical properties (see Background 2.3, Figure 9). This can further be linked to the retention and storage capacity of soils, and consequently, the potential of AOCs to re-volatilize from soil to air (Cabrerizo, A. et al. 2011).

SOM, determined by loss-on-ignition, and characterizing the soil, showed that there was a wide variation in SOM content for the whole sample set (Figure 17). SOM varied from 4% to 98%, showing no clear north-to-south trend, i.e. both low and high SOM contents were found along the entire north-to-south gradient in Norway.

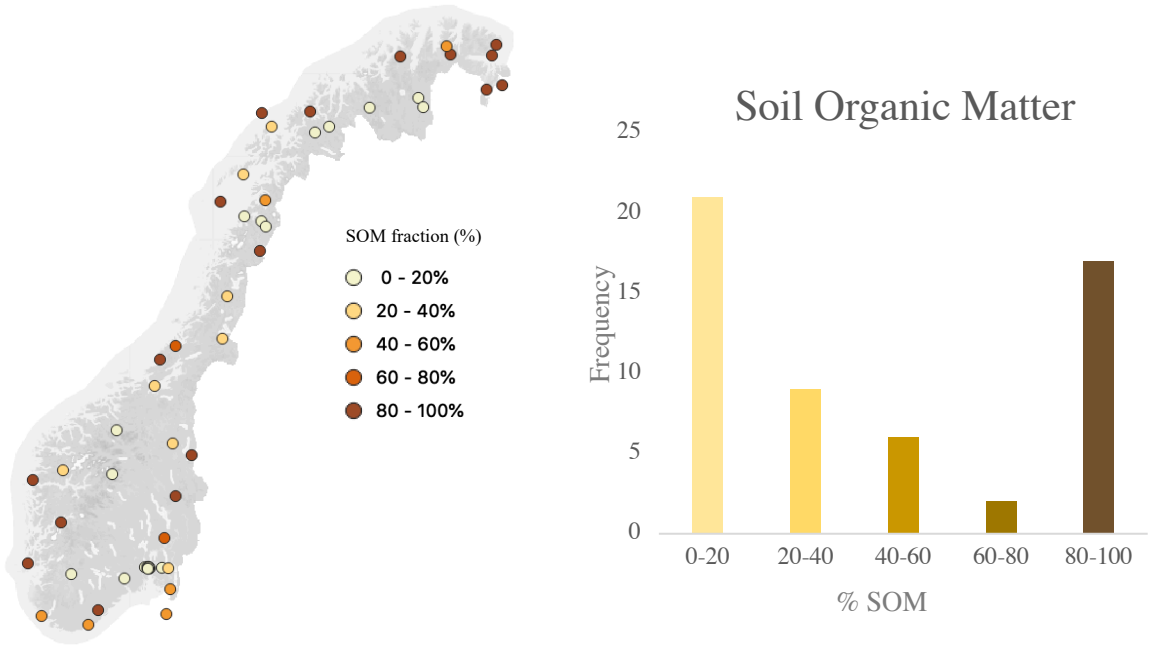

Figure 17: Distribution of SOM content for all soil samples included in this study, were x-axis is % SOM content intervals, and y-axis is the soil sample frequency within the intervals. The majority of the soil samples with 0-20% SOM were from the Oslo area urban soils. The number of samples with 80-100% SOM make up about 30% of all samples.

For investigating the relationship between concentration levels and SOM, correlation analysis for the compound groups of interest and the fraction of SOM was applied. This analysis can be used to study and explain the environmental behavior and fate of AOCs (see Background 2.3).

4.3.1 Relationship between AOC concentration levels and SOM

The relationship between the concentration of AOCs and the fraction of SOM was plotted and tested through a statistical correlation analysis for the background sites (Figure 18 to 24). This approach revealed in general a strong positive correlation between the concentration levels of AOCs and the SOM fraction ($r>0.3$, $p<0.05$) (see Appendix B.3.3). The strongest association was found for dechlorane plus ($DP_{syn\&anti}$), with $r>0.8$ and $p<0.001$ (Figure 24), and the weakest for NBFRs and CPs ($r\sim0.3$ and $p<0.05$) (Figure 22 and 23). These findings are also supported by results from linear regression analysis, where the increase in concentration per fraction of SOM was strongest for $DP_{syn\&anti}$ ($y=0.013x+2.1$, $p<0.001$), and weakest for CPs ($y=0.004x+3.3$, $p<0.05$).

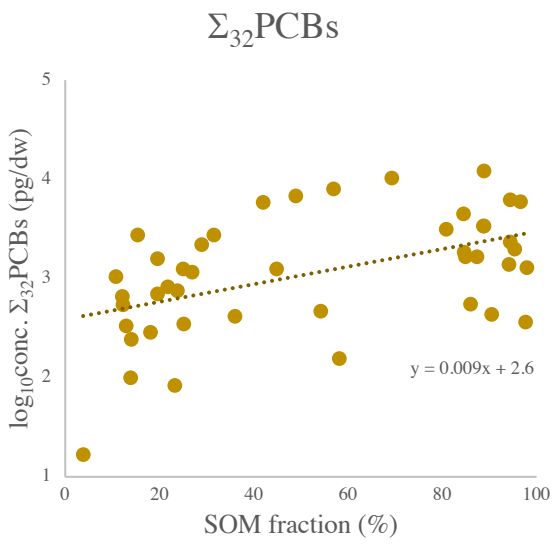

Figure 18: The relationship of Σ_{32}PCBs with SOM content in n=44 soil samples. The strength of linear relationship through correlation test was found to be r=0.5 and p<0.001.

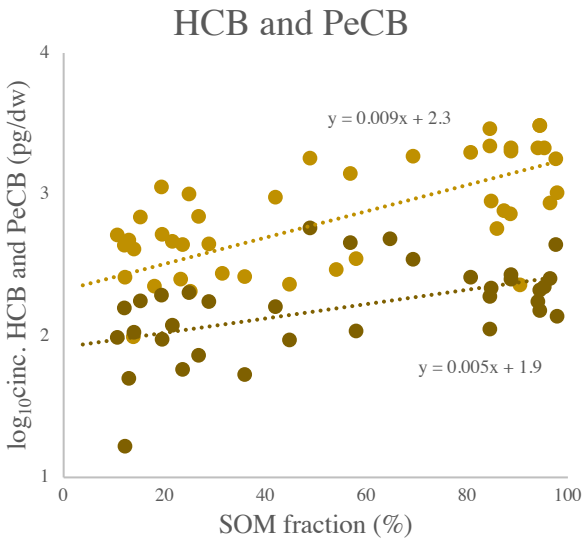

Figure 19: The relationship of HCB (top dots and line) and PeCB (lowest dots and line) with SOM content. The strength of linear relationship was found to be 0.6 and 0.5 for HCB and PeCB respectively (p<0.05). This figure also show that HCB has a higher concentration level than PeCB.

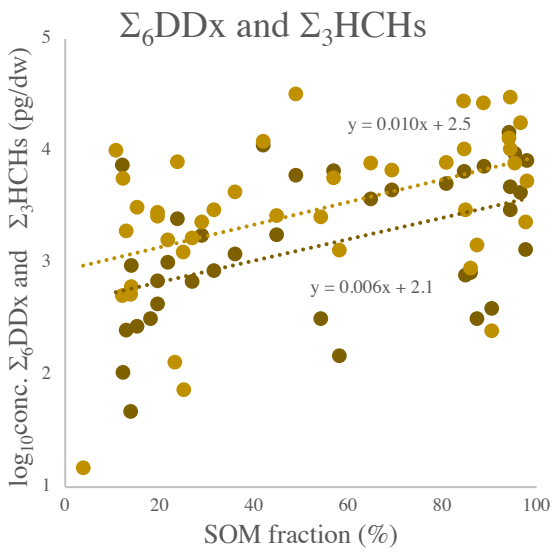

Figure 20: The relationship of Σ_6DDx (upper dots and line) and Σ_3HCHs (lower dots and line) with SOM content in n=42 and 40 soil samples, respectively. The strength of linear relationship through correlation test was found to be r=0.5 and 0.3 (p<0.05), respectively.

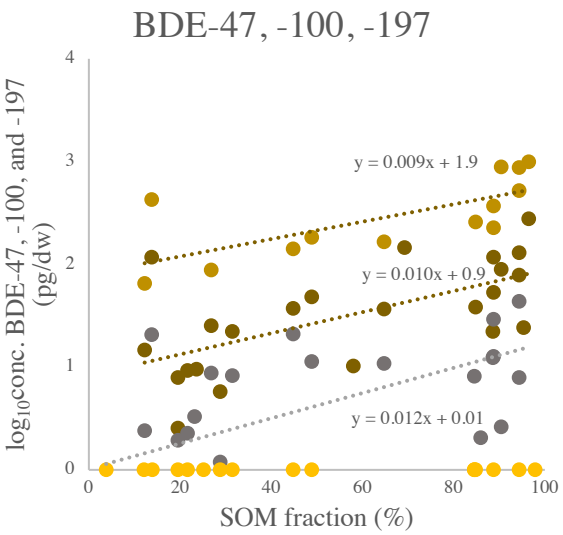

Figure 21: The relationship of selected indicator PBDE-congeners: from top to bottom dots and line: BDE-47, -100, and -197. The orange dots represent the values <MDL, where there is a higher frequency of these samples at lower SOM content. The strength of linear relationship through correlation test was found to be r=~0.6 (p<0.05) for all congeners assessed. This figure also show that the concentration of PBDE-congeners decreases from BDE-47 to -197.

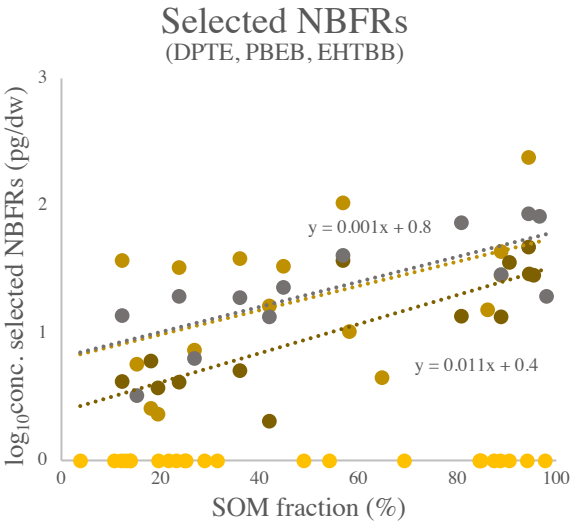

Figure 22: The relationship of selected NBFRs: from top to bottom dots and line: DPTE, EHTBB, and PBEB. The orange dots represent the values <MDL, where there is a slightly higher frequency of these samples at lower SOM content. The strength of linear relationship through correlation test was found to be 0.3 (p<0.05).

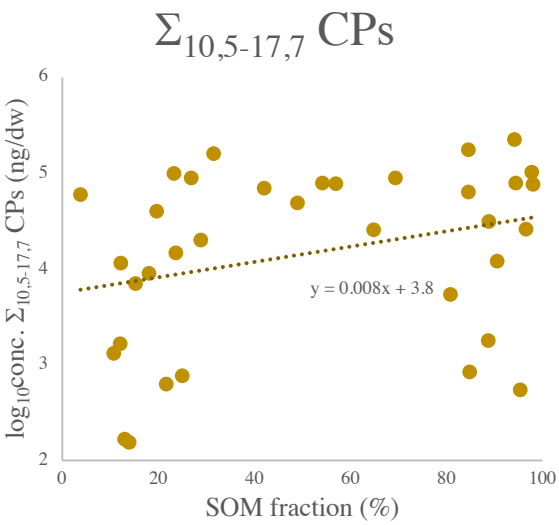

Figure 23: The relationship of $\Sigma_{10,5\text{-}17,7}$CPs with SOM content. The strength of linear relationship was found to be significant for SCCPs separately (r=0.3, p<0.05), but not for MCCPs (r=0.2 and p>0.05).

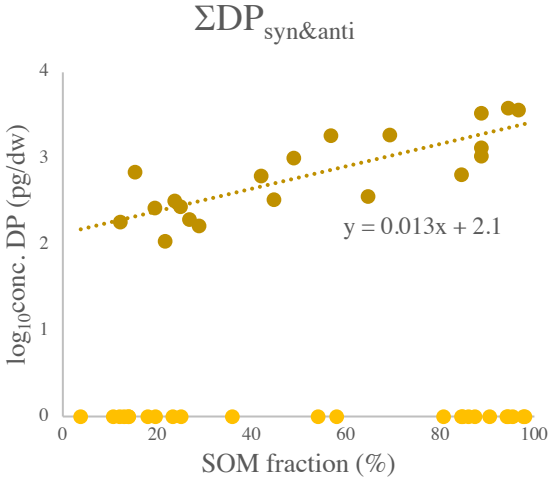

Figure 24: The relationship of $\Sigma DP_{syn\&anti}$ with SOM content. The orange dots represent the values <MDL, where there is a nearly equal amount at low and high SOM content. The few samples <MDL observed at mid-SOM content could be related to the few samples with this SOM content (Figure 17). The strength of linear relationship was found to be r=0.8 and p<0.001.

The strong relationships found between concentration of AOCs and the SOM fraction (Figure 18 to 24), suggest that these compounds are mainly associated with the SOM fraction in soil environments. The mechanism behind this is related to the compounds' physicochemical properties, such as their lipophilicity and low-water solubility. The strong relationship seen for the legacy POPs (PCBs, DDTs, HCHs, HCB, and PBDEs), and also the new POP-like compound DPs, can be attributed to their high $\log K_{OA}$ and low $\log K_{AW}$ (see Background 2.3, Figure 9). The weak relationship found for CPs can be caused by the complexity of the group (see Background 2.1.5, and Materials and Methods 3.5.1), and the resulting large range of $\log K_{OA}$ and $\log K_{AW}$ values. SOM is therefore an important factor influencing the concentration levels of AOCs in soils. The burden of AOCs can therefore be expected to be larger in SOM-rich soils. This agrees with earlier studies and has been explained with the role of terrestrial vegetation as a scavenger of AOCs from the air (Moeckel et al. 2008; Ockenden et al. 2003) (see also Background 2.3, and Materials and Methods 3.2).

The Norwegian terrestrial ecosystems included in this study are hemi-boreal, boreal and polar, where these ecosystems may have an effect on the burden of AOCs. These ecosystems are characterized with generally high carbon stocks and climatic factors limiting biotic- and soil formation processes (Holten & Carey 1992). The rate of these processes differs along the Norwegian latitudinal gradient, where the north of Norway may be even more limited than in the south due to lower temperatures (Figure 32). This affect the age of the SOM, where northern soils have a slower vegetation growth and degradation compared to the south, resulting in an older SOM (Brady & Weil 2010a; Brady & Weil 2010b). The burden of AOCs can be affected by this because historical emissions can be present in surface soils over a longer time period in older SOM. Consequently, aged SOM in the most northern soils might have a higher AOC-burden. This is further discussed in the factors influencing the spatial distribution (4.5) and the air to soil exchange assessment (4.7.2).

The characteristics of the terrestrial ecosystems included creates a suitable environment for sorption and storage of AOCs. The sorption of AOCs to SOM is driven by the chemical nature of these compounds, such as their hydrophobicity and low water-solubility, and environmental factors favoring deposition (e.g. low temperatures, vegetation available to scavenge AOCs from the air). These factors influence the burden of AOCs in these northern soils, where AOCs are deposited, retained, and possibly stored over many decades. The association of AOCs with SOM can be compared with the bioaccumulation of these compounds (see Background 2), for example in fat-rich aquatic organisms (e.g. tuna, salmon) where they are stored and accumulated over time. The globally emitted AOCs may be long-range transported to northern terrestrial ecosystems, where they may deposit at surfaces, such as living vegetation and thereafter deposited and accumulated on soil surfaces, due to environmental factors (e.g. temperature) limiting further transport and/ or degradation. This, in combination with the factors suggested above, gives adequate conditions for AOC-accumulation and storage in the terrestrial ecosystems found in Norway.

4.4 Spatial distribution of AOCs from south to north in Norway

In order to illustrate the spatial distribution of the AOCs included in this study, concentration levels from the background and urban sites were mapped along the Norwegian latitudinal gradient (Figure 25a to 32a). Possible relationships between latitude and AOC concentration levels were assessed, providing information about the compound's atmospheric transport potential. In this assessment, only the background soils were included in the statistical analysis (Figure 25&26b, 27&28, and 29b-32b). The reason for this approach is that the background sites are assumed to be distant from small-scale local sources and AOCs are expected to have undergone atmospheric transport from large-scale source regions, for instance Central Europe. This assessment of AOCs' spatial distribution in background sites can therefore provide information on, and evidence, of possible environmental behaviors in relation to latitude-depending factors, such as temperature, precipitation, population density and influence of source regions. This will allow to identify possible factors that may contribute to the variability seen in the results overview (Table 3).

The results are reported as mass unit AOC per mass unit SOM in this spatial distribution assessment because of the findings presented in section 4.3. It was found that AOCs are mainly associated with the SOM fraction in soil environments and that the soils' SOM content therefore explain some of the variability of the AOC concentrations. Consequently, accounting for this by using AOC concentration levels on a per unit SOM basis, allows to study the effect of other parameters. The concentration levels were further converted to a logarithmic scale, $\log_{10}$ pg/g SOM, because of the large disparities in concentration levels and their right tailed density distributions (Appendix B.2.1). As a result of this, the data was normalized and statistical analysis that require normal distribution, such as the Pearson correlation test and two sample t-test, could be applied. To study differences between ecosystems in the southern and northern of Norway, a fictive line was drawn at 66° N, where <66° N is referred to as south, and >66° N as north. This separation was chosen because of the Nordic Polar circle at 66° N, where the area above this latitude is defined as the Artic (Tjernshaugen 2018). The well-studied legacy POP, PCBs, are initially presented in this section, followed by OC-pesticides, novel and historical BFRs, DPs, and CPs.

4.4.1 The spatial distribution of polychlorinated biphenyls (PCBs)

The concentrations of PCBs in Norwegian soils show a trend decreasing from south to north (Figure 25). The PCB concentrations were highly variable, ranging from around 2 to 5 $\log_{10}$ pg/g SOM, with highest concentrations found in the urban soils. The mapping of PCB-concentrations in Norway illustrates that there is a higher frequency of high concentrations (darker dots, 3.5-5.0 $\log_{10}$ pg/g SOM) in the south of Norway compared to higher latitudes, with some of these dark dots representing the urban sites in, or close to Oslo. The difference between south (<66°N) and north (>66°N) concentration levels in the background soils was found to be significant ($p<0.01$) (see Appendix B.3.2), and there is a strong association between concentration level and latitude ($r= -0.5$ and $p<0.001$) (Figure 25b) (see Appendix B.3.4). This implies that there is a decreasing presence of PCBs in background soils with increasing latitude.

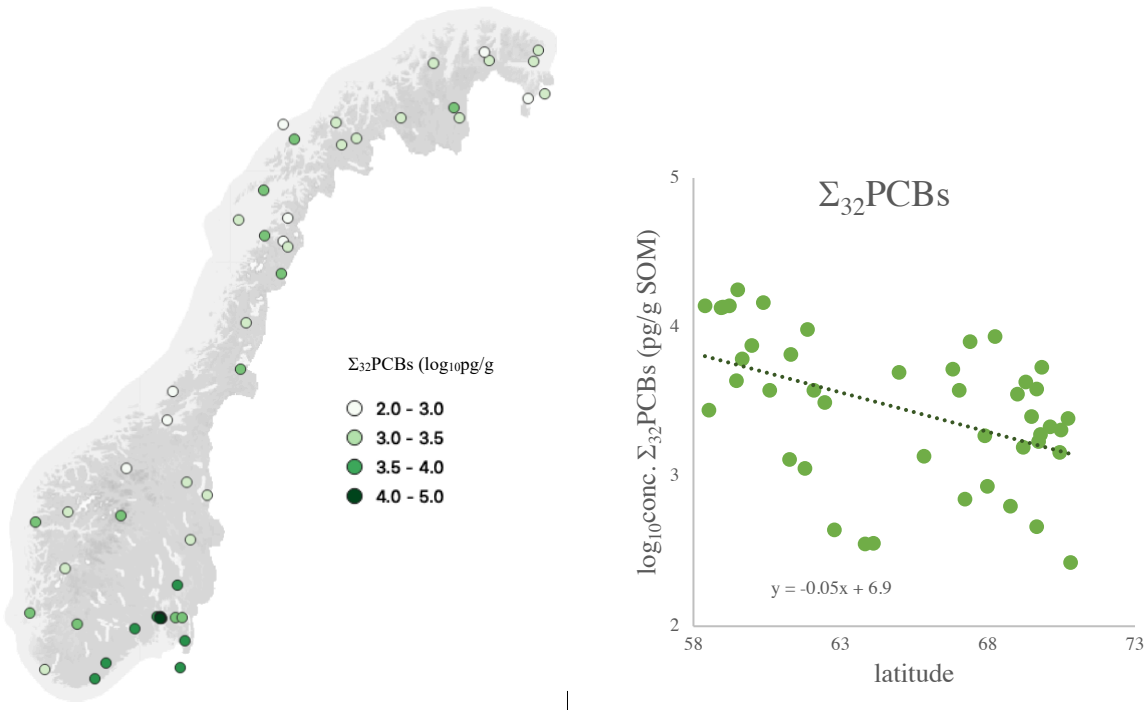

Figure 25: a) Map of concentration levels of the PCBs in Norwegian background and urban soils (left). b) Plot graph of background soils on the right side with a trend line. For both a) and b), all 32 congeners of PCBs analyzed are included.

The spatial distribution of individual PCB-homologue groups (tri- to octa-PCBs) is assessed in section 4.6. This is done to study differences in physicochemical properties (e.g. volatility, hydrophobicity) for the PCB-homologue groups.

4.4.2 The spatial distribution of organochlorine (OC) pesticides

Σ_6DDx' spatial distribution shows a decreasing concentration trend with increasing latitude (Figure 26). For Σ_6DDx, the concentrations varied from approx. 2 to 5 $\log_{10}$ pg/g SOM. The color gradient from light- to dark green, representing concentration levels from low to high, shows a higher abundance of lighter dots in the north of Norway compared to the south. This difference between south and north of Norway was found to be statistically significant ($p<0.01$) (see Appendix B.3.2), and there is a substantial association between latitude and concentration levels ($r=-0.4$, $p<0.01$) (Figure 26b) (see Appendix B.3.4). Consequently, there is a decreasing abundance of DDT and their metabolites with increasing latitude.

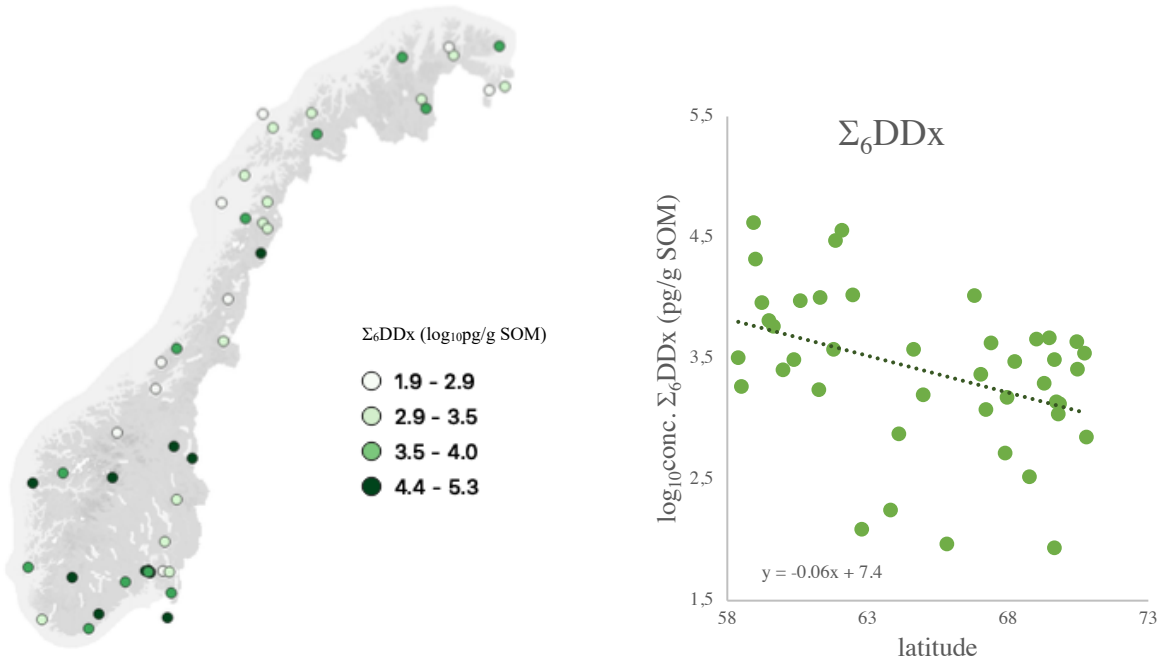

Figure 26: a) Map of concentration levels of DDTs and its metabolites, DDE and DDD, in Norwegian background and urban soils (left). b) Plot graph of background soils on the right side with a trend line. For both a) and b), Σ_6DDx analyzed are included.

The contribution of the individual DDTs and their metabolites in the concentration levels found is assessed in section 4.6.3.1 to provide information on environmental processes.

The occurrence and trend for the sum of DDTs and their metabolites is similar to the distribution seen for the PCBs (Figure 25). The concentration levels for these two legacy POP-groups (PCBs and DDTs) are similar (2-5 $\log_{10}$pg/SOM), but the highest concentration level (darkest green dot) is more abundant for Σ_6DDx. The similar spatial trend observed for PCBs and DDTs may be related to similar environmental behavior. This suggestion is assessed in section 4.6.

For HCHs, the relationship between concentration level and latitude was very weak for β- and γ-HCH (r=-0.1), and no relationship was found for α-HCH (Figure 27). The lack of trend for HCHs with latitude can indicate that they travel quite easily and are consequently relatively homogenously distributed in the atmosphere. The weak, negative relationship for β-HCHs can be caused by its somewhat lower volatility compared to the γ- and α-HCH (Willett et al. 1998), possibly resulting in a slightly lower atmospheric transport potential of β-HCHs compared to the other two HCH isomers. However, the ratio between γ- and α-HCH revealed a clear spatial trend, and this is assessed in section 4.6.

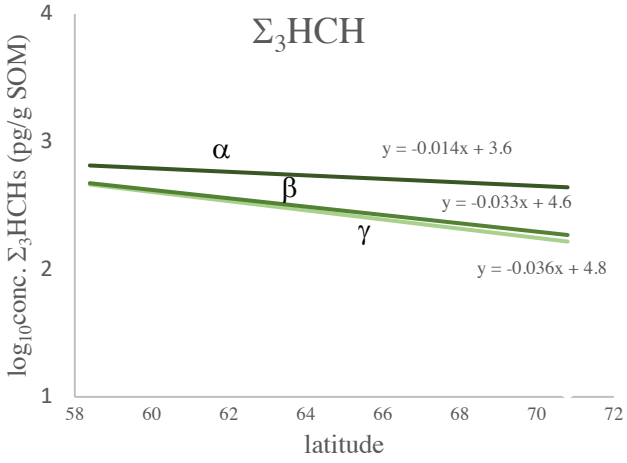

Figure 27: The concentration of the HCHs (α, β, and γ) in Norwegian background soils.

The PeCB and HCB concentrations showed no strong relationship to latitude (r=-0.1 and r=0.2 respectively) (Figure 28). Here, the concentration levels were nearly similar along the Norwegian latitudinal gradient, i.e. no relationship between HCB and PeCB with latitude was found in this study. Both HCB and PeCB are highly mobile in the atmosphere and as a result of this, they are relatively easily and homogenously distributed in the atmosphere compared to other compounds, such as DDTs and DPs (Barber et al. 2005). HCB was the only compound studied that shows a weak positive relationship with latitude, indicating a possible increase from south to north, which is expected according to HCB's volatile nature (see Background 2.1.2, and 2.3, Figure 9). However, at higher latitudes with lower temperatures (Figure 34), the vapor pressure of HCB decreases, and deposition to surfaces is expected to be enhanced. Therefore, higher soil concentrations are likely to occur in colder regions. Earlier global studies on HCB have shown that the concentration is clearly increasing towards the Northern Hemisphere (Meijer et al. 2003), but within the limited latitudes assessed in this study (59-71^{0}N), this is not statistically significant.

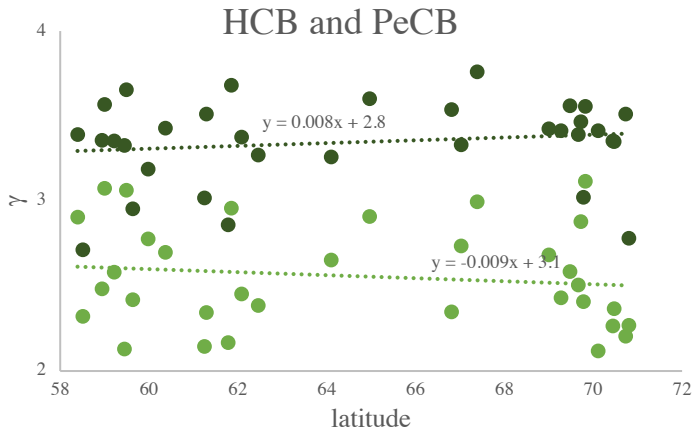

Figure 28: The concentration of HCB (dark green) and PeCB (light green) in Norwegian background soils. This figure also illustrates that the concentration levels for HCB is higher than for PeCB.

4.4.3 The spatial distribution of brominated flame retardants (PBDEs and NBFRs)

The spatial distribution of PBDEs and NBFRs from south to north in Norway (Figure 29 and 30) indicates a decreasing presence of these compounds with increasing latitude. Sites with concentrations <MDL are spread all over the latitudinal gradient, but with a greater occurrence at higher latitudes. This can imply that the concentration levels in the northern regions are lower than in the southern, which would be consistent with the trend found in earlier studies (Hassanin et al. 2004). From the correlation analysis, the relationship between latitude and Σ_{25}PBDEs concentration (>MDL) was not found to be statistically significant ($p>0.05$), but with a negative correlation of -0.3. However, for NBFRs, the correlation was significant ($p<0.05$ and $r=-0.4$) (see Appendix B.3.4). The difference between south and north was not significant ($p>0.05$) for any of the groups.

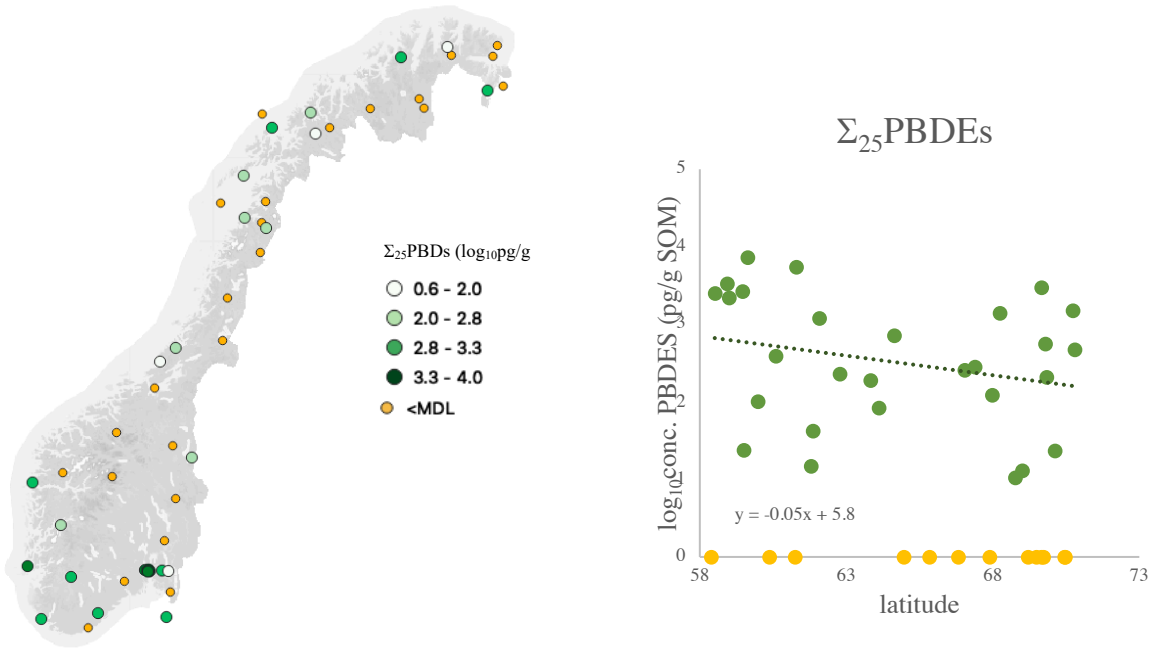

Figure 29: a) Map of concentration levels of the PBDEs in Norwegian background and urban soils (left). b) Plot graph of background soils on the right side with a trend line. For both a) and b), all 25 congeners of the PBDEs analyzed are included.

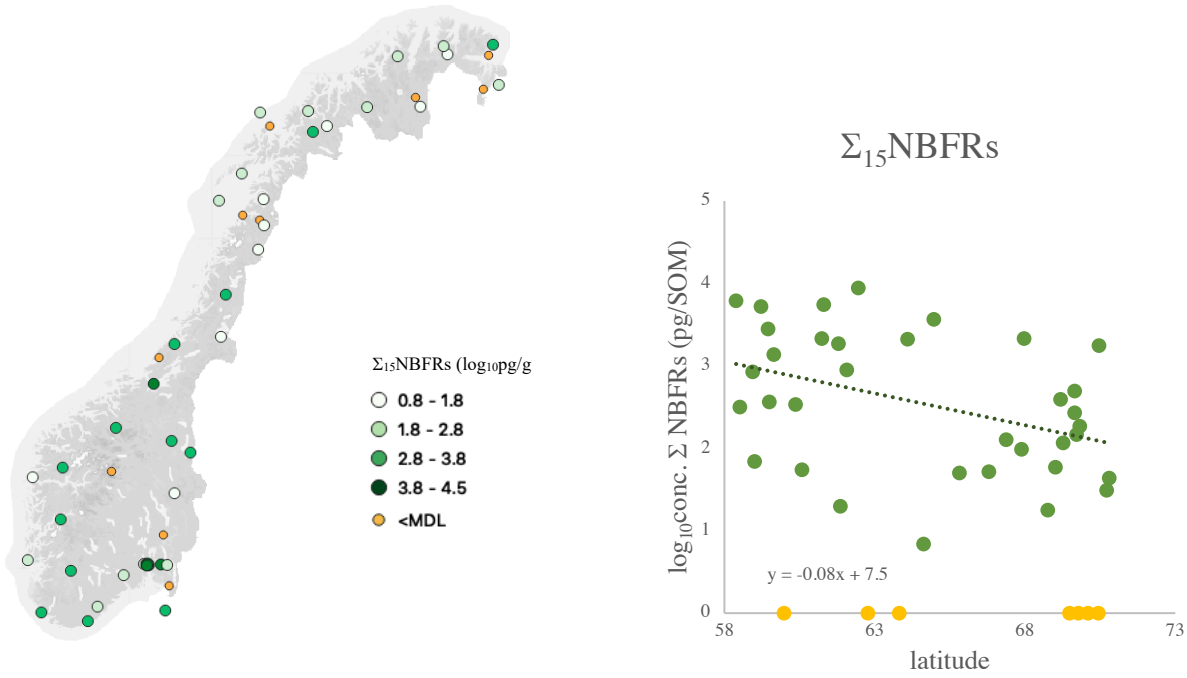

Figure 30: a) Map of concentration levels of NBFRs in Norwegian background and urban soils (left). b) Plot graph of background soils on the right side with a trend line. For both a) and b), all the 15 NBFRs compounds analyzed are included.

4.4.4 The spatial distribution of dechlorane plus (DPs)

In Norway, dechlorane plus show a decreasing presence of these compounds with increasing latitude (Figure 31). The difference between the south and north was found to be significant ($p<<0.001$), and there was a clear relationship between latitude and concentration level for DPs ($r=-0.5$, $p<0.05$) (Figure 31b) (see also Appendix B.3.2&4). The number of samples <MDL have a clear higher frequency at norther latitudes, indicating that DPs were not present at quantifiable levels in many of the soils from such latitudes. However, DPs have been detected in Artic regions, showing that LRAT is occurring (Wang et al. 2016).

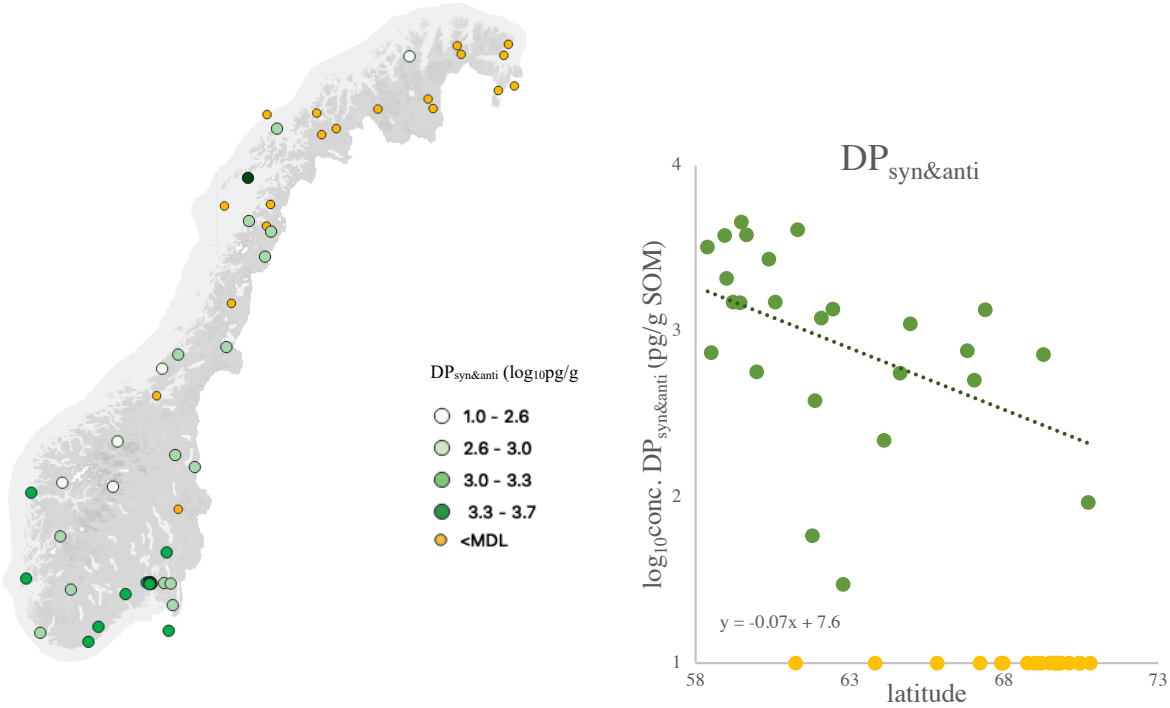

Figure 31: a) Map of concentration levels of DPs in Norwegian background and urban soils (left). b) Plot graph of background soils on the right side with a trend line.

The physicochemical properties of DPs (high K_{OA}, low volatility and water solubility) limit their atmospheric transport (Wang et al. 2016). This is supported by their spatial distribution found in the present study. Deposition to soil- and vegetation surfaces is likely to dominate their environmental fate. After deposition, these compounds will most likely not re-volatilize and act as secondary sources because of their strong hydrophobic and low volatile properties (see Background 2.3, Figure 9). This is also in accordance with the strong relationship found between DP-concentrations and SOM content (see Results and Discussion 4.3, Figure 24).

4.4.5 The spatial distribution of chlorinated paraffins (CPs)

The distribution of $\Sigma_{10,5\text{-}17,7}$CPs in Norwegian background soils shows both a decreasing and slightly increasing trend from south to north (Figure 32). The relationship of CPs with latitude was found to be significant and negative for SCCPs ($r=-0.4$, $p<0.05$) (see Appendix B.3.4). However, for MCCPs, a slight increase with latitude was found, but this was not significant ($r=0.3$, $p>0.05$). The difference between the south and north for CPs was found to be significant for SCCPs ($p<0.05$), but not for MCCPs ($p>0.05$). The concentrations of MCCPs in the soil samples are higher than those of SCCPs. This differs from levels found in indoor environments (see Results and Discussions 4.1), where SCCPs>MCCPs, but not for outdoor environments (see Background 2.1.5). The volatility of these compounds decreases with higher chlorination degree and carbon chain length, and as a result of this, sorption to surfaces, such as soil, vegetation, and dust particles, may increase accordingly. This should result in a lower atmospheric mobility of MCCPs compared to SCCPs. From the trend found, this is however not consistent, and the findings indicate that MCCPs have a stronger atmospheric mobility compared to SCCPs. However, there is a higher frequency of values <MDL for MCCPs at northern latitudes compared to the south. How to interpret these findings for MCCPs is today (2019) difficult because knowledge on CPs' environmental behavior is spars and further research is required, and more robust data processing. Analysis and data processing for CPs is complicated and the uncertainty of these results is higher than for all the other compound groups analyzed (see Materials and Methods 3.5.1).

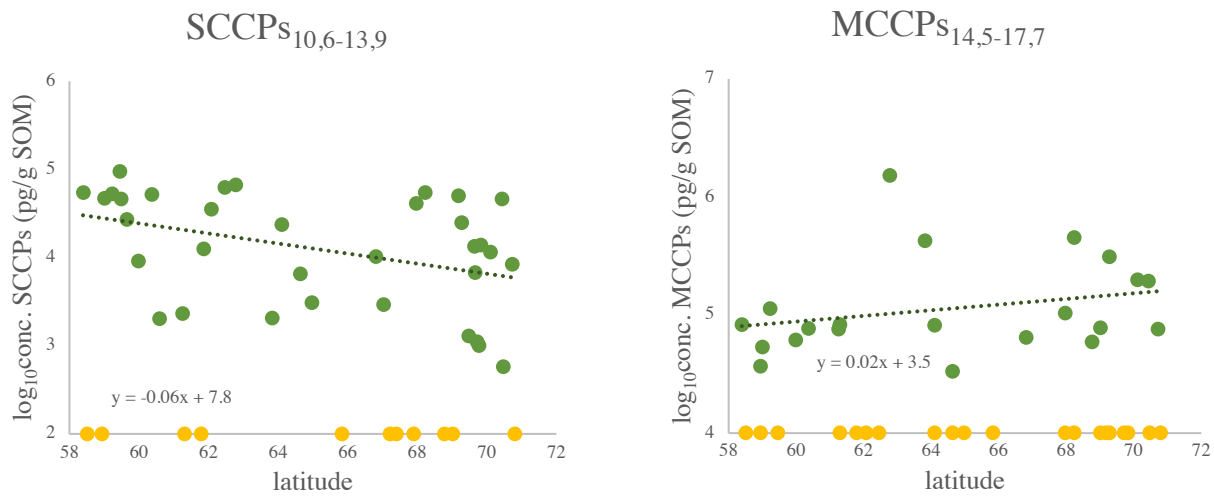

Figure 32: The spatial distribution of the SCCPs (left) and MCCPs (right) in Norway. A decline in concentration with latitude is seen for the SCCPs. However, for the MCCPs, a weak increase is observed.

4.4.6 Summarized spatial distribution of the assessed AOCs

The spatial distribution of the studied AOCs shows a generally decreasing concentration level from south to north in Norway (Figure 33). The strongest decline in concentration per latitude was found for NBFRs (y=-0.08x+7.5), followed by DPs (y=-0.07x+7.6), while the weakest decline was found for the PCBs (y=-0.05x+6.9). The similarity in trends observed suggest that the compounds originate from similar source regions, show similar behavior in the environment and experience therefore a similar environmental fate. Relationships between concentration levels in relation to parameters that are linked to latitude, such as population density, temperature, precipitation, and proximity to source regions are assessed in section 4.5 below.

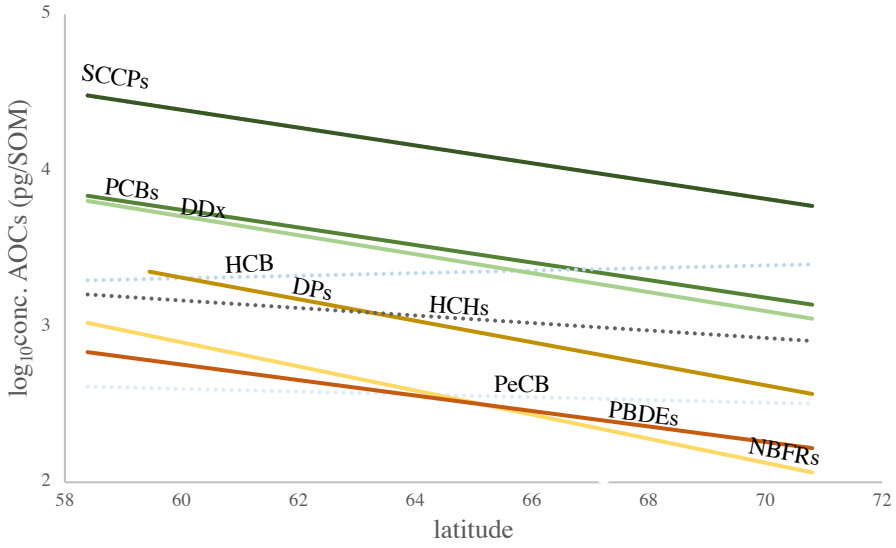

Figure 33: Summarized spatial distribution of the assessed background concentration levels of the AOCs in this study.

4.5 Factors influencing the spatial distribution and trends of AOCs

Population density, proximity to source regions, and climatic factors (e.g. temperature and precipitation) are factors that may influence the occurrence, spatial distribution and trends observed for AOCs. In this section, these factors are discussed, providing potential explanations for the occurrence and spatial trend observed in section 4.4 for the assessed AOCs in this study.

4.5.1 The influence of population density and local sources on AOCs

Several of the studied AOCs are applied in products used by people (e.g. PCBs, CPs, PBDEs, DPs), such as in construction materials and household products. As a result of this, areas with a high population density are then expected to act as local sources and to have a higher burden of AOCs compared to areas with fewer people. Population density can therefore be used as a measure of urbanization. The burden of pesticide-AOCs is however not expected to be as closely related to population density. This is because cultivated areas are often found in a certain distance from urban locations and depend also on climate and soil properties.

In Norway, the population density decreases along the latitudinal gradient (Figure 34), and this may have an impact on AOCs' occurrence and spatial distribution. The decrease in population density was found to be significant for background and urban sites combined ($p<0.05$) (Figure 34a), but not for background sites alone ($p>0.05$) (Figure 34b). Further, a significant difference was found between the urban Oslo sites and the background sites population densities ($p<0.05$) (see Appendix B.3.6).

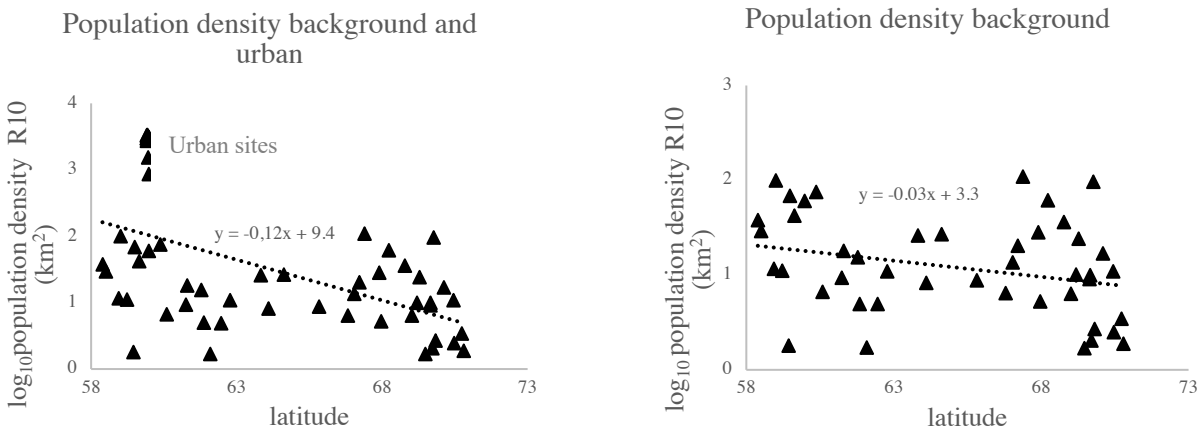

Figure 34: a) Relative population density in a 10km² radius (R10km²) at urban and background sampling sites (y-axis) with latitude (x-axis). b) Relative population density in a 10km² radius (R10km²) at background sampling sites (y-axis) with latitude (x-axis This figure show that the population density decreases with increasing latitude. This decrease was only significant for a).

Against this background, the relationship between concentration levels and population density was assessed for the studied AOCs to provide information on the influence of population densities and proximity to source areas on AOCs' occurrence and spatial distribution.

The relationship between population density and concentration levels of AOCs showed that highly populated areas seems to influence the burden of AOCs (Figure 35). The assessment of AOC concentrations in urban and background soils combined showed that they are related to population densities, as an increase in population density gave an increase in the levels of AOCs (Figure 35a). The relationship between concentration level and population density was found to be significant and positive for the non-pesticide AOCs, and significantly negative for the pesticide-AOCs ($p<0.05$). The occurrence of AOCs in urban and background soils is further significantly different from each other, with the highest concentration levels in the urban soils (Figure 35b) (see also Result overview 4.2). This suggests that the city of Oslo acts as a local source, and that it is strong enough to significantly affect non-pesticide AOC concentrations and determine the burden of AOCs in these soils. As a result of this, other factors, such as temperature and precipitation, may have a comparably weak impact on the concentration levels and trend observed. This confirms findings from other urban areas (Cachada et al. 2009) (Harrad & Hunter 2006), showing that highly populated regions can be expected to have a strong impact on the burden of AOCs in their vicinity, i.e. urban environments act as local source regions of AOCs.

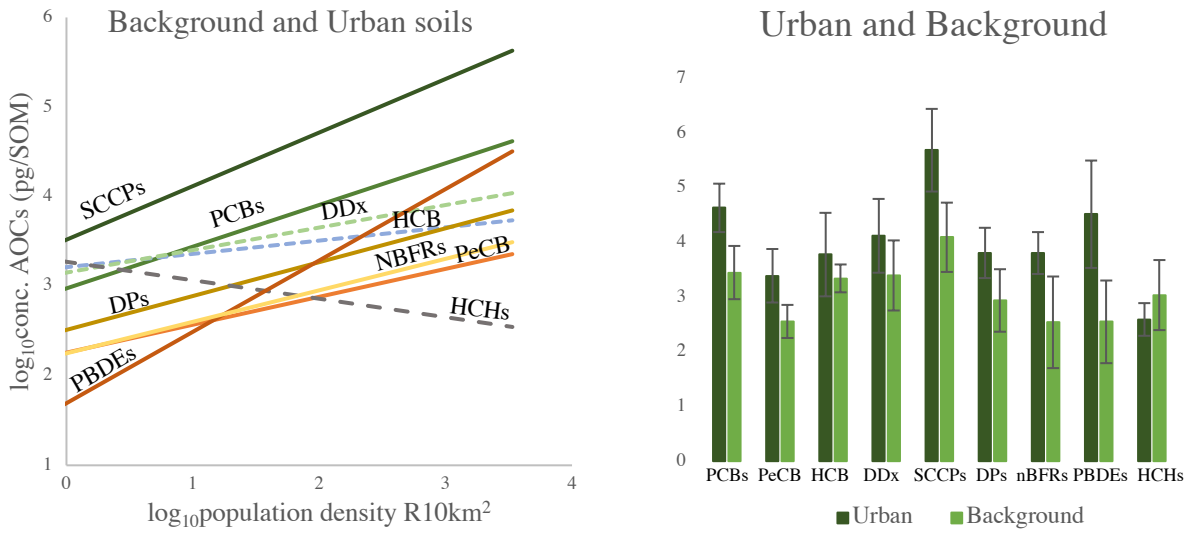

Figure 35: a) Relationship between concentration levels of AOCs and population density (relative population density, 10km² radius (R10km²)) in background and urban soils (left). b) Comparison of average concentration levels (y-axis, log_{10}pg/g SOM) of the AOCs (x-axis) in background and urban soils.

The urban samples were then excluded from the dataset in order to assess whether the "background" sample sites really are background sites, i.e. not significantly affected by local sources but rather by long-range transport. To identify measurement sites that are not influenced by local sources is of fundamental importance for models used to predict the fate of AOCs in the environment. The relationship between population density and the burden of AOCs in the remaining (i.e. background) samples was weak and not significant (Figure 36). This implies that the urban samples from the Oslo area have a great influence on the strong relationship seen in Figure 35a.

The background soils' weak relationship with population density suggests that LRAT rather than local sources determines the AOCs burden found in these soils (Figure 36). This means that the occurrence and distribution of AOCs in the atmosphere and therefore also in soils is predominantly determined by distance from sources, and linked to this, to the compounds' LRAT potential, and climate.

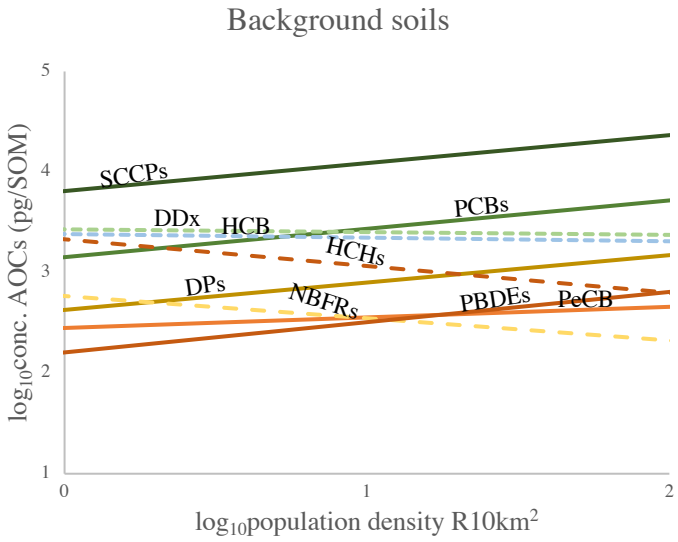

Figure 36: Relationship between concentration levels of the AOCs and population density (relative population density, 10km² radius (R10km²)) in background soils. There is no significant relationship between the assessed AOCs and the population density for the background soils alone.

4.5.2 The influence of distance from large-scale source regions

Large-scale source regions are found with different distances from the study sites, and this impact the concentration gradient observed in Norway. The distance between densely populated regions in western, central and eastern Europe and the north of Norway is approximately 2.5 to 3 times longer than that between those areas and the south of Norway. As AOCs are transported in the atmosphere over long distances, they get diluted on their way from the large-scale source areas. Since AOCs continue to be emitted from these areas (Gasic et al. 2009), this effect has been identified as the most likely explanation for the concentration gradients observed with latitude. In addition, predominating westerly winds make it more likely for the south than for the north of Norway to receive emissions from the UK. Over time, the strength of those sources will become weaker because of restrictions and bans of the chemicals. Atmospheric mixing processes may then result in a nearly uniform distribution of the compounds in the atmosphere. However, such a uniform distribution will only occur for the most volatile AOCs (e.g. HCB)(Brown & Wania 2008). Compounds with lower volatility and stronger affinity to organic matter for instance will be limited in their ability to travel long distances because they deposit soon to surfaces and irreversibly absorb to organic matter.

The LRAT potential of different AOCs is expected to have an effect on concentrations in environmental media already now (Brown & Wania 2008). Compounds with a high LRAT potential are more readily transported over long distances than those with a low LRAT potential. The LRAT potential depends on AOCs' physicochemical properties, and these properties change along a latitudinal gradient due to climatic factors (see Background 2.3). Against this background, climatic factors that potentially influence the occurrence and distribution of AOCs observed, are discussed below.

4.5.3 The influence of climatic factors on the environmental fate and behavior of AOCs

Climatic factors, such as temperature and precipitation, vary with latitude and longitude in Norway, and this is likely to affect the environmental fate and behavior of the AOCs. The average summer temperature (June to August) from each study site decreases with increasing latitude (Figure 37). This average summer temperature is applied because the sampling campaign was within these summer months (see Materials and Methods 3.1), and these temperatures have been estimated for the SERA-project.

Temperature has a substantial influence on the volatility of these compounds, where higher temperatures give a higher volatility (see Background 2.3). As a result of this, deposition to surfaces is enhanced with decreasing temperature because of reduced volatility, increased adsorption to surfaces and partitioning to highly hydrophobic compounds, such as cuticular waxes of plants and SOM. This effect is strongest for the less volatile compounds such as DDTs, DPs, highly halogenated: PCBs, CPs, and PBDEs. For the more volatile compounds (e.g. HCHs, PeCB, HCB, lowly chlorinated SCCPs) this effect is weaker, and they have a higher LRAT potential. This results in a more uniform distribution in the atmosphere of the whole northern hemisphere, and for these volatile compounds, slightly higher SOM-normalized concentrations can be expected in soils from the north compared to those from the south. Consequently, a possible mechanism contributing to the decreasing concentrations observed with latitude for the less volatile compounds, can be that low temperatures limit the atmospheric transport of AOCs to higher latitudes. This mechanism is likely to be the more pronounced the less volatile the compounds are.

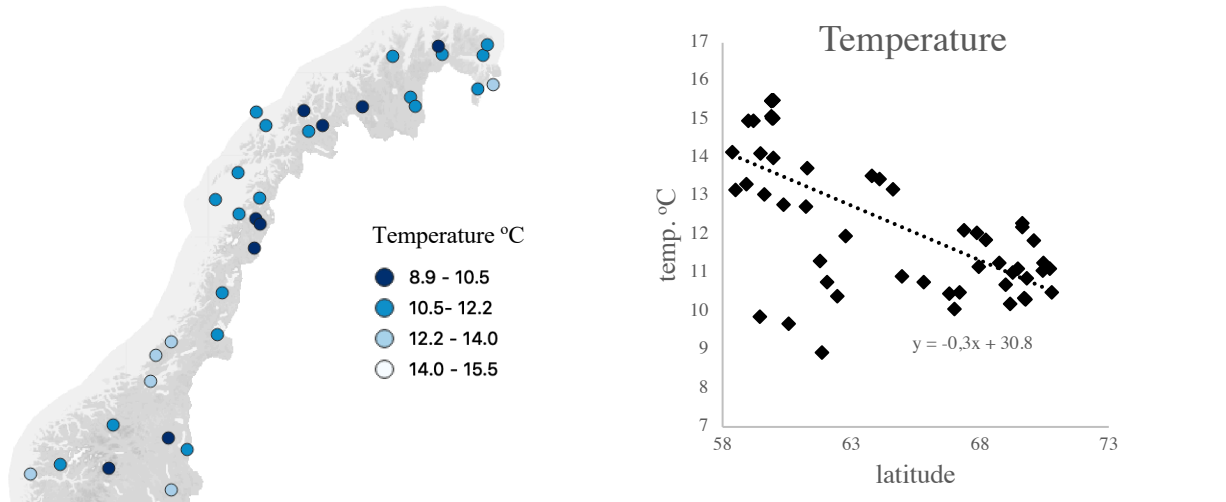

Figure 37: Summer temperature averages (June to August) for each sampling site along the Norwegian latitudinal gradient. This figure (graph and map) shows that the temperature (y-axis) decreases with increasing latitude (x-axis).

Apart from temperature, precipitation is another climatic factor that can directly affect the occurrence and distribution of AOCs in terrestrial ecosystems. The precipitation pattern in Norway is characterized by higher precipitation in the south-west compared to the central and northern parts (Norwegian Climate Service Senter 2019). Precipitation has previously been shown to augment deposition of heavy metals and PAHs by increasing wet particle deposition (Meijer et al. 2002). It is likely that the same process is occurring for AOCs with similar properties as the PAHs (e.g. PCBs, DDTs, PBDEs, DPs). Air contains aerosols and particles, such as volatile organic compounds, and these may interact with the AOCs. The AOCs can be sorbed to the particles and condense. Rain will wash these particles out of the air (Blanco-Alegre et al. 2018), resulting in wet deposition of AOCs with precipitation. Therefore, the elevated precipitation in south-west Norway can contribute to the higher occurrence of AOCs in these regions. This factor can however not be distinguished from the effect of temperature with the current dataset available.

Both the temperature gradient and precipitation differences in Norway support the spatial pattern observed in concentrations of AOCs, i.e. generally decreasing levels with increasing latitude (Figure 33). However, it is possible that other climate-related effects cause a contrasting trend at the same time and may therefore weaken the magnitude of the effect of proximity to large-scale source areas as well as that of the effect of temperature and precipitation on the air-to-surface deposition behavior of AOCs. With the data obtained in this study it is not possible to isolate these effects. However, when the results are used in chemical fate models later, it may be necessary to consider such effects in order to reflect the magnitude of spatial differences correctly. Overall, the results indicate that LRAT of AOCs from distant sources determines the concentrations at the "background" sites included in this study. This confirms that the sampling sites can generally be considered to be background sites, meaning that the mechanisms described under Background 2.4 apply.

Two factors were identified that could potentially cause a weakening of the south-north concentration gradient of AOCs in soil caused by the effects discussed so far. Firstly, the degradation rate of the AOCs themselves will depend on temperature, with higher rates generally expected at higher temperature (Mackay et al. 2006). This effect on its own should result in lower concentrations in soils in the south of Norway compared to the north. However, degradation of AOCs in soils under aerobic conditions is generally very slow due to their persistency, and this may therefore affect the concentrations comparably little.

Secondly, climate also impacts the rate of vegetation growth and decomposition, and therefore the average age of SOM (Brady & Weil 2010a). This is likely to affect the spatial distribution observed for the assessed AOCs (see Results and Discussions 4.3.1). Colder regions are characterized by a lower biomass production, leading to a slower formation of SOM. The soils' microbial activity is also lower, which reduces decomposition rates of SOM. Given the sampling strategy used (top 5 cm of the soil), a sample from the north of Norway may contain organic matter of a higher average age than a sample from the south. This sample therefore represents a longer period of biomass growth, SOM accumulation and hence also of AOCs' accumulation.

As seen in Background, Table 1, several of the assessed AOCs are restricted and regulated, and therefore their peak usage time, and consequently greatest emission and deposition time, may have been several decades ago (e.g. PCBs and HCB in the 1970s). Hågvar (2016) estimated for a spruce forest in the south of Norway that needles pass through the top 5 cm of the litter layer within roughly 20 years. Even when adding a few more years to account for the time when they constituted living biomass, samples from this area may contain comparably small percentages of biomass that had grown during the period of highest emissions for many AOCs. In northern Norway on the other hand, where organic matter production and decomposition is slower, the top 5 cm soil layer may contain a larger fraction of SOM originating from this time. This effect may result in higher than expected AOC concentrations in the soil samples from colder areas, considering factors like the samples SOM content or the compounds' atmospheric transport potential and partitioning behavior. The age of the SOM content, determined by carbon to nitrogen ratios (C:N) analysis, in the soil environments could therefore have been of interest in this study. The age would reveal net primary production at the study sites, and this could have provided evidence for the discussion on the age of SOM's impact on the burden of AOCs.

The chemical composition of the SOM may also differ between sampling sites as it is affected by the vegetation type, which in turn is related to climatic factors such as temperature and precipitation, and the availability of nutrients. Certini et al. (2015) found for instance that SOM originating from *Calluna vulgaris* is more hydrophobic than litter from other heathland plants (Certini et al. 2015). Such differences in organic matter quality affect the SOM decomposition rate (Brady & Weil 2010b), and may then also impact the SOM's storage capacity for AOCs and therefore the AOC concentrations found in the soil samples.

4.6 Associations within and between different groups of AOCs

Evidence of similarities and differences in environmental fate and behavior, and evaluation of environmental processes, can be provided by the assessment of associations within and between different AOC-groups. Firstly, the environmental fate and behavior with respect to varying physicochemical properties within compound groups was assessed for PCB-homologue groups (tri- to octa-PCBs) (4.6.1). PCB-homologue groups span over a wide range of K_{OA} and K_{AW} ($logK_{OA}$ 7-11) (Li et al. 2003). Based on this, assessment of PCB-homologue groups' spatial distribution can reveal the effect of this range on their behavior. Secondly, evaluation of the contribution of DDT and its metabolites relative to the p,p'- Σ_3DDx can provide information on environmental processes, such as degradation (4.6.2). Thereafter, assessment of ratios between isomers of HCHs and DPs on a latitudinal gradient can also provide information on environmental processes, such as degradation and fractionation due to differences in physicochemical properties. This information can be obtained in such assessment because the ratios of HCHs and DPs isomers in products are known and determined from the production processes. Consequently, evidence of similarities and differences in environmental fate and behavior, and environmental processes, are provided below from these assessments.

Evaluating relationships between selected AOC-groups can provide information on similar source regions and environmental behaviors. A positive relationship between different groups suggests that they generally share common sources, have similar transportation pathways and behaviors in the environment, and/or are similarly retained in soils (e.g. high SOM content may retain AOCs and retard re-emission and degradation) (Nam et al. 2008). Consequently, assessment of such associations of AOCs provides information on their behavior and fate in the environment, and source patterns (4.6.3).

4.6.1 Variations in physicochemical parameters

The influence of variation in PCB-homologue groups' physicochemical properties on their environmental fate and behavior was assessed by investigating their spatial distribution along the latitudinal gradient in Norway. This assessment was done by plotting the homologue groups, tri- to octa-PCBs, with latitude (Figure 38). The plots revealed an increasing concentration of the lower chlorinated PCBs (tri- and tetra-PCBs) with latitude, and a decreasing concentration for the more chlorinated PCBs (hepta- and octa-PCBs).

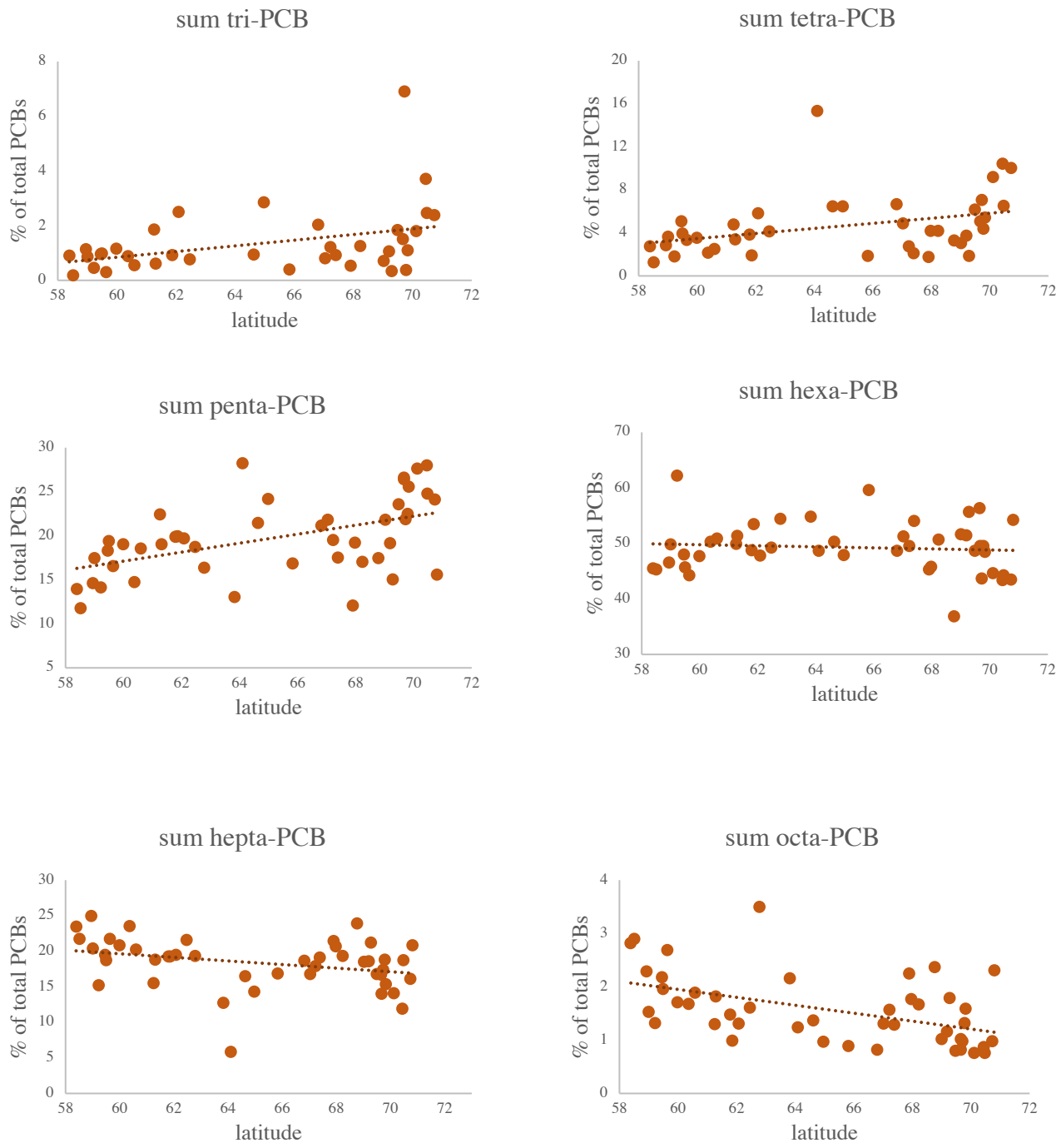

Figure 38: The spatial distribution the PCB-homologue groups, tri to octa, for the Norwegian background soils. There was found a significant relationship ($p<0.05$) between latitude and concentration level as % of total PCBs for 5/6 homologue groups), and the absolute correlation coefficient was >0.3, with strongest relationship for penta- and octa-PCBs. Hexa-PCBs was the only group with $r<0.3$ and $p>0.05$. These figures also show that hexa-PCBs is the highest contributor to all homologue groups, followed by penta- and hepta-PCBs.

From Figure 38, it seems as PCB-fractionation in soils with latitude is occurring, and this can be explained by their variation in physicochemical properties (see Background 2.3, Figure 10). The chlorination degrees affect physicochemical properties, where the less chlorinated congeners are more volatile than the highly chlorinated ones. This may therefore prevent the highly chlorinated PCBs from traveling long distances, compared to the less chlorinated ones. As a result, they are rather deposited and retained closer to source areas. This trend has also been emphasized for PCBs in a study by Ockenden (2002) and Meijer et al. (2003) from the UK-Norway soil transect in 1998 (Meijer et al. 2002; Ockenden et al. 2003).

The spatial trend explained by the differences in volatility for PCB-homologue groups can also be applicable for the PBDEs. The bromine degree impacts the PBDEs' environmental behavior in a similar way as seen with the chlorination degree for the PCBs. When evaluating the spatial distribution of the tetra-brominated BDE-47 with the penta-brominated BDE-99 alone, a slight increase in concentration with increasing latitude for BDE-47, and a weak decrease for BDE-99, was seen. However, due to the limited number of observations >MDL, this trend may not be fully reliable for the dataset available in this study. Even though this finding is less certain than for PCBs in this study, they are in agreement with an equal assessment in a study from the 1998 UK-Norway transect, were such spatial distribution between congeners of different bromine content with latitude was reported with certainty (Hassanin et al. 2004).

4.6.2 Evaluation of environmental processes

4.6.2.1 DDT and its metabolites in Norwegian terrestrial ecosystems

The relative abundance of p,p'-DDT and its metabolites, DDE and DDD to $\Sigma_{p,p'}$DDx can provide information on source areas and degradation processes (Cabrerizo, A. et al. 2011). The ratios of (p,p'-DDE + p,p'-DDD)/p,p'-DDT have been used to distinguish DDT sources, and to identify if degradation has occurred. A ratio >1, i.e. the metabolites DDE and DDD are present in larger amounts than DDT, is often interpreted as documentation of historical usage of DDT. This conclusion can be drawn because the degradation for DDT is slow and DDE and/or DDD require time to occur to a noticeable extent. A ratio of <1 on the other hand, indicates fresher inputs of DDT as the contribution of the metabolites is low.

The ratios between DDT and its metabolites were found to be <1 for about 50% and 60% of the background- and urban soils, respectively. The average ratio was 1.0 and 1.4, ranging from 0.2 to 6 and 0.6 to 3, for background- and urban soils, respectively (Table 5). The relatively high frequency of (p,p'DDE + p,p' DDD)/p,p'-DDT ratios <1 appears to indicate that new inputs might be occurring, and/or that only a limited degradation processes contribute to a continually high abundance of DDT compared to its metabolites. The latter is likely since the soil sampling sites are characterized by a relatively cold climate, degradation happens more slowly than in warmer areas where DDT was used extensively (Mackay et al. 2006). Consequently, low abundances of metabolites compared to parent DDT may not necessarily indicate current use. The age of the SOM in the soil samples might therefore also impact the ratios observed, where older SOM may have received DDT at a time when it was used in large parts of Europe.

Table. 5 The average ratios and ranges of (p,p'DDE+ p,p' DDD)/p,p'-DDT for background and urban soils.

Soil type	$Ratio_{(DDE/D)/DDT}$	Median	Range	% of sites with ratio <1
Background	1.0	0.4	0.2 – 6	50
Urban	1.4	2.9	0.6 – 3	60

In air samples collected at the same sites as the soil samples, the ratio between DDT and its metabolites was found to be around 3, i.e. a higher abundance of the metabolites. A possible explanation for this is that DDE and DDD are more volatile than DDT (Spencer & Cliath 1972).

This may influence a larger abundance of DDE and DDD in air, and higher deposition and adsorption of DDT to vegetation, and further storage in soil with SOM.

Degradation processes are likely to have occurred if the abundance of the metabolites DDE and DDD are higher than DDT compared to the technical mixture composition. Generally, technical mixtures of DDT contain about 90% DDT, and the remaining percentages are DDE and DDD. For the background soils, approx. 70% DDT, followed by 25% DDE and 5% DDD was found (Figure 39). This relatively high abundance of DDT compared to its metabolites is also reflected by the ratios in Table 5. In the urban soils, DDE was found in highest abundance, with approx. 60%, thereafter 35% DDT and 5% DDD, which also matches the average ratio and median found for these DDT-compounds (Table 5). These findings can be related to the age of the SOM in the background soils and their proximity to source areas, while the urban soils are possibly more strongly affected by local, historical sources within the wider Oslo area and possibly "younger" SOM. However, for both soil types, there is an indication of degradation processes when comparing to the technical mixture composition. It is also possible that the degradation has occurred at source areas, where higher temperatures and concentrations may have given more adequate conditions for biotic degradation. On the background of this, it is difficult to ascertain where and if degradation is occurring in the Norwegian soil environments.

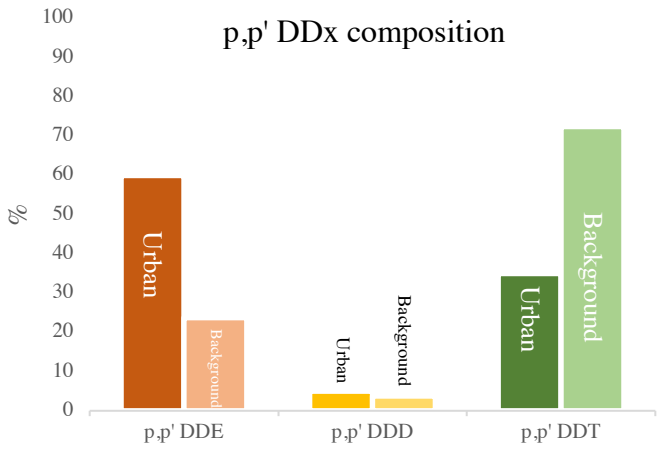

Figure 39: The distribution of p,p'DDE, DDD and DDT in urban and background soils. From this figure it is clear that p, p'DDT (green, 72%) is the largest contributor for sum p,p'DDX for the background sites, while it is p,p'DDE (brown-red 60%) in the urban soils. For both, p,p' DDD (yellow, 5%) has the lowest contribution for both soil types.

4.6.2.2 The relationship between HCH ratios and latitude in Norway

The application of different HCH mixtures (e.g. technical HCH with all its isomers, or lindane) can be monitored by estimating the ratios between different HCH isomers (Vijgen et al. 2010; Wenzel et al. 2002). In technical HCH mixtures, which was banned in the late 1970s, the ratio between α- and γ-HCH was between 4 to 12. Lindane, which was used more recently, contains almost exclusively γ-HCH (see Background 2.1.2). The α/γ-HCH ratio can be used as a tool to distinguish the source of HCHs found in the soil, either they originate from (older) technical HCH mixtures, or from more recent lindane applications. If the α/γ-ratio is well above 4 it would suggest that usage of the technical HCH-mixtures in source regions has affected the soil samples in the current study. In contrast, very low ratios, i.e. α-HCH being almost absent, would indicate predominant influence of lindane. For all the background and urban sites, the ratio was found to be generally <4 (Figure 40), but rarely below 1, except for samples from the urban sites where the majority was <1 (Figure 40b). This indicates that both the usage of technical HCH formulations and lindane contribute to the HCH burdens found in the soils in this study. The low ratios found in the urban Oslo samples may indicate use of lindane.

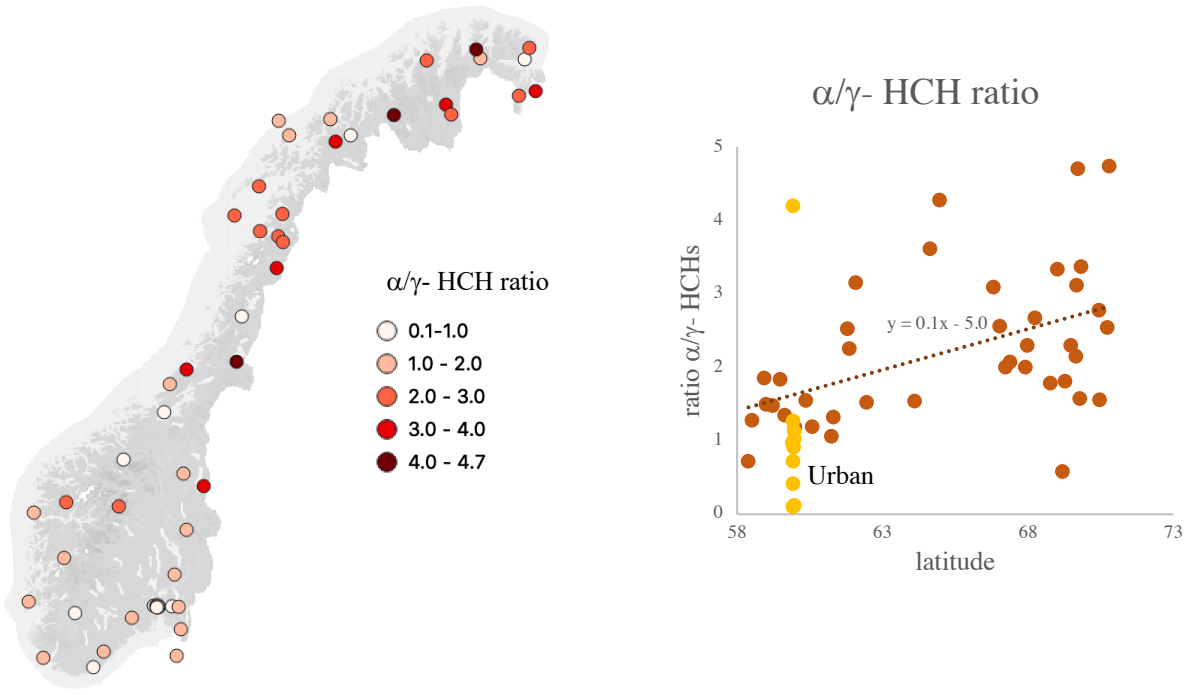

Figure 40: a) Map of the spatial distribution of α/γ- HCHs ratios. The difference between south and north was found to be significant ($p<0.01$). b) Graph of the spatial distribution, where the x-axis is the ratio and y-axis is the latitude. The urban sites are indicated in orange dots. The map and graph illustrate that the ratio between α- and γ increases from south to north.

The distribution of α/γ-HCH ratio on a latitudinal gradient can provide information on environmental fate and behavior, and further indicate sources and usage patterns. Along the Norwegian gradient from south to north a significant increase in α/γ-HCH ratio ($p<0.001$) was found (Figure 40), and also a significant difference between north and south ($p<0.05$). The relative contribution of these two HCH-isomers showed that there was a higher abundance of γ-HCH relative to α-HCH in the south, compared to the north. This can be related to their differences in physicochemical properties, where γ is the less volatile isomer (vapor pressure $1.3\text{-}9.9\text{x}10^{-2}$Pa), and α-HCH is the more volatile (vapor pressure 2.9-8.0 Pa) (Xiao et al. 2004). These differences can therefore have caused a stronger transport of α-HCH to higher latitudes compared to γ-HCH.

Another factor that may play a role in the trend observed, is that technical HCH with all its isomers (see Background 2.1.2) was used until it was banned in the late 1970-80s. The usage of all isomers started at the same time, however, the usage of γ-HCH has continued for a longer time in the form of lindane. Fresh releases of γ-HCH into the environment have therefore occurred more recently. Thus, α-HCH has had more time to get evenly distributed because there was no more freshly applied α-HCH coming from a certain point on, while there was still fresh γ-HCH coming from the usage of lindane. This allowed less time for γ-HCH to reach a uniform distribution. It can therefore be assumed that most of the α-HCH released to the environment have had about six to eight decades to become well distributed, and to accumulate at higher latitudes, unless illegal usage took place or technical HCH leaked out of old stockpiles.

The ratio between α- and β-HCH can provide information on degradation processes (Wenzel et al. 2002). The ratio decreases as degradation proceeds due to the greater persistency, and lower volatility of β-HCH compared to α-HCH. Along the latitudinal gradient, this ratio was found to increase towards the north (Figure 41). This may indicate that the HCHs deposited at soil surfaces has been degraded more slowly in the north than in the south, potentially because of lower temperature, and the age of SOM. The lower volatility of β-HCH (vapor pressure β-HCH = 2.5-3.3x10^{-2} Pa, and α-HCH = 2.9-8.0 Pa)(see also Background 2.3, Figure 9&10) gives a weaker LRAT potential for the β-HCH, and may therefore not have travelled as far north, hence leading to higher α/ β-HCH ratios in the north. This difference in LRAT potential may also consequently be a possible explanation for the trend seen. Based on this, the trend in ratio seen for the α- and β-HCHs can be due to the higher degradation of α-HCH, and/or limited transport of β-HCH to the north.

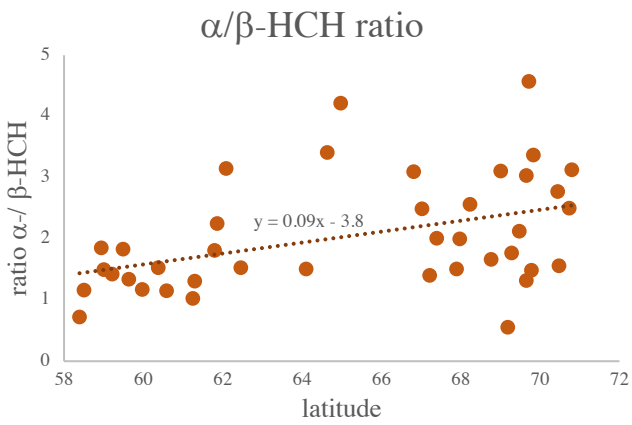

Figure 41: The spatial distribution of α/β-ratios along the latitudinal gradient in Norway. The graph show that the ratio increases with increasing latitude.

4.6.2.3 The relationship between dechlorane plus anti/syn ratios and latitude in Norway

The ratio between anti- and syn-DP can be used to assess the fate and distribution of DPs in the environment (Wang et al. 2016). The average ratio for the urban and background sites was found to be 5, and there was a decrease in this ratio from south to north in Norway (Figure 42). When evaluating the anti- and syn-DP separately, both isomers where found to decrease from south to north, but with a steeper decline for the anti-DP. The mechanism behind this difference in decline is that the syn-DP has a lower K_{OA}-value than the anti-DP (Möller et al. 2010). This difference will affect the compounds' LRAT potential, i.e. syn-DP is expected to have a higher ability to travel in the air compared to anti-DP, which may contribute to the decreased ratio towards the northern parts of Norway. In addition to LRAT, the anti/syn-DP ratio may change slowly compared to the ratio found in the commercial mixture. The reason for this is that the syn-DP is more stable than the anti-DP (Möller et al. 2010), leading to a stronger depletion of the anti-DP compared to the syn-DP in the environment.

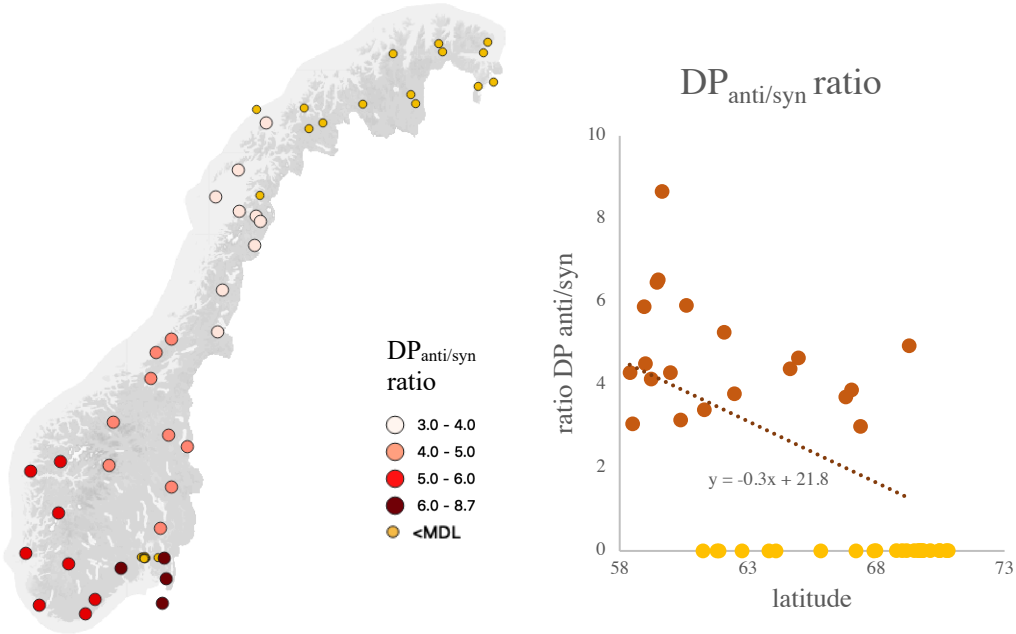

Figure 42: The spatial distribution of $DP_{anti/syn}$ ratios in Norway.

4.6.3 Evaluation of similarities and differences in sources

Evaluating relationships between selected AOC-groups can provide information on similar source regions, as well as environmental behaviors. PCB- and PBDE-homologue groups were found to have similar environmental behaviors (see Results and Discussions 4.6.1). Based on this, the relationship between these two AOC-groups' concentration levels was searched. A positive, significant relationship between PCBs and PBDEs was found ($r=0.5$, $p<0.01$), similar to what has been reported by Hassanin et al. (2004). This support the opinion that PCBs and PBDEs have common source areas, and similarities in atmospheric distribution, deposition, and retention in soils. PCBs and DDTs were also found to be strongly correlated ($r=0.7$ and $p<0.001$) (Figure 43), implying that these two compound groups may behave similarly in the environment, and that they most probably share common source areas. Several of the other assessed AOC-groups were also correlated, such as HCHs and DDTs ($r=0.7$, $p<0.01$), and HCB and PeCB ($r=0.6$, $p<0.01$). These relationships are not that surprising as they all are associated with SOM, they share similar spatial trends, and are most probably influenced by the same environmental factors (see Results and Discussion 4.3, 4.4, and 4.5).

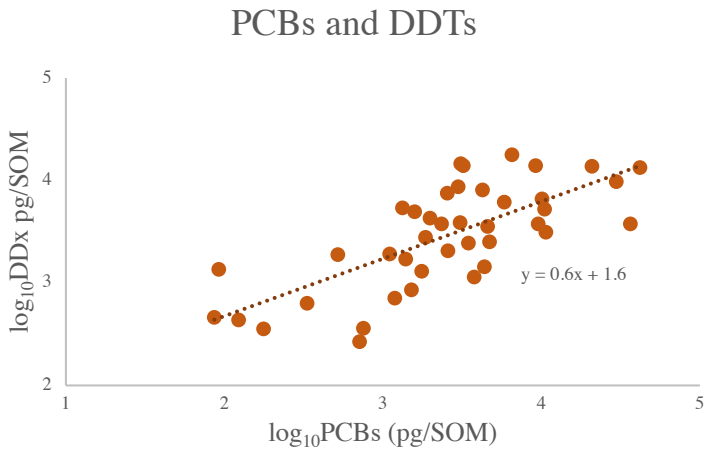

Figure 43: The relationship between the concentration levels of PCBs (x-axis) and DDTs (y-axis) in background soils. Similar plots were found for PBDEs and PCBs, HCHs and DDTs, and HCB and PeCB.

4.7 Air to soil exchange of PCBs in Norway

The burden of AOCs in background soils are mainly driven by mechanisms of inputs and outputs between air and soil (see Background 2.4). Soil- and vegetation surfaces interact with the atmosphere, and between these two environmental compartments, AOCs are exchanged. To increase the knowledge of this interaction, both air and soil were sampled at the same sites in 2016, as part of the SERA-project. These soil and air samples allowed for the assessment of air to soil exchange, where the main direction of exchange, soil storage capacities, and the extent of soils as secondary sources of AOCs, can be found. In this study, this assessment was applied for PCBs. The air to soil exchange for PCBs might then be extrapolated to other AOCs with similarities in physicochemical properties.

4.7.1 The soil to air equilibrium partition coefficient (KSA) for PCBs

The exchange of AOCs between soil and air is driven by a gradient in chemical potential, expressed as K_{SA} – the soil to air equilibrium partition coefficient (Cabrerizo, Ana et al. 2011; Li et al. 2010) (see also Background 2.3, and Materials and Methods 3.6.4). For the PCB-congeners evaluated (28, 52, 101, 153, 180), the K_{SA} estimates increase with chlorination degree for background- and urban sites (Table 6).

Table 6. Estimated air to soil exchange parameters for PCBs.

Parameter	PCB-28 Tri-Cl	PCB-52 Tetra-Cl	PCB-101 Penta-Cl	PCB-153 Hexa-Cl	PCB-180 Hepta-Cl
logK_{SA}	7.3	7.7	8.2	8.9	9.7
logfs	-2.9	-3.0	-2.9	-3.2	-4.2
logfa	3.3	3.4	3.2	3.0	2.3
logff	-6.1	-6.4	-5.9	-6.1	-6.1

The strength of soil retention and exchange between air and soil is dependent on the PCB-congeners' physicochemical properties, which than affects the environmental fate and behavior of the PCBs. The estimated K_{SA} for the evaluated PCB-congeners were all found to be significantly different from each other ($p<<0.001$), indicating that the partitioning to soil compared to air increases with higher degree of chlorination, lower volatility, and higher

hydrophobicity of the PCB-congeners (from PCB-28 to -180). In Figure 38, section 4.6.1, which shows the spatial distribution of PCB-homologue groups with latitude, it can be seen that the less chlorinated, more volatile PCBs are increasing with latitude (tri- to penta-PCBs), and vice-versa for the more chlorinated PCBs (hexa- to octa-PCBs). K_{SA} may play a role in this trend, where higher K_{SA}-values give a higher deposition to, and stronger retention, in soils. The trend found for the PCBs' and latitude, partly explained by the partitioning between air and soil, is then also linked to the congener's differences in physicochemical properties (e.g. volatility, hydrophobicity). Consequently, the strength of retention in soil and individual congeners' chemical characteristics are the main factors influencing their air to soil exchange and thus the spatial distribution of PCBs in the environment.

4.7.2 The fugacity- factors (f_A and f_A) and fractions (*ff*) for PCBs

Comparison of estimated fugacity factors for air (f_A) and soil (f_S), and the fugacity fraction (*ff*), can provide indicative information on the direction and the equilibrium status of the air to soil exchange (see Materials and Methods 3.6.4). In the evaluation of air to soil exchange, it has to be taken into account that there is a considerable uncertainty associated with the calculations of fugacity factors (Bruhn et al. 2003). These uncertainties are related to environmental factors, and the determination of PCBs concentration levels in air and soil, where both the stages of sample collection, and the chemical analysis. The environmental factors considered are the differences between the nature of these two media, where air is a much more dynamic medium than soil. Therefore, the variability of concentrations in time might be larger for air, while variability in space is likely to be larger for soil. The analytical procedure for analyzing PCBs in air differs from that for soil, and consequently, these approaches can cause uncertainty when evaluating both medias. However, as f_A is much higher than f_S (Table 6), it is suggested that the PCB-congeners move in the direction from air to soil because the chemicals tend to move from a media where their fugacity is high to media where it is low. Based on these findings, a net deposition from ambient air to soil surfaces and/ or vegetation is most likely to occur.

The very low *ff*s ($ff = f_S/f_A$) suggest that the equilibrium between air and soil for PCBs is far from being reached (Table 6). The 5 cm of topsoil sampled at each study site contained generally a high amount of SOM (Figure 17), where the SOM may range from a few years to hundreds of years in age. Most of these 5 cm of soil are not in direct contact with air. During the peak time of PCB-usage (1970-80s), substantial amounts of PCBs may have been deposited form air to soil, and thereafter been bound to the SOM fraction and retained. This aged SOM is probably no longer in direct contact with air because it might be covered by fresh, and newly degraded litter inputs. Therefore, underlying SOM masses may contain historical PCBs, and possibly in a higher amount than fresh litter at the time of sampling (2016). If historical PCBs should be released from the aged SOM by volatilization, they will most likely be trapped and retained by the fresh litter lying above. As a result of this, historical PCBs will probably not reach air masses and contribute as a secondary source.

Leaching of compounds from the sampled O/A-horizons to the underlying soil horizons (e.g. through the E- to the B horizon) can have transported PCBs further away from the soil surface and the direct contact with air masses (Moeckel et al. 2008). The least chlorinated PCB congeners (tri- to penta-) are most volatile and also more water soluble than the higher chlorinated PCB-congeners. Low chlorinated PCBs can then easily be transported downward with the percolating soil water and accumulate in the underlying soil horizons. Then, these PCBs are lastingly locked away from contact with the atmosphere. Dissolved organic matter may also carry the less water-soluble PCBs downwards in the soil profile, where they either can be retained or further leached (e.g. to groundwater or nearest river system). Thus, and despite the uncertainties associated with those calculations, the downward transport of PCBs, in combination with SOM burial and ageing, support the results from the fugacity calculations, that the soils included in this study do not act as secondary sources of PCBs to air, despite the uncertainties associated with those calculations. Consequently, the soils investigated are able to take up and retain substantial amounts of PCBs. This emphasize the large storage capacity of these soils for PCBs, and potentially other AOCs with similar properties, such as DDTs, PBDEs, and DPs.

4.8 Temporal variations

Soils are sinks and reservoirs, and potential secondary sources, for the global burden of AOCs. The AOCs in this study were found to be strongly associated with the SOM fraction in soil environments (see Results and Discussion 4.3). Based on this, evidence of AOCs' sorption to soils was provided. From the air to soil exchange assessment of PCBs (see Results and Discussions 4.7), these soils were also found to act as storage reservoirs of AOCs, and that these soils are unlikely to act as secondary sources. The emissions and atmospheric loadings of AOCs have changed over time because of restrictions and regulations on legacy POPs, and due to the introduction of new POP-like compounds. Soil- and vegetation surfaces are in direct contact with the atmosphere, and therefore the terrestrial ecosystems respond to these changes. This response is evaluated with respect to the UK- Norway transect data from 1998 and 2008 (Schuster et al. 2011), where the Norwegian background soil and the results obtained in the current study (2016) are evaluated.

The temporal variations of AOCs in Norwegian background soils from 1998 to 2016 appear to show a slightly decreased burden of these contaminants in soil environments (Table 7) over that time period. The sampling- and analytical methods applied in 1998 and 2008 are comparable with the one used in this study. However, for SCCPs, a different analytical method was applied in 2008, and consequently, there are large uncertainties in the comparison.

Table 7. Concentration levels (mean with standard deviation and range in ng/g SOM) and difference (Diff.) between 1998 and 2018 for selected AOCs from Norwegian background soils in 1998, 2008 and 2016.

Compound	1998	2008	2016	Diff. mean 1998-2016
PCBs	8.5 ± 8.8 0.7 - 40	7.8 ± 6.4 0.2 - 27	2.8 ± 4.0 0.2 - 22	-5.7
HCB	1.6 ± 1.2 0.1 – 5.5	1.4 ± 1.0 0.2 – 4.6	1.3 ± 2.0 0.03 – 1.8	-0.3
p,p' DDT	5.7 ± 8.6 0.4 - 39	7.7 ± 18.6 0.04 - 80	3.4 ± 6.2 0.01 – 27	-2.3
p,p' DDE	1.5 ± 1.1 0.2 – 4.3	1.2 ± 1.4 0.02 – 6.8	1.2 ± 1.5 0.06 – 6.1	-0.3
Σ_5PBDEs	1.3 ± 0.8 0.3 – 2.9	0.3 ± 0.4 0.01 – 1.6	0.4 ± 0.7 0.5 – 7.2	-0.9
SCCPs	No observation	22 ± 87	15 ± 16	-7

The reduction in the burden of AOCs is found to be generally low (Table 7, Diff. 1998 to 2016). The large standard deviations indicate that there are uncertainties in the decrease, especially for SCCPs, where the standard deviation in 2008 is very high and there is large spreading in the dataset. The variation is most likely attributed to the variation along the Norwegian transect, as also found for the latitudinal gradient in this study. The slow reduction of AOCs indicates that it will take a long time for concentrations in soil environments to drop, even though the concentrations have been found to decrease more substantially in air (Hung et al. 2016). Reduction rates of AOCs in soil and air differ because air is more dynamic than soil when it comes to responses of AOCs. Concentrations of AOCs in the air can change within hours (Halse et al. 2013) while they are relatively stable in soils which contain organic matter of a wide range of ages, spanning typically several decades. This, in combination with soils' much larger reservoir capacities for AOCs compared to the air, and the limited degradation in these northern soils, results in even slower responses to changes of AOCs emissions from source areas. The highest difference between 1998 and 2016 was found for PCBs and therefore, this compound group's temporal trend is assessed more closely below.

There is a slight decreased burden of PCBs in surface soils at equal study sites from 1998 to 2016 (Table 7, and Figure 44). The reductions from both 1998 to 2016 (diff. mean = - 3.2 ng/g SOM), and from 2008 to 2016 (diff. mean = -3.6 ng/g SOM), were found to be statistically significant ($p<0.05$), but there was no significant decrease between 1998 and 2008 (diff. mean = 0.4 ng/g SOM). This suggests that regulations work in a sense that concentrations appear to decline. However, this decrease is slow, presumably because soil degradation processes in these climate zones are slow, and because several source regions might continue to emit AOCs even though they have been banned for several years. This is apparent for the sampling sites where concentration levels measured have increased since 1998 (Figure 44, light- to dark red colored dots on the map).

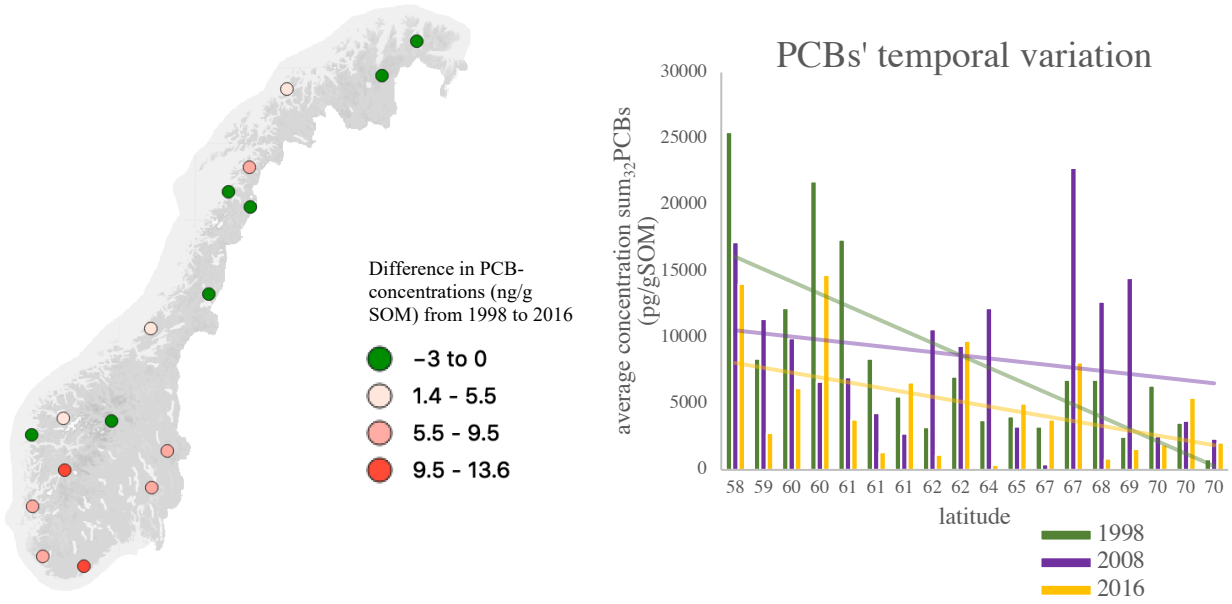

Figure 44: a) The map on the left side show the difference in concentration levels of PCBs from 1998 to 2016 (pg/g SOM 1998 – pg/g SOM 2016). The green dots represent the sites were the concentrations have decreased. The red dots, from light to darker, show sites where an increase is observed. b) The histogram on the right side show the average concentration in pg/g SOM (y-axis) from 1998, 2008 and 2016 with their respective trend lines.

5. Conclusion and future perspectives

The occurrence of AOCs in Norwegian terrestrial ecosystems indicates that these contaminants have been, and/ or are still today (2019), used and emitted from old and new sources. According to threshold values from the Norwegian guidelines on soil classification, the background, and also the urban soils, are of good environmental quality and there are today (2019) no human health risks associated with the concentration levels found, where such thresholds were available. For some compounds, as e.g. the CPs and DPs, such threshold values have not been established yet because there is not sufficient knowledge on these compounds. CPs, and especially the MCCPs, where found in highest concentrations in the background and urban soils, and therefore, this knowledge gap should be considered in the case of sensitive usage of these soils. This is consequently a matter that should be addressed in the future to ascertain safety for sensitive organisms and ecosystems, and generally a good environmental status.

The strong relationship found between AOCs and SOM shows that vegetation scavenges these contaminants from the air, and that they are further deposited and stored in the soil organic matter fraction in these environments. This suggests that the soils in the areas investigated (e.g. high carbon stock, cold climate) are important storage compartments for old, as well as more currently used, organic chemicals and that a significant proportion of the emitted AOCs will eventually end up there. Being very far from reaching equilibrium between air and soil also indicates that AOCs will continue to deposit from the air, and that the soils are unlikely to act as secondary sources, even if the concentrations in air decrease further in the near future. Moreover, cleaner litter layers will then deposit on top of more polluted litter and possibly trap chemicals that potentially evaporate from older, more polluted, layers. This effect will further inhibit the release of these chemicals to the atmosphere.

The AOCs analyzed were found to be long-range transported from large-scale source areas. During this transport, the compounds are diluted on their way, and their volatility decreases as they travel from the south to the north of Norway due to the decreasing air temperatures. As a result of this, there is a decreasing abundance of the contaminants with increasing latitude in the Norwegian background soils. The finding of new POP-like compounds, such as DPs, NBFRs and MCCPs, in the remote background soils indicates that also these compounds have the ability to be long-range transported, such as for the legacy-POPs. This is one of the criteria for being classified as POPs and to be regulated thereafter. Bioaccumulation is another criterion needed to be labeled as a POP. This is investigated in another part of the SERA-project in order to increase our knowledge on these contaminants' environmental fate and behavior.

Several of the studied AOCs included in this study have been regulated and restricted in order to prevent harmful effects on ecosystems and our health. The soils' response to this is presumably slow and the occurrence of legacy-POPs in terrestrial ecosystems appeared to have only decreased slightly over the last two decades. This can largely be attributed to vegetation and soils' sorption and storage capacities of AOCs, and also the lower rate of degradation processes occurring in these cold regions. Based on this, the AOC-concentrations in the soils are therefore not expected to decrease markedly in the near future. The production and usage of such chemicals with similar properties in the years to come should therefore be evaluated carefully because, as seen in this study, they persist in the environment, are long-range transported, and their presence may cause adverse and possibly unforeseen effects to our ecosystems.

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Appendix

Appendix A

This appendix contains tables of solvents, reagents, and materials used at NILU Kjeller, Laboratory for organic analysis, Environmental Chemistry department. Detailed information on sample preparation procedures is given in chapter A.2.

A.1 Chemical analysis

A.1.1 Solvents, reagents and materials

All materials used in the laboratory work and analysis is listed in table.1 below.

Table A.1.1. Solvents, reagents and materials used in laboratory work and analysis

	Producer/origin	**Size**	**Purity grade**	**Use**
Acetone Pestinorm	VWR Chemicals	2,5L	99,70%	Cleaning of all material
Alkaline soap (Extrane)	Mereck (Darmstadt, D)	1L		Cleaning of glassware
Aluminium foil	Caterwrap	450mx150mm		Storage of soil samples
Aluminium foil sheets	Korff	100x100mm		Cover for glassware during preparation
Cotton wool	Vernon Carus	500g		Stopper in chromatography column used in silica clean-up
Diethyl ether SupraSolv	Mereck (Darmstadt, D)	1L		Extractions
GC vials (brown& clear)	Chromacol (USA)	300µL		Analytical procedure (GC)
Glass centrifuge tubes w/ glass stopper	Schott Duran (D)	10mL		Acid clean-up
Glass columns	Schott Duran (D)	15mm diam.		Silica clean-up
Glass vial, conical	Chromacol (USA)	1mL		Volume reduction N_2 and storage of samples
Glassware (Erlenmeyer flasks, beakers, measuring cylinders etc.)	Schott Duran (D)			General laboratory work
Helium gas (He)	Paraxair (NO)		5,0	Analytical procedure (GC/MS)
Hypodermic needles Microlance	Becton Dickinson Medical			Volume reduction using N^2 gas
Iso-Octane Emsure	Mereck (Darmstadt, D)	1L	99,50%	Solvent used for samples during GC analysis
Latex tops for Pasteur pipettes	Svenska latex AB (SE)			General laboratory work
Micropipettes	Balubrand (D)	20, 50, 100µL		Transfer of standards to samples, transfer of samples to GC vials

N^2	Paraxair (NO)			Volume reduction of samples and ASE
N^2 evaporation system				Volume reduction of samples
n-Hexane Pestinorm	VWR Chemicals	2,5L	95,00%	Extractions, rinsing of glassware
Nitrile gloves	Ansell			General laboratory work
Ovens				Glassware cleaning, burning of silica, copper, sodium sulfate, florisil
Pasteur pipettes	Scherf prazision GMBH			General laboratory work
PTV inlet	Agilent (USA)			Sample introduction GC
Silica gel 60Å	Mereck (Darmstadt, D)	1kg		Silica column clean-up
Sodium sulfate	Mereck (Darmstadt, D)	1kg		Water removal agent in ASE extraction cells and silica column clean-up
Sulfuric acid Emsure	Mereck (Darmstadt, D)	100mL	95-97%	Acid clean-up of samples
Turbovap 500	Zymark			Sample volume reduction
Turbovap glasses	Biotage	200mL		Sample volume reduction on Turbovap 500
Ultrasonic bath	VWR			Cleaning ASE cells
Whirl mixer	VWR			Mixing during acid clean-up, sample homogenization
Ziploc bags	Polynova			Sampling material storage

Table A.1.2. Components of ^{13}C-PBDE present in the standard mixture

Component	**Concentration (pg/µL)**
^{13}C PBDE-28	254
^{13}C PBDE-47	269
^{13}C PBDE-99	244
^{13}C PBDE-153	255
^{13}C PBDE-183	257
^{13}C PBDE-197	255
^{13}C PBDE-206	257
^{13}C PBDE-209	1232

Table A.1.3. Components of ^{13}C-DDT/HCH present in the standard mixture

Component	**Concentration (pg/µL)**
^{13}C alpha-HCH	994
^{13}C beta-HCH	200
^{13}C gamma-HCH	1004

^{13}C delta-HCH	1002
^{13}C p,p' DDE	318
^{13}C p,p' DDD	319
^{13}C p,p' DDT	321

Table A.1.4. Components ^{13}C-PEST I present in the pesticide standard mixture

Component	**Concentration (pg/µL)**
^{13}C tr.Nanachlor	108
^{13}C Cis.Nonachlor	49.3
^{13}C tr.Chlordane	49.2
^{13}C cis. Chlordane	98.7
^{13}C Oxychlordnae	676
^{13}C Heptachlor epoxid	815
^{13}C HeptaChlor	1386
^{13}C Dieldrin	1292
^{13}C Mirex	765
^{13}C Endosulfan I	108
^{13}C Endosulfan II	128
^{13}C Endosulfan Sulfate	69.5
^{13}C Trifluralin	70.5
^{13}C Endrin	987
^{13}C Aldrin	1250
^{13}C Isodrin	2536

Table A.1.5. Components ^{13}C-CP-DEC I present in the CPs standard mixture

Component	**Concentration (pg/µL)**
C10-C13 55% Cl	18671
C14-C17 55% Cl	18996
13C 10 Dechlorane Plus syn	4.77

Table A.1.6. Components ^{13}C-PCBs present in (PCB I) standard mixture

Component	Concentration (pg/µL)
^{13}C PeCB	98.8
^{13}C HCB	98.2
^{13}C PCB-28	237
^{13}C PCB-52	239
^{13}C PCB-101	236
^{13}C PCB-105	240
^{13}C PCB-114	237
^{13}C PCB-118	236
^{13}C PCB-123	242
^{13}C PCB-138	238
^{13}C PCB-153	238
^{13}C PCB-156	236
^{13}C PCB-157	236
^{13}C PCB-167	238
^{13}C PCB-180	239
^{13}C PCB-189	237
^{13}C PCB-209	237

Table A.1.7. Components^{13}C-NBFRs present in the standard mixture

Component	Concentration (35.18) (pg/µL)	Concentration (46.17) (pg/µL)
^{13}C BTBPE	989	986
^{13}C HBB	988	986
^{13}C d17 EHTBB	994	1022
^{13}C DBDPE	995	965
^{13}C PBBZ	992	1000

Table A.1.8. Recovery standard

Component	Concentration (pg/µL)
1,2,3,4 TCN	96.2

A.2 Sample preparation

A.2.1 Accelerated Solvent Extractor (ASE)

Prior to extraction, the composite soil samples from each site had to be homogenized to attain a representative sample. Soil sample homogenization was done with the use of a large glass bowl (2L), scalpel and metal spoon to mix the soil. All material used was precleaned with acetone and washed before and between each sample with alkaline soap.

Sample preparation for ASE requires packing of extractions cells and internal standard addition. Stainless steel extraction cells were precleaned with acetone in ultrasound bath for 15 minutes, three times before use. Thereafter, ASE cells were packed for each soil sample in the following way from the bottom: two cellulose filter papers, ≈ 5 g of florisil (activated magnesium silicate, $MgSiO_3$), one cellulose filter paper, ≈ 5-15 g soil dried with burned anhydrous sodium sulfate powder (Na_2SO_4), internal standard solution, and one cellulose filter paper at the top, as presented in Figure A.2.1.1 below. All weights had an accuracy of 0.01 g. Internal standard was added to monitor recovery rates for the sample preparation pathways and later to be used to quantify analytes of interest. These standards contained ^{13}C labeled compound groups of interest: PCBs, PBDEs, NBFRs, pesticides, and CPs. The compound groups standard mixture concentrations are given in appendix A.1.2 Solvents, reagents and materials.

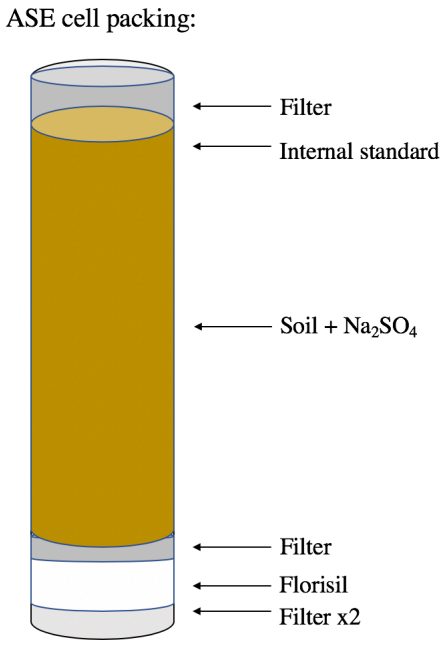

Figure A.2.1.1: ASE cell packing illustration.

Anhydrous sodium sulfate was used to chemically dry the soil. This was achieved by grinding soil and sodium sulfate in a mortar until a free-flowing powder was obtained before transferring to ASE cells. For efficient chemical drying, the powdered sodium sulfate was burned at 550°C for 8 hours before use to completely dry the salt and remove potential contaminants. Florisil was included in ASE cells because of its absorbing property of non-analytes. As a result of this, florisil can clean the extracted solution to some extent before the extracted solution is collected. Florisil was burned at 450°C for 9.2 hours to remove contamination and to obtain maximum free sites on florisil's large surface area.

Each cell was tightly closed with stainless steel lids at each end. To avoid air-filled space in ASE cells, sodium sulfate was used to fill up dead volume in some samples before placing cellulose filter. Blank samples were prepared equally to identify any potential contamination pathways in the analytical procedures. Per approximately 8 sample, one blank-sample was prepared with anhydrous sodium sulfate powder without soil in ASE cells.

The extraction parameters applied on the ASE apparatus is given in table 9 below.

Table A.2.1.1 ASE extraction parameters on Dixon ASE200 apparatus.

Solvent	Acetone-hexane 1:1 v/v
Pressure	1500Psi (10,3MPa)
Temperature	100°C
Cycle	2 x static cycle* of 10minutes
Purge of sample	N_2 gas**

*Static cycle implies that the cell is filled with a certain amount of solvent and then heated for the set static cycle time.

**The extract sample was purged to their respective collection vials with the use of compressed Nitrogen gas (N_2).

A.2.2 Sample clean-up

After extraction with ASE method, the extracts were cleaned to remove soil matrix compounds that can interfere with the quantitative analyses. Sample clean-up is a step-wise procedure and in this project, acid clean-up, followed by silica-based SPE were chosen as suitable methods for this purpose.

Acid clean-up

Acid clean-up aims to remove matrix compounds from extracted sample solution. To enable acid clean-up, the sample extracts needed to be concentrated and solvent-exchanged from the ASE acetone/hexane to hexane. This was done with the use of a turbovap (Turbovap 500). Turbovap 500 Concentration Evaporator is an evaporation system, where the use of a helical gas flow and sensor endpoint detection technology gives automated sample concentration and solvent recovery (Biotage 2019). The extract in the extraction solvent hexane: acetone (1:1) was therefore transferred from the ASE collection vial to turbovap glasses and evaporated down to 0,5mL concentrated sample. To make sure that compounds were not lost in this process and that complete solvent exchange was achieved, 2 Pasteur pipettes à 1mL hexane was added to rinse turbovap glasses and was evaporated to 0,5mL sample in hexane solvent. This was repeated two times.

When the concentrated 0,5mL sample in hexane solvent was obtained, the sample was transferred to glass centrifuge tubes. Turbovap glasses were rinsed three times with hexane using a 1mL Pasteur pipette to ensure that all analytes are transferred to the centrifuge tube. In these centrifuge tubes, one pipette of concentrated sulfur acid (H_2SO_4) was added and mixed thoroughly on a vortex mixer.

To allow for better separation between the two phases, hexane and H_2SO_4, the sample stood over night after the first acid addition. Thereafter, the sulfuric acid (the lower layer in the glass centrifuge tube) was removed using a Pasteur pipette This acid addition and removal procedure was repeated four times to remove as much soil matrix compounds as possible. Prior to each acid removal, centrifugation (20min, 2000rpm) was used to achieve a sufficient separation between the acid and hexane phase before removing acid. This was necessary because of the frequent formation of emulsions.

To remove any traces of acid from the extracts, one pipette of water (milli Q) was added to each sample after the last acid take-out. After mixing and centrifugation, the hexane phase was pipetted out and transferred to a new, clean glass centrifuge tube. This procedure was repeated three times to completely remove all traces of acid and to clean out the glassware used. Thereafter, acid-washed copper powder (≈0,25g) was added to remove elemental sulfur. Elemental sulfur may be present in a soil sample if anaerobe conditions occurred, usually caused by waterlogging, such as in marshes. A color change of copper from rust to black indicated elemental sulfur presence in the sample. In all 55 extracts, unreacted copper was still present in the extracts. Therefore, no further addition was necessary. If this wouldn't have been the case, copper powder would have been added until no further color change. After this clean-up, the samples were ready for silica-based SPE clean-up. An illustration of the summarized acid clean-up from ASE collection vials to acid-cleaned sample is presented in figure 13 below.

Silica-based Solid-Phase Extraction (SPE)

Silica-based SPE clean-up efficiency is dependent on the silica particle properties (e.g. pore volume, surface area and number of unreacted functional groups). In this project, 60 Å pore diameter with 63-200µm irregular particle size, 0,75cm^3/g pore volume, and ~500 m^2/g surface area was applied as acceptable particle properties for efficient clean-up. Silica particles' functional groups for attachment points of interfering compounds are silonal polar groups (Si-OH). To increase the efficiency of these functional groups and the silica particles, silica gel was activated by burning the powder at 550 degrees to obtain maximum surface area and number of unreacted silonal groups.

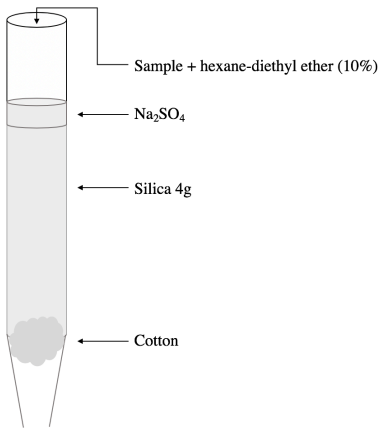

Figure A.2.2.1: Set-up of silica-based SPE clean-up method.

The silica columns were dry-packed as presented in Figure A.2.2.1 above. Before the sample was added on top, the column was rinsed and wetted with 30mL elution solvent hexane-diethyl ether 10%. By closing the tap, we ensured that the columns did not run completely dry at this stage. A 60 mL collection vial was placed under the column before each sample was added to their respective silica column with three small hexane-diethyl ether washes. The samples were then eluted with 30mL of hexane-diethyl ether 10%. This volume was collected and later evaporated on a turbovap until 0,5mL concentrated sample. The solvent was changed from hexane-diethyl ether to isooctane during this procedure by rinsing the turbovap glass walls three times with ca. 1 mL of isooctane and evaporating the solvent after each addition. The 0,5mL sample was then transferred to small conical vials à 1mL with two small isooctane washes to rinse out the turbovap glasses in order to ensure quantitative transfer of all analytes. Thereafter, the sample was blown down with nitrogen gas (N_2) to obtain a ca. 150µL sample. 20µL recovery standard solution, containing 98,8 pg/µL tetrachloronaphthalene, was added to the samples.

Wax removal by centrifugation at low temperature

The extraction method and the high soil organic matter content in the soil samples, it became clear that the cleaned extracts still contained large amounts of waxes. These were most likely cuticular waxes from decomposing tree leaves or needles. These waxes are acid-stable and were hence not removed during the sulfuric acid clean-up, and they were not efficiently retained by the silica column either. This became evident when white flakes were found in the cleaned extracts after they had been stored at 4 °C. These waxes also interfered with the instrumental analysis even when the wax flakes dissolved as the samples reached room temperature again. Therefore, it was necessary to further clean the samples before instrumental analyses. To achieve this, the chilled samples were centrifuged at -9 degrees and 2500 rpm for 20 min and then kept cold until further processing. Using disposable capillary glass pipettes, aliquots à 20 µL were quickly transferred from the 150 µL samples to chromatographic injection vials. Care was taken to avoid transfer of any of the waxes that had accumulated at the conical bottom of the vials during cold centrifugation. This is an efficient and cost-effective method to remove waxes and prevent complications in the instrumental analysis.

A.2.3 Soil characterization by soil organic matter (SOM) determination

A prior to determination of soil organic matter (SOM %), all soil samples were oven-dried. For each sample, about 15-20 g wet soil with 0.01 g accuracy was taken out and transferred to an aluminum form. Thereafter, the samples were oven-dried at 80 °C until no further change in weight. This was done by controlling the masses after ca. 24h and 40h. The temperature was chosen to obtain an efficient drying without loss of material through chemical reactions, such as oxidation of organic material (O'Kelly 2005). When the samples were completely dried after about 48h, they were cooled down to room temperature (21°C) in a desiccator before being weighed to 0.01 g accuracy. These weights were used to calculate POP concentrations in soil extracts based on dry weight.

Soil organic carbon in each sample was determined by the loss on ignition method (LOI). For each sample, ca. 3-15 g with 0,0001 accuracy soil was taken out to their respective porcelain crucible and placed in an oven. As a consequence of the high SOM content in a majority of the soil samples, a temperature program with increasing temperature (105- to 575 °C) per time (0-5h) needed to be used to avoid rapid burning and upwelling of ash (Sluiter et al. 2008). This could have caused a loss of sample and consequently, incorrect measurement of SOM. The temperature program is presented in Table A.2.3.1 below. After the temperature program was completed, the samples were weight with 0.0001 accuracy and amount SOM was calculated using equation A.2.3.1 below.

Eq. A.2.3.1

$$SOM\ \% = \left(\frac{(dry\ weight\ 80°C\ \ (g) - LOI\ weight\ 575°C\ (g))}{dry\ weight\ 80°C\ (g)} \right) x\ 100\ \%$$

Table A.2.3.1 Loss-on-ignition temperature program

Rate °C/min	**Temperature °C**	**Hold time hour.**
	105	0.5
10	250	2.0
10	575	4.0
	105	2.0

A.3 Instrumental analysis

A.3.1 Gas chromatography parameters

Table A.3.1.1 GC column parameters applied for the analysis of the compound groups.

Analyte group	**GC-column**				
	stationary phase	length [m]	inner diameter [mm]	film thickness [µm]	injector
DDT & HCH	ZB Multiresidue-1	30	0,25	0,25	programmable temperature vaporizer (PTV), see Table A.3.1.3 for parameters
PCB & chlorobenzenes	HT-8	50	0,22	0,15	
PBDE	Rtx 1614	15	0,25	0,1	
Nybrom	Rtx 1614	15	0,25	0,1	
CP & dechloranes	HP-5MS UI	2x15	0,25	0,25	PTV

Table A.3.1.2 GC program.

mobile phase	ramp 2 [°C/min]	oven temperature 3 [°C]	hold time 3 [min]	initial hold time [min]	ramp 1 [°C/min]	oven temperature 1 [°C]	hold time 1 [min]	ramp 1 [°C/min]	oven temperature 2 [°C]	hold time 2 [min]	ramp 2 [°C/min]	oven temperature 3 [°C]	hold time 3 [min]	ramp 2 [°C/min]	oven temperature 3 [°C]	hold time 3 [min]
He				1	22	280	3,13									
He				2,7	25	170	1	3	210	0	100	320	5,6			
He				2,5	22	220	0	7	280	0	40	300	5,6			
He				2,5	22	220	0	7	280	0	40	300	7			
He	70	325	10	2	70	280	1	10	280	1	10	310	0	70	325	10

The samples were introduced with the use of a programmed temperature vaporization (PTV) inlet in solvent vent mode, as presented in Table A.3.1.3 below. The temperature program injects the sample without destroying compounds present. More volatile compounds will first be vaporized (e.g. solvents) and travel through the column. Thereafter, less volatile compounds will follow because of differences in the compounds' vapor pressure.

Table A.3.1.3 Injector programmable temperature vaporizer – PTV parameters

Analyte group	vent pressure [psi]	vent flow [mL/min]	vent time [min]	purge flow [mL/min]	purge time [min]	initial temperature [°C]	initial hold time [min]	rate 1 [°C/min]	temperature 1 [°C]	hold time 1 [min]	rate 2 [°C/min]	temperature 2 [°C]	hold time 2 [min]	rate 3 [°C/min]	hold time 3 [min]
DDT & HCH	2,5	10	0,2	50	1	60	0,2	550	220	8	100	240	5,5		
PCB & chlorobenzenes	1,5	30	0,4	50	2	50	0,35	300	285	3	300	310	45	300	0,8
PBDE	1,5	30	0,4	50	2,15	50	0,35	250	300	25	50	50			
Nybrom	1,5	30	0,4	50	2,15	50	0,35	250	300	25	50	50			
CP & dechloranes	0,4	15	0,3	50	2	60	0,35	500	320	3	10	290	5		

A.3.2 Mass spectrometer parameters

Table A.3.2.1 General Mass spectrometer parameters

MS parameters Autospec	
MS mode	Electron impact ionisation (EI)
Interface temperature	DDT & HCH: 270 °C
	PCB & chlorobenzenes: 285 °C
	PBDE: 280 °C
	Nybrom: 280 °C
Ion source temperature	DDT & HCH: 270 °C
	PCB & chlorobenzenes: 285 °C
	PBDE: 280 °C
	Nybrom: 280 °C
Acceleration voltage	7500 V
Detector voltage	385 V
MS lock mass standard	Perfluorokerosene (PFK)
MS parameters Q-ToF	
MS mode	ECNI
Interface temperature	280 °C
Ion source temperature	120 °C
Quadrupole temperature	106 °C

Table A.3.2.2 General Mass spectrometer parameters for the different compound groups.

DDT & HCH								
SIM function	start time [min]	end time [min]	isomer group	^{12}C mass 1	^{12}C mass 2	^{13}C mass 1	^{13}C mass 2	lock mass
1	8	10,89	HCH	216,9145	218,9116	222,9347	224,9317	218,9856
2	10,89	15	TCN	263,9067	265,9038			242,9856
			DDE	246,0003	247,9974	258,0406	260,0377	
			DDD	235,0081	237,0052	247,0484	249,0454	
			DDT	235,0081	237,0052	247,0484	249,0454	
PCB & chlorobenzenes								
SIM function	start time [min]	end time [min]	isomer group	^{12}C mass 1	^{12}C mass 2	^{13}C mass 1	^{13}C mass 2	lock mass
1	7	17,8	PeCB	249,8491	251,8462	255,8693	257,8663	242,9856
2	17,8	23	HCB	283,8102	285,8072	293,8244	295,8214	280,9825
3	23	32,4	TCN	263,9067	265,9038			280,9825
			tri-CBs	255,9613	257,9584	268,0016	269,9986	
			tetra-CBs	289,9224	291,9194	301,9226	303,9597	
4	32,4	38,35	penta-CBs	325,8804	327,8775	337,9207	339,9177	330,9792
			hexa-CBs	359,8415	361,8385	371,8817	373,8788	
5	38,35	46,5	hexa-CBs	359,8415	361,8385	371,8817	373,8788	380,97605
			hepta-CBs	393,8025	395,7995	405,8428	407,8398	
			octa-CBs	427,7635	429,7606			

6	46,5	49,4	nona-CBs	461,7246	463,7217			480,9697
			deca-CB	497,6867	499,6798	509,7229	511,7199	
PBDE								
SIM function	start time [min]	end time [min]	isomer group	^{12}C mass 1	^{12}C mass 2	^{13}C mass 1	^{13}C mass 2	lock mass
1	3,5	7,7	TBA	343,7870	345,7850			330,9792
2	7,7	9,5	TCN	263,9067	265,9038			268,9825
3	9,5	10,4	tri-BDEs	405,8027	407,8007	417,8429	419,8409	416,9760
4	10,4	12,1	tetra-BDEs	483,7132	485,7112	495,7534	497,7514	492,9697
5	12,1	13,55	penta-BDEs	563,6217	565,6197	575,6619	577,6598	580,9633
6	13,55	15,6	hexa-BDEs	641,5322	643,5302	653,5724	655,5704	654,6901
7	15,6	17,75	hepta-BDEs	721,4407	723,4386	733,4809	735,4788	742,9537
8	17,75	21,4	octa-BDEs	799,3511	801,3491			754,9537
			nona-BDEs	719,4250	721,4230			
9	21,4	24,3	deca-BDE	797,3355	799,3335	809,3757	811,3737	792,9505
Nybrom								
SIM function	start time [min]	end time [min]	isomer group	^{12}C mass 1	^{12}C mass 2	^{13}C mass 1	^{13}C mass 2	lock mass
1	7	8,4	ATE	369,8027	371,8007			380,976
2	8,4	10,05	TCN	263,9067	265,9038			268,9825
			TBECH	264,9227	266,9207			
			BATE	329,7714	331,7693			
			PBBz	469,5975	471,5954	479,6135	481,6115	
3	10,05	10,6	PBDE 28			417,8429	419,8409	480,976
			PBT	485,6111	487,609			
			PBEB	499,6267	501,6247			
4	10,6	11,7	DPTE	329,7714	331,7693			430,9728
			PBDE 47			495,7534	497,7514	
			HBB	547,501	549,506	559,522	561,52	
5	11,7	13,6	EHTBB	418,674	420,672	426,6921	428,69	430,9728
6	13,6	17,3	BTBPE	356,7948	358,7928	362,8149	364,8129	354,9792
7	17,3	19,8	BEHTBP	462,6639	464,6619			454,9728
8	19,8	26,2	DBDPE	484,6033	486,6012	491,6267	493,6247	492,9697

A.4 Quantification

The quantification of individual compound in MassHunter and TargetLynx was performed based on the following principles:

A relative response factor, RRF_i, is calculated for individual components relative to the ISTD on the basis of analysis of quantification standard with known concentration.

Eq.A.4.1

$$RRF_i = \frac{amount_{ISTD} * area_i}{amount_i * area_{ISTD}}$$

Where $amount_{ISTD}$ is the concentration of ISTD multiplied with volume injected, $amount_i$ is the concentration of component *i* multiplied with volume injected, and the $area_{i \text{ and ISTD}}$ is area of component *i* and the ISTD. The sample quantification is determined based on the RRF, the amount of ISTD added, and the area of individual components *i*.

Eq.A.4.2

$$Amount_i = \frac{amount_{ISTD} * area_i}{RRF_i * area_{ISTD}}$$

The ISTD recoveries are calculated based on the amount of recovery standard added before instrumental analysis and quantification. The relative response factor based on the recovery standard, RRF_g, is calculated form each ISTD-component on the basis of quantification standard analysis.

Eq.A.4.3

$$RRF_g = \frac{amount_{GSTD} * area_{ISTD}}{amount_{ISTD} * area_{GSTD}}$$

Where $amount_{GSTD}$ is the concentration of the recovery standard multiplied with injection volume, and $area_{GSTD}$ is the area of the recovery standard.

Eq.A.4.4

$$Rec\ \% = \left(\frac{amount\ found\ (pg)}{amount\ added\ (pg)}\right) * 100$$

Appendix B

B.1 Sampling sites

Table B.1.1 Sampling site locations and classifications in Norway.

Sample nr:	Sampling site:	Soil type:	Lat:	Long:	Dry weight	SOM fraction
1	Bærum	Urban	59,95	10,49	13,10	0,15
2	Holmenkollen	Urban	59,98	10,68	15,76	0,07
3	Maridalen	Urban	59,97	10,77	8,33	0,19
4	Skøyen	Urban	59,92	10,69	12,66	0,09
5	Sofienbergparken	Urban	59,92	10,77	14,26	0,11
6	Alnabru	Urban	59,92	10,84	14,09	0,09
7	Gamle Oslo, svartedalsparken	Urban	59,90	10,79	15,32	0,11
8	Botanisk Hage	Urban	59,92	10,77	13,49	0,14
9	Dronninparken	Urban	59,92	10,72	12,13	0,10
10	Kjeller	Urban	59,98	11,05	8,11	0,10
11	Grøtfjorden	Background	69,78	18,60	1,67	0,85
12	Karpdalen	Background	69,66	30,42	0,70	0,81
13	Neiden	Background	69,65	29,47	0,43	0,90
14	Ekkerøy	Background	70,11	30,18	2,14	0,85
15	Vardø	Background	70,44	30,86	1,21	0,94
16	Vestre Tana	Background	70,47	27,95	1,30	0,95
17	Hopseidet	Background	70,80	27,73	2,10	0,58
18	Lakselv	Background	69,83	25,16	8,45	0,12
19	Karasjok	Background	69,48	25,48	4,41	0,13
20	Slåtten	Background	70,73	24,60	1,03	0,94
21	Kvænangsbotn	Background	69,72	22,07	4,99	0,14
22	Tamokdalen	Background	69,19	19,78	3,19	0,18
23	Øverbygd	Background	69,01	18,98	3,66	0,20
24	Innhavet	Background	67,97	15,97	2,06	0,54
25	Bø i Vesterålen	Background	68,77	14,67	1,39	0,86
26	Andøya	Background	69,28	16,01	4,69	0,27
27	Svolvær	Background	68,23	14,51	2,53	0,32
28	Moskenes	Background	67,90	13,06	0,91	0,87
29	Bodø	Background	67,39	14,66	3,98	0,20
30	Øvrevatn	Background	67,22	15,59	4,73	0,14
31	Balvatn	Background	67,03	15,99	3,32	0,22
32	Junkerdal	Background	66,81	15,43	1,69	0,85
33	Tustervatn	Background	65,83	13,91	4,37	0,25
34	Namsvatn	Background	64,97	13,59	2,22	0,25

35	Aglen	Background	64,63	11,07	1,61	0,65
36	Nomyra	Background	64,10	10,51	1,32	0,98
37	Bjørndalselva	Background	63,82	10,24	2,57	0,23
38	Hummelfjell	Background	62,46	11,30	4,24	0,24
39	Valldalen	Background	62,08	12,12	2,16	0,89
40	Osen	Background	61,25	11,74	1,22	0,98
41	Lom	Background	61,86	8,87	7,66	0,11
42	Kårvatn	Background	62,78	8,88	11,96	0,04
43	Utvikfjellet	Background	61,79	6,49	2,57	0,36
44	Furumeset	Background	61,30	5,04	1,11	0,94
45	Ulvik	Background	60,59	6,86	1,00	0,89
46	Vatnedalen	Background	59,45	7,39	8,12	0,12
47	Utbjoa	Background	59,64	5,59	0,95	0,97
48	Ualand	Background	58,51	6,37	2,46	0,45
49	Birkenes	Background	58,39	8,25	2,74	0,57
50	Solheimsfjell	Background	58,94	8,83	1,66	0,89
51	Hvittingfoss	Background	59,49	9,79	7,21	0,15
52	Prestebakke	Background	59,00	11,53	2,86	0,49
53	Aremark	Background	59,22	11,73	4,20	0,42
54	Aurskog	Background	59,98	11,50	3,67	0,29
55	Hurdal	Background	60,37	11,08	2,20	0,69

B.2 Raw data

Table B.2.1 Concentrations for HCB, PeCB, and the PCB-homologue groups tri to penta, and the indicator PCB-congeners: 28, 52,101, and 118 in pg/g dw for all sampling sites (n=55).

Sampling site	PeCB	HCB	PCB (28)	Totals Tri PCB*	PCB (52)	Totals Tetra PCB**	PCB (101)	PCB (118)	Totals Penta PCB***
1	99,12	246,50	2,39	11,75	5,24	47,77	79,61	67,93	448,91
2	200,41	16727,44	1,55	9,89	4,28	32,96	44,19	69,31	282,58
3	216,71	457,92	14,58	60,68	58,05	387,48	506,24	536,43	2623,14
4	488,74	459,86	13,59	77,16	203,32	677,19	956,30	639,10	4163,32
5	980,47	8526,17	27,00	150,17	97,09	427,45	476,96	431,16	2112,95
6	226,20	201,68	13,75	74,81	32,62	202,73	341,10	345,18	1558,53
7	1236,97	789,15	29,91	155,32	66,07	356,17	373,58	392,50	1817,64
8	475,22	382,02	114,89	435,87	138,49	739,57	665,06	519,01	3276,85
9	239,26	303,39	36,75	196,15	151,95	979,08	758,04	625,97	3073,23
10	30,25	109,16	<MDL	<MDL	3,63	14,26	31,83	30,28	130,09
11	217,20	895,35	<MDL	<MDL	14,77	71,93	129,38	131,15	369,13
12	259,17	1985,96	16,48	<MDL	38,36	159,57	239,34	321,31	837,82
13	<MDL	228,46	<MDL	<MDL	<MDL	<MDL	37,45	39,01	<MDL
14	111,18	2194,61	18,66	<MDL	52,44	168,78	177,04	170,08	<MDL
15	173,96	2131,60	21,41	<MDL	51,47	143,02	128,42	129,28	<MDL
16	222,50	2130,57	21,97	<MDL	28,38	129,20	150,65	173,07	<MDL
17	108,54	350,68	<MDL	<MDL	<MDL	<MDL	6,35	8,28	<MDL
18	158,03	435,93	2,17	<MDL	23,95	35,80	66,10	56,99	168,22
19	49,90	472,43	3,61	<MDL	4,88	20,36	31,96	23,72	77,68
20	151,25	3063,75	18,23	55,02	72,02	233,15	182,20	189,20	<MDL
21	105,86	411,39	6,02	16,58	3,38	17,04	17,96	18,38	<MDL
22	<MDL	225,37	<MDL	<MDL	2,02	10,67	19,13	21,54	<MDL
23	94,61	523,71	2,28	<MDL	5,48	21,46	53,40	55,82	152,65
24	<MDL	294,63	<MDL	<MDL	7,39	19,65	37,22	26,18	<MDL
25	<MDL	575,59	<MDL	<MDL	7,48	<MDL	36,24	33,19	<MDL
26	72,73	695,17	1,81	<MDL	4,09	21,58	37,26	72,90	<MDL
27	<MDL	277,11	9,67	34,53	36,36	114,90	159,23	163,97	468,17
28	<MDL	763,58	<MDL	<MDL	11,64	29,23	51,74	90,43	<MDL
29	193,03	1130,32	4,01	14,63	6,24	33,58	77,00	108,49	276,25
30	<MDL	98,93	<MDL	<MDL!	<MDL	<MDL	6,45	7,08	<MDL
31	118,62	467,25	3,27	<MDL	4,77	40,10	60,27	65,12	<MDL
32	189,30	2913,51	43,85	<MDL	65,94	296,97	339,10	322,28	942,50

33	<MDL	205,64	<MDL	<MDL	1,58	6,50	21,46	16,19	58,11
34	202,82	1002,27	10,89	35,41	18,33	80,73	109,31	116,21	<MDL
35	485,46	13012,34	59,59	<MDL	299,37	1422,28	1232,32	1872,27	<MDL
36	439,80	1787,60	<MDL	<MDL	34,50	54,17	48,93	23,86	<MDL
37	<MDL	251,62	<MDL	<MDL	<MDL	<MDL	6,04	2,57	<MDL
38	57,82	441,95	2,99	<MDL	6,16	31,07	45,81	53,81	<MDL
39	252,06	2125,20	34,61	83,73	67,62	195,59	258,41	228,20	<MDL
40	137,32	1024,26	6,55	<MDL	23,73	61,71	120,68	89,81	<MDL
41	97,65	516,57	1,65	9,65	3,90	20,18	85,13	59,46	208,14
42	<MDL	6,34	<MDL	<MDL	<MDL	<MDL	1,31	0,74	<MDL
43	53,09	262,01	<MDL	<MDL	4,86	15,85	31,45	29,93	<MDL
44	210,07	3066,54	8,16	<MDL	94,25	212,55	416,76	432,98	<MDL
45	<MDL	729,25	7,30	<MDL	23,09	84,46	222,71	221,83	626,33
46	16,50	260,33	1,40	<MDL	9,51	27,30	38,21	35,45	<MDL
47	254,80	869,08	9,42	<MDL	63,08	200,20	322,50	383,56	<MDL
48	93,90	232,40	<MDL	<MDL	7,48	<MDL	50,69	57,54	<MDL
49	457,52	1405,99	30,20	71,54	44,21	219,96	297,50	500,14	1118,28
50	270,18	2021,57	50,63	136,05	117,76	345,33	538,46	713,37	1756,74
51	176,59	692,88	15,97	<MDL	15,03	108,36	161,25	225,68	532,02
52	581,53	1810,80	21,37	57,85	82,44	245,21	451,20	415,41	1175,84
53	161,02	952,13	7,44	26,41	17,42	106,81	293,86	325,22	832,61
54	173,89	445,05	9,42	25,31	10,86	78,01	133,27	170,73	416,64
55	348,24	1865,03	31,23	89,52	46,95	223,33	463,52	608,10	1506,34

*Tri-PCBs: congener number 18, 28, 31, 33, and 37.

**Tetra-PCBs congener number 52, 47, 66, and 74.

***Penta-PCBs: congener number 99, 101, 105, 114, 122, 118, 123.

Table B.2.2 Concentrations for the PCB-homologue groups hexa to nona, and the indicator PCB-congeners: 153, 138, and 180 in pg/g dw for all sampling sites (n=55).

Sampling site	PCB (153)	PCB (138)	Totals 1 Hexa PCB*	PCB (180)	Totals Hepta PCB**	PCB (194) (octa)	PCB (206) (nona)	PCB (209) (nona)
1	443,21	444,18	871,41	225,70	683,71	33,96	26,00	49,84
2	285,32	307,83	582,81	146,72	515,81	33,44	45,80	166,19
3	1282,69	1447,88	3160,51	591,92	1842,53	85,02	56,39	75,99
4	2152,13	2299,65	7259,62	1800,54	5832,46	279,17	97,84	25,51
5	1136,39	1033,61	2824,95	871,08	2853,33	325,01	324,78	54,46
6	830,02	1025,03	1930,20	411,20	1317,46	67,03	37,32	14,96
7	1279,38	1341,37	2974,25	625,90	1987,94	99,14	74,72	53,59
8	1957,66	2262,10	6097,77	1395,02	4552,62	218,98	151,87	122,83

9	1352,69	1318,44	3560,72	637,57	2181,53	84,75	39,47	17,69
10	108,76	98,55	228,37	39,47	117,33	6,15	5,26	12,12
11	267,91	239,88	811,62	106,31	308,12	21,57	11,26	39,54
12	500,21	554,05	1556,53	190,07	441,75	25,63	21,40	56,92
13	87,52	70,75	#VERDI!	27,79	<MDL	4,25	1,56	9,14
14	275,93	235,70	818,07	85,61	258,52	13,92	10,91	23,35
15	201,55	178,02	593,91	57,85	<MDL	11,93	7,50	16,49
16	278,26	310,49	872,31	162,14	369,16	14,89	17,69	33,84
17	26,09	20,52	84,20	9,35	32,30	3,58	3,07	7,91
18	100,47	102,96	318,63	44,23	100,80	10,42	8,67	8,00
19	50,54	52,81	159,88	24,25	<MDL	2,64	2,03	5,19
20	373,86	286,38	1007,66	141,77	373,41	22,67	19,14	48,43
21	33,08	36,77	104,92	13,98	41,90	2,35	1,69	3,51
22	47,23	52,12	145,95	18,98	52,67	3,30	3,75	10,07
23	107,43	136,80	360,65	52,36	129,26	7,14	7,89	15,24
24	75,83	57,64	214,07	37,26	96,68	8,28	14,23	25,46
25	72,76	54,29	201,52	35,13	130,90	12,97	19,29	69,45
26	267,34	216,96	646,42	102,66	246,59	20,75	15,06	32,53
27	469,59	525,38	1390,94	234,56	531,63	45,76	46,31	114,68
28	262,48	301,09	748,06	140,66	354,43	37,12	59,26	217,65
29	274,46	315,01	851,86	129,10	300,95	20,32	22,92	56,20
30	18,33	13,36	48,95	6,41	<MDL	1,55	1,71	5,71
31	154,80	124,52	420,13	58,33	<MDL	10,73	9,67	16,07
32	681,36	768,32	2161,90	309,19	827,84	36,20	29,03	63,04
33	59,43	79,94	204,98	23,70	58,07	3,04	3,63	8,34
34	198,96	225,04	597,28	69,89	178,23	12,11	12,22	29,29
35	4271,57	3408,15	11006,79	1634,36	3602,20	299,67	256,63	406,29
36	59,51	47,16	<MDL	<MDL	<MDL	4,37	<MDL	2,76
37	18,40	14,86	<MDL	5,28	<MDL	1,79	3,77	10,52
38	134,10	114,97	366,45	66,66	160,54	11,96	10,27	19,82
39	537,64	484,52	1603,17	291,85	<MDL	43,95	43,39	73,63
40	192,75	209,73	640,09	84,37	<MDL	16,60	34,99	19,14
41	165,58	195,47	557,49	86,13	200,61	10,32	11,77	25,26
42	3,41	2,42	<MDL	1,41	<MDL	0,59	0,72	0,35
43	75,23	58,32	200,79	30,99	<MDL	6,08	6,94	21,23
44	1185,67	1053,34	3194,76	527,73	<MDL	112,96	90,52	224,00
45	559,44	663,35	1716,59	289,39	682,29	63,51	62,45	120,29
46	89,49	74,99	257,98	52,95	<MDL	11,70	8,45	23,94
47	918,00	812,39	2634,19	592,57	1294,72	160,11	155,86	507,27

48	188,18	192,82	565,69	113,83	271,61	36,19	41,67	169,47
49	1301,59	1091,77	3634,44	872,02	1872,08	225,33	168,76	677,48
50	1668,80	2072,33	5582,36	1384,35	2995,23	273,88	199,90	713,25
51	475,05	335,58	1250,13	215,50	512,58	53,66	48,53	207,69
52	1056,44	1247,29	3348,75	613,49	1369,49	103,09	90,77	341,21
53	705,43	847,34	3651,85	407,82	890,72	77,44	68,61	218,27
54	331,55	384,38	1044,77	206,22	455,21	37,41	30,68	101,85
55	1625,52	1894,91	5125,48	1028,30	2400,17	171,07	172,56	516,30

* Hexa-PCBs: congener number: 153, 141, 149, 138, 167, 128, 156, 157.
** Hepta-PCBs: congener number: 180, 170, 183, 187, 189.

Table B.2.3 Concentrations for Σ_6DDx and the HCHs in pg/g dw for all sampling sites (n=55).

Sampling site	o,p'-DDE	p,p'-DDE	o,p'-DDD	p,p'-DDD	o,p'-DDT	p,p'-DDT	sumDDX	a-HCH	b-HCH	g-HCH
1	12,57	1429,26	3,38	9,54	123,34	444,28	2022,36	11,21	3,66	12,20
2	1,91	249,47	1,99	5,44	94,62	273,88	627,31	21,83	37,55	21,25
3	7,07	2757,99	4,08	31,40	468,13	1823,90	5092,58	25,75	10,39	22,67
4	3,73	437,58	8,65	43,23	84,31	630,64	1208,14	12,52	4,68	9,82
5	56,32	14792,13	50,31	209,74	1098,91	5072,01	21279,42	59,44	12,13	14,15
6	0,82	123,86	2,14	4,85	34,72	143,53	309,93	4,74	2,95	6,53
7	6,51	590,45	8,86	36,81	116,33	634,79	1393,76	10,69	2,82	10,88
8	35,43	2473,27	259,15	1087,93	1841,65	6095,98	11793,42	10,21	14,56	98,55
9	3,08	241,46	6,64	22,02	68,41	300,61	642,20	8,82	2,70	20,87
10	1,08	41,19	1,92	<MDL	4,44	26,23	74,85	5,46	<MDL	42,53
11	2,31	278,67	<MDL	33,67	293,25	332,17	940,07	106,31	71,56	67,35
12	19,69	466,38	114,04	187,67	1702,80	<MDL	2490,58	985,29	325,23	315,26
13	<MDL	78,29	<MDL	<MDL	<MDL	<MDL	78,29	55,79	42,27	25,87
14	107,03	391,88	36,85	20,84	917,69	1805,70	<MDL	1285,07	394,74	391,46
15	32,50	335,30	76,52	177,61	1477,46	2022,07	4121,46	2701,41	975,67	969,89
16	<MDL	410,97	45,48	116,99	375,33	1504,89	2453,66	1314,93	847,30	841,91
17	<MDL	34,53	<MDL	4,77	328,58	45,61	413,49	30,63	9,80	6,46
18	0,80	30,03	1,33	3,18	37,25	88,67	161,27	1485,91	441,69	440,86
19	4,76	54,68	6,38	15,23	287,42	241,89	610,36	41,62	19,66	18,07
20	36,03	496,26	71,81	111,40	1422,87	1152,28	3290,65	847,13	339,09	332,32
21	0,80	32,12	3,26	7,43	60,09	90,28	193,98	208,69	45,71	44,31
22	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0,00	22,51	40,37	38,18
23	4,41	133,95	14,49	28,13	328,67	386,60	896,26	84,14	27,10	25,19
24	8,36	252,63	15,57	17,94	297,58	226,32	818,40	51,78	25,90	22,49
25	2,41	70,16	4,11	10,69	84,21	113,99	285,57	119,68	71,98	66,94
26	2,20	234,54	4,45	12,79	52,92	225,44	532,35	102,37	57,99	56,50

27	5,93	417,90	3,39	32,47	121,90	359,11	940,69	152,44	59,63	56,87
28	2,92	291,91	4,67	15,78	38,06	101,90	455,25	46,51	30,91	23,20
29	10,15	292,28	2,82	6,24	471,71	49,58	832,77	111,17	55,28	53,52
30	<MDL	14,89	<MDL	<MDL	150,69	MDL	165,58	6,78	4,86	3,38
31	1,32	178,71	<MDL	<MDL	224,83	104,28	509,14	178,46	71,61	69,50
32	27,14	690,99	53,73	100,84	5070,38	2909,41	8852,47	5857,02	1894,68	1890,54
33	1,38	16,17	0,39	<MDL	4,87	0,46	23,28	2,14	<MDL	<MDL
34	1,95	63,85	8,01	13,13	169,77	138,46	395,16	804,73	191,03	187,87
35	14,42	920,65	159,04	355,19	440,71	563,61	2453,61	265,19	77,72	73,38
36	13,19	137,66	5,41	12,53	282,08	283,68	734,56	339,95	225,93	220,61
37	<MDL	27,97	<MDL	<MDL	13,21	<MDL	41,18	<MDL	<MDL	<MDL
38	7,42	410,79	15,84	42,97	855,09	1197,41	2529,52	1125,96	736,88	735,23
39	77,02	2991,33	151,49	358,91	9021,64	19735,19	32335,58	8016,61	2544,46	2541,22
40	44,47	511,04	9,34	21,59	613,05	517,49	1716,98	130,40	127,70	121,94
41	21,64	490,25	28,31	109,57	835,68	1710,55	3196,01	499,00	221,95	221,03
42	<MDL	4,69	<MDL	<MDL	<MDL	<MDL	4,69	<MDL	<MDL	<MDL
43	4,81	428,03	32,00	165,38	202,05	530,38	1362,66	17,14	9,49	6,77
44	25,18	3123,53	193,47	1046,29	785,57	4391,86	9565,89	537,83	410,78	404,48
45	11,54	5374,82	18,03	91,98	690,51	2274,40	8461,28	210,08	182,77	175,76
46	3,52	263,92	11,62	41,61	448,49	1025,38	<MDL	703,80	699,71	698,85
47	11,99	943,12	45,01	76,19	1030,10	3546,58	5652,99	933,08	696,85	689,50
48	3,01	445,58	<MDL	12,68	66,74	309,10	837,12	32,38	28,02	25,17
49	6,91	557,36	8,28	24,27	478,53	751,18	1826,53	508,36	703,14	700,58
50	64,54	4257,21	126,43	489,09	7933,83	24258,51	37129,61	1703,96	922,03	917,81
51	2,06	374,82	4,07	9,90	252,02	349,85	992,72	266,91	146,06	145,09
52	21,70	1810,43	31,59	310,20	1414,40	6622,86	10211,17	609,76	408,54	406,10
53	9,20	1527,52	13,63	6,74	1042,08	1262,38	3861,55	56,36	39,55	37,88
54	2,42	180,87	6,45	20,31	167,05	360,47	737,56	192,55	164,32	162,41
55	7,89	361,97	<MDL	56,70	1022,02	692,88	2141,46	203,62	133,90	130,72

Table B.2.4 Concentrations for the PBDE-congeners analyzed at all sampling sites (n=55) in pg/g dw (see also Table B.2.5 below)

Sampling site	PBDE-17	PBDE-28	PBDE-49	PBDE-71	PBDE-47	PBDE-66	PBDE-77	PBDE-100	PBDE-119	PBDE-99	PBDE-85	PBDE-126	PBDE-154
1	0,19	2,17	9,50	<MDL	170,76	5,37	<MDL	40,70	<MDL	131,25	3,34	2,33	7,68
2	<MDL	0,04	2,40	1,68	34,47	2,71	0,32	15,59	<MDL	40,76	1,62	<MDL	3,01
3	2,08	9,89	40,42	<MDL	560,11	48,24	3,63	127,49	5,19	415,96	13,74	9,32	23,96
4	<MDL	1,44	16,04	<MDL	292,06	5,72	<MDL	78,07	<MDL	292,81	<MDL	<MDL	23,70
5	<MDL	1,36	18,11	441,93	318,48	7,12	0,39	103,70	<MDL	410,44	12,60	<MDL	31,30
6	0,58	3,18	8,90	<MDL	163,91	26,64	2,45	52,18	<MDL	213,97	8,63	5,82	7,88

7	<MDL	0,34	4,49	112,55	75,62	2,35	0,32	16,60	<MDL	49,35	0,66	<MDL	3,17
8	0,72	3,03	15,65	<MDL	248,99	6,50	<MDL	81,59	<MDL	243,66	<MDL	<MDL	14,73
9	<MDL	0,51	8,82	204,30	141,44	3,18	<MDL	29,60	<MDL	88,87	2,39	<MDL	5,13
10	<MDL	0,69	3,20	<MDL	33,44	1,35	<MDL	13,35	<MDL	30,45	<MDL	<MDL	2,41
11	<MDL	<MDL	14,79	<MDL	257,83	6,10	<MDL	38,66	<MDL	151,14	<MDL	<MDL	<MDL
12	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13	<MDL	<MDL	36,79	14,39	891,18	18,76	<MDL	89,50	<MDL	321,38	<MDL	18,37	<MDL
14	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	4,46	<MDL	6,92	<MDL	<MDL
15	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
16	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	24,29	<MDL	63,36	<MDL	<MDL	<MDL
17	<MDL	<MDL	9,46	3,27	<MDL	4,51	<MDL	10,30	<MDL	<MDL	<MDL	4,08	<MDL
18	<MDL	<MDL	<MDL	12,19	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	12,39	<MDL
19	<MDL	<MDL	<MDL	<MDL	<MDL	3,90	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
20	<MDL	27,39	31,07	<MDL	876,76	19,47	<MDL	78,64	<MDL	312,33	<MDL	<MDL	<MDL
21	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
22	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
23	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	2,54	<MDL	<MDL	<MDL	<MDL	<MDL
24	<MDL	<MDL	<MDL	32,43	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	33,26	<MDL
25	<MDL	<MDL	<MDL	2,89	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	4,11	<MDL
26	<MDL	<MDL	5,11	<MDL	88,16	2,77	<MDL	25,39	<MDL	73,23	2,09	<MDL	3,74
27	<MDL	<MDL	9,03	<MDL	<MDL	7,03	<MDL	22,24	<MDL	99,05	2,75	<MDL	5,73
28	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
29	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	876,28	<MDL	<MDL	<MDL	<MDL	1095,45
30	<MDL	6,51	23,57	<MDL	426,16	27,03	<MDL	118,43	<MDL	465,89	16,13	<MDL	19,99
31	<MDL	<MDL	3,14	<MDL	<MDL	3,95	<MDL	9,35	<MDL	28,00	<MDL	<MDL	<MDL
32	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
33	<MDL	<MDL	<MDL	<MDL	<MDL	19,01	<MDL	<MDL	<MDL	<MDL	0,70	<MDL	1,77
34	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
35	<MDL	<MDL	17,70	<MDL	167,33	10,18	<MDL	37,02	<MDL	151,17	<MDL	<MDL	<MDL
36	<MDL	<MDL	11,66	5,13	<MDL	14,21	<MDL	<MDL	<MDL	<MDL	<MDL	6,42	<MDL
37	<MDL	<MDL	<MDL	17,35	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	18,01	<MDL
38	<MDL	<MDL	4,54	<MDL	<MDL	2,44	<MDL	9,57	<MDL	27,40	<MDL	<MDL	<MDL
39	5,28	10,34	32,62	9,14	228,33	19,31	<MDL	53,39	<MDL	163,92	8,71	9,93	5,31
40	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
41	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
42	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
43	<MDL	<MDL	<MDL	2,32	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	2,98	<MDL
44	<MDL	14,72	108,90	<MDL	527,28	81,27	<MDL	131,09	<MDL	843,48	<MDL	<MDL	<MDL
45	<MDL	<MDL	15,85	<MDL	<MDL	16,95	<MDL	22,36	4,38	145,69	6,64	<MDL	7,50

46	<MDL	2,37	11,39	<MDL	65,13	6,58	<MDL	14,82	<MDL	72,11	<MDL	<MDL	<MDL
47	9,54	36,18	178,38	<MDL	994,30	261,38	<MDL	277,35	<MDL	1321,27	<MDL	<MDL	95,28
48	<MDL	<MDL	28,79	3,21	141,70	24,43	<MDL	37,37	<MDL	215,18	<MDL	3,91	<MDL
49	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
50	<MDL	<MDL	46,69	<MDL	372,24	39,07	<MDL	117,30	178,48	504,65	4,14	<MDL	22,90
51	<MDL	<MDL	1,57	<MDL	<MDL	1,36	<MDL	<MDL	<MDL	<MDL	0,58	<MDL	<MDL
52	<MDL	<MDL	16,08	<MDL	185,05	17,08	<MDL	48,18	<MDL	214,42	5,48	<MDL	10,02
53	<MDL	<MDL	9231,61	9039,19	6660,61	89452,67	<MDL	46,74	<MDL	421,54	<MDL	9039,59	13,32
54	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	5,78	<MDL	19,94	<MDL	<MDL	<MDL
55	<MDL	1,28	16,79	-0,27	301,23	14,92	<MDL	100,66	<MDL	322,17	9,92	0,50	13,96

Table B.2.5 Continued concentrations for the PBDE-congeners analyzed at all sampling sites in pg/g dw (n=55).

Sampling site	PBDE-153	PBDE-138	PBDE-156	PBDE-184	PBDE-183	PBDE-191	PBDE-202	PBDE-197	PBDE-196	PBDE-207	PBDE-206	PBDE-209
1	14,34	<MDL	<MDL	1,03	14,42	<MDL	2,70	10,84	10,40	30,40	20,54	297,43
2	6,68	1,74	<MDL	0,69	8,80	0,81	3,11	6,14	6,70	30,63	36,91	886,32
3	51,17	<MDL	<MDL	4,47	49,37	<MDL	7,75	29,56	32,00	108,35	111,52	2342,34
4	54,68	<MDL	<MDL	ND	70,57	<MDL	<MDL	145,32	371,94	5306,15	52981,26	1389574,09
5	48,61	6,59	<MDL	1,25	15,40	<MDL	6,07	19,46	16,10	87,29	109,13	2089,55
6	29,83	0,00	<MDL	1,76	28,28	<MDL	<MDL	12,96	18,33	28,36	29,90	272,16
7	8,40	1,13	<MDL	0,54	11,69	<MDL	1,81	10,60	6,36	25,17	24,48	501,18
8	32,72	ND	<MDL	1,86	23,92	<MDL	7,72	22,12	19,77	125,49	143,71	3921,04
9	8,13	0,98	<MDL	0,59	4,64	<MDL	3,04	7,11	4,39	34,20	44,17	898,08
10	5,96	<MDL	<MDL	1,15	9,71	<MDL	3,44	8,17	6,65	43,09	61,91	3230,43
11	<MDL	<MDL	<MDL	<MDL	7,96	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
12	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	2,63	<MDL	<MDL	<MDL	1321,46
14	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	8,17	<MDL	<MDL	<MDL	<MDL
15	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
16	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	242,15
18	<MDL	<MDL	<MDL	0,51	<MDL	<MDL	<MDL	0,15	0,07	<MDL	<MDL	<MDL
19	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
20	<MDL	<MDL	<MDL	<MDL	10,75	<MDL	<MDL	7,90	<MDL	41,36	<MDL	<MDL
21	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
22	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
23	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
24	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

25	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	2,06	<MDL	<MDL	<MDL	<MDL
26	15,61	<MDL	<MDL	<MDL	13,89	<MDL	<MDL	8,80	9,45	45,19	62,01	3491,04
27	15,10	<MDL	<MDL	<MDL	13,90	<MDL	<MDL	8,29	6,20	31,31	17,48	198,61
28	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
29	1,12	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0,81	2,08	<MDL	<MDL	<MDL
30	53,30	<MDL	<MDL	2,50	51,57	<MDL	<MDL	20,80	31,34	42,80	63,97	593,10
31	4,73	<MDL	<MDL	<MDL	3,91	<MDL	<MDL	2,29	<MDL	<MDL	<MDL	<MDL
32	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
33	<MDL	<MDL	<MDL	2,30	2,65	<MDL	<MDL	2,41	2,52	7,79	<MDL	153,12
34	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	-0,93	<MDL	<MDL	<MDL	<MDL
35	23,17	<MDL	<MDL	<MDL	23,75	<MDL	<MDL	10,94	<MDL	20,15	<MDL	<MDL
36	<MDL	<MDL	<MDL	<MDL	11,54	<MDL	<MDL	<MDL	<MDL	<MDL	32,55	<MDL
37	<MDL	<MDL	<MDL	3,44	<MDL	<MDL	<MDL	3,33	1,88	<MDL	<MDL	<MDL
38	<MDL	<MDL	<MDL	<MDL	6,19	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
39	28,43	<MDL	<MDL	4,44	26,60	<MDL	<MDL	12,70	12,35	27,11	30,85	369,91
40	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
41	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
42	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0,20	0,10	4,09	4,25	<MDL
43	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
44	141,70	<MDL	<MDL	<MDL	117,89	<MDL	<MDL	43,96	298,06	309,33	667,84	1860,63
45	30,79	<MDL	<MDL	<MDL	24,80	<MDL	<MDL	12,45	10,85	44,56	<MDL	<MDL
46	9,64	<MDL	<MDL	<MDL	7,71	<MDL	<MDL	2,40	3,28	8,88	9,90	107,60
47	223,56	<MDL	<MDL	<MDL	237,68	<MDL	<MDL	139,74	126,62	300,96	256,50	2605,00
48	36,89	<MDL	<MDL	<MDL	27,48	<MDL	<MDL	21,07	14,33	48,67	28,87	489,29
49	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
50	68,00	<MDL	<MDL	<MDL	103,55	<MDL	<MDL	29,13	43,06	97,37	103,33	1213,82
51	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0,10	<MDL	<MDL	<MDL	<MDL
52	25,57	<MDL	<MDL	<MDL	28,98	<MDL	<MDL	11,42	49,62	29,78	50,08	384,95
53	58,21	<MDL	<MDL	<MDL	54,80	<MDL	<MDL	26,42	34,95	55,96	60,06	668,33
54	<MDL	<MDL	<MDL	<MDL	2,34	<MDL	<MDL	1,20	<MDL	<MDL	<MDL	<MDL
55	39,89	<MDL	<MDL	0,39	41,53	<MDL	<MDL	17,23	32,84	41,45	43,63	505,70

Table B.2.6 Concentrations for SCCPs (10,5 - 13,9) and MCCPs (14,5 – 17,7) at all sampling sites (n=55) in pg/g dw.

Sampling site	SCCPs (10,5 - 13,9)	MCCPs (14,5 – 17,7)
1	4603,49	6862,01
2	18096,53	17533,82
3	42876,64	52683,30
4	45922,19	151797,58
5	45469,07	144607,23
6	43188,13	40895,59
7	25365,49	37611,88
8	4687584,71	316175,03
9	78052,19	81625,61
10	64181,22	19922,13
11	845,79	<MDL
12	5456,82	<MDL
13	12031,98	<MDL
14	9714,62	167534,56
15	43282,92	183543,01
16	552,63	<MDL
17	<MDL	<MDL
18	1666,88	<MDL
19	167,14	<MDL
20	7855,94	71689,12
21	154,90	<MDL
22	8999,95	<MDL
23	25252,99	15274,63
24	22170,73	56556,11
25	24894,71	51042,64
26	6699,24	83288,58
27	17244,52	143293,15
28	<MDL	<MDL
29	<MDL	<MDL
30	<MDL	<MDL
31	627,08	<MDL
32	8658,12	54847,72
33	<MDL	<MDL
34	770,81	<MDL
35	4239,77	21691,45
36	23051,50	80297,79
37	477,24	99517,49
38	14713,79	<MDL
39	31427,97	<MDL

40	2254,77	74813,34
41	1328,00	<MDL
42	2521,62	57676,10
43	<MDL	<MDL
44	64199,83	78528,80
45	1796,78	<MDL
46	11568,62	<MDL
47	26029,86	<MDL
48	<MDL	<MDL
49	30842,41	47440,75
50	65000,00	32792,02
51	7056,80	<MDL
52	22862,13	26164,78
53	22114,56	47884,40
54	2607,88	17653,32
55	35649,70	53628,68

Table B.2.7 Concentrations for all the NBFRs analyzed at all sampling sites (n=55) in pg/g dw.

Sampling site	ATE (TBP-AE)	a-TBECH	b-TBECH	g/d-TBECH	BATE	PBT	PBEB	PBBZ	HBB	DPTE	EHTBB	BTBPE	BEHTBP	DBDPE
1	<MDL	<MDL	<MDL	<MDL	0,00	<MDL	<MDL	<MDL	<MDL	<MDL	2,99	43,24	19,22	<MDL
2	<MDL	<MDL	<MDL	<MDL	0,00	<MDL	<MDL	<MDL	<MDL	<MDL	2,21	37,01	<MDL	<MDL
3	<MDL	1,33	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	47,06	<MDL	342,61
4	5,45	2,65	<MDL	0,97	2,15	1,49	4,37	11,24	12,17	<MDL	54,05	31,52	1137,25	0,13
5	<MDL	5,84	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	114,40	200,32	869,50
6	<MDL	1,23	<MDL	<MDL	<MDL	1,63	0,64	1,18	<MDL	<MDL	<MDL	217,37	12,53	1483,01
7	<MDL	8,20	<MDL	<MDL	<MDL	<MDL	0,47	<MDL	<MDL	<MDL	<MDL	60,65	22,60	181,12
8	<MDL	38,18	92,48	4,33	<MDL	0,84	<MDL	<MDL	<MDL	<MDL	<MDL	57,54	32,27	281,41
9	<MDL	5,05	0,80	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0,59	<MDL	72,54	39,39	670,97
10	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	1365,48	<MDL	<MDL
11	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
12	<MDL	23,22	22,83	9,13	8,12	13,92	13,67	<MDL	<MDL	<MDL	74,17	<MDL	<MDL	<MDL
13	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	413,80	<MDL
14	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
15	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
16	<MDL	<MDL	9,69	<MDL	6,82	10,78	28,49	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	1616,07
17	<MDL	7,48	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	10,30	<MDL	<MDL	<MDL	<MDL
18	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	22,34	<MDL
19	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

20	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	29,41	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
21	2,39	4,83	3,13	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
22	5,26	6,15	5,93	3,81	7,25	7,19	6,06	4,90	<MDL	2,57	<MDL	<MDL	<MDL	<MDL
23	2,33	<MDL	3,48	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
24	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	1164,96
25	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	15,36	<MDL	<MDL	<MDL	<MDL
26	2,04	3,63	2,72	<MDL	1,02	<MDL	<MDL	<MDL	<MDL	7,35	6,38	<MDL	<MDL	<MDL
27	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	5999,01
28	9,02	<MDL	22,19	<MDL	11,20	12,28	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
29	1,60	<MDL	4,68	<MDL	2,76	3,61	3,74	<MDL	<MDL	2,32	<MDL	<MDL	<MDL	<MDL
30	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	2396,98	<MDL	9151,24	<MDL	<MDL
32	5,71	<MDL	8,73	7,49	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
33	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	12,67	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
34	3,13	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	907,39
35	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
36	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	2077,92
37	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
38	3,54	10,39	5,46	<MDL	5,12	8,07	4,13	10,04	23,04	32,72	19,43	477,86	403,32	1080,30
39	15,51	12,90	8,96	<MDL	2,92	6,92	<MDL	15,30	28,44	44,12	28,91	591,89	<MDL	<MDL
40	21,93	22,92	25,76	5,96	7,82	<MDL	<MDL	15,08	<MDL	<MDL	19,61	<MDL	<MDL	1901,98
41	<MDL	<MDL	1,07	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
42	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
43	8,38	25,10	8,56	7,68	5,16	9,61	5,09	12,90	<MDL	38,65	19,04	191,71	286,53	<MDL
44	45,65	89,93	63,34	46,37	54,67	85,86	47,72	78,89	153,35	240,58	87,17	1376,13	475,71	2193,11
45	8,17	<MDL	12,53	<MDL	7,52	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
46	3,70	14,28	5,13	3,58	4,75	8,84	4,19	9,17	18,46	37,43	13,83	116,49	80,80	<MDL
47	26,66	57,61	14,81	<MDL	<MDL	8,58	<MDL	17,20	<MDL	<MDL	82,81	1015,46	<MDL	<MDL
48	5,60	19,35	6,77	<MDL	4,16	6,40	<MDL	11,73	<MDL	33,60	22,98	<MDL	<MDL	<MDL
49	37,88	67,67	64,38	48,36	50,51	58,69	37,37	89,05	124,34	106,22	40,98	1244,86	545,73	759,61
50	28,72	20,62	19,73	4,50	13,09	10,60	13,43	<MDL	<MDL	28,65	<MDL	547,24	<MDL	<MDL
51	<MDL	<MDL	<MDL	<MDL	<MDL	1,45	<MDL	<MDL	<MDL	5,71	3,24	45,75	<MDL	<MDL
52	<MDL	7,98	7,69	<MDL	2,56	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
53	2,68	4,90	2,51	<MDL	1,75	5,65	2,04	4,93	<MDL	16,33	13,48	915,37	427,72	785,74
54	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
55	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	9,65	<MDL	<MDL	<MDL	228,10	<MDL	<MDL

Table B.2.8 Concentrations for all the dechloranes analyzed at all sampling sites (n=55) in pg/g dw.

Sampling site	Dechlorane 602	Dechlorane 603	Dechlorane 604	Dechlorane 601	Dechlorane plus syn	Dechlorane plus anti
1	61,14	<MDL	<MDL	<MDL	36,18	223,95
2	39,79	4,80	<MDL	<MDL	109,92	873,73
3	195,60	46,30	<MDL	<MDL	380,21	2224,96
4	2,05	<MDL	<MDL	63,56	290,64	<MDL
5	21,31	18,21	<MDL	<MDL	112,52	631,55
6	70,58	4,34	<MDL	<MDL	178,49	1106,01
7	31,76	9,25	<MDL	<MDL	173,88	938,89
8	65,40	138,46	<MDL	<MDL	669,12	2938,23
9	52,90	3,90	<MDL	<MDL	98,98	336,63
10	<MDL	109,98	<MDL	<MDL	22,05	70,40
11	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
12	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
13	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
14	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
15	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
16	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
17	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
18	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
19	<MDL	5,88	<MDL	<MDL	<MDL	<MDL
20	<MDL	<MDL	<MDL	<MDL	87,30	<MDL
21	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
22	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
23	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
24	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
25	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
26	17,20	<MDL	<MDL	<MDL	32,70	161,59
27	82,76	<MDL	<MDL	<MDL	2491,50	25973,07
28	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
29	14,52	<MDL	<MDL	<MDL	65,97	197,66
30	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
31	31,33	<MDL	<MDL	<MDL	22,57	87,42
32	70,51	38,52	<MDL	88,83	137,19	507,91
33	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
34	<MDL	<MDL	<MDL	<MDL	48,96	227,69
35	33,34	<MDL	<MDL	<MDL	67,39	294,96
36	<MDL	<MDL	<MDL	<MDL	<MDL	215,39

37	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
38	35,31	<MDL	<MDL	<MDL	67,58	255,19
39	123,71	<MDL	<MDL	<MDL	170,03	894,85
40	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
41	5,67	<MDL	<MDL	<MDL	<MDL	40,80
42	<MDL	<MDL	<MDL	<MDL	<MDL	1,13
43	<MDL	<MDL	<MDL	<MDL	<MDL	20,99
44	238,10	<MDL	<MDL	<MDL	877,83	2979,08
45	42,92	<MDL	<MDL	<MDL	191,57	1131,34
46	10,18	1,86	<MDL	<MDL	24,31	157,03
47	215,10	27,96	<MDL	<MDL	381,12	3299,63
48	27,79	8,84	<MDL	<MDL	81,90	249,71
49	91,81	18,46	<MDL	<MDL	345,08	1481,86
50	130,54	31,73	<MDL	<MDL	488,83	2872,77
51	38,20	6,01	<MDL	<MDL	92,51	603,83
52	42,87	10,66	<MDL	<MDL	184,70	831,85
53	37,76	9,68	<MDL	<MDL	122,44	507,02
54	19,25	6,79	<MDL	<MDL	30,96	132,98
55	177,10	20,08	<MDL	<MDL	452,77	1425,14

B.2.1 Box- and density plots of the raw data

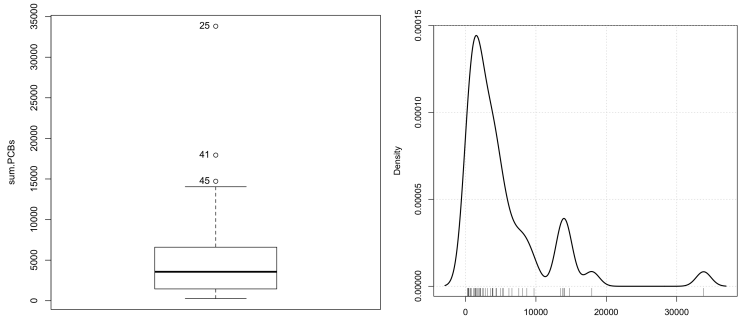

Figure B.2.1.1: Box- (left) and density (right) plots for PCBs. The numbers indicated: 25, 41, and 45, are: 35 (Aglen), 51 (Hvittingfoss), and 55 (Hurdal), respectively.

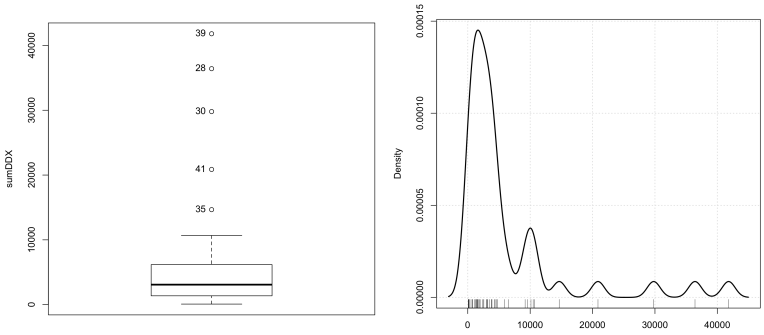

Figure B.2.1.2: Box- (left) and density (right) plots for DDTs. The numbers indicated: 39, 28, 30, and 41 are: 49 (Birkenes), 38 (Hummelfjell), 40 (Osen), 45 (Ulvik), respectively.

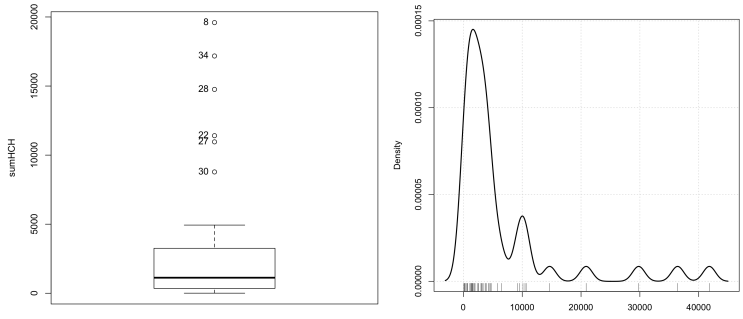

Figure B.2.1.3: Box- (left) and density (right) plots for DDTs. The numbers indicated: 30, 27, 22, 28, 34, 8 are: 40 (Osen), 37 (Bjørndalselva), 32 (Junkerdal), 38 (Hummelfjell), 44 (Furumset), and 18 (Lakselv).

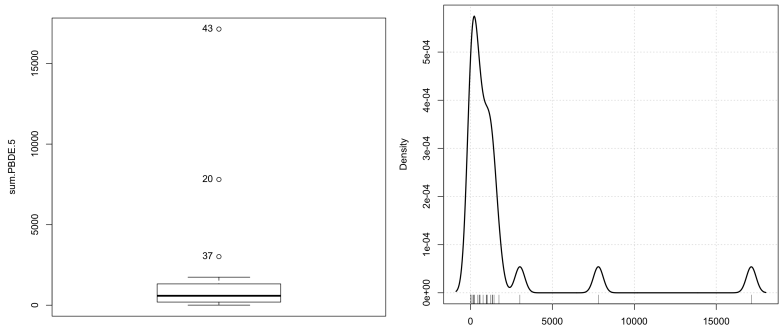

Figure B.2.1.4: Box- (left) and density (right) plots for the indicator PBDEs (congener number 47, 99, 100, 153, and 154). The numbers indicated: 43, 20, and 37 are: 53 (Aremark), 30 (Øvrevatn), and 47 (Utbjoa).

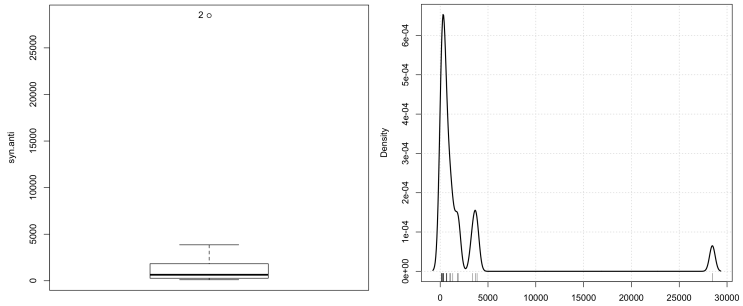

Figure B.2.1.5: Box- (left) and density (right) plots for DPs (syn and anti). The number indicated: 2 is: 27 (Svolvær).

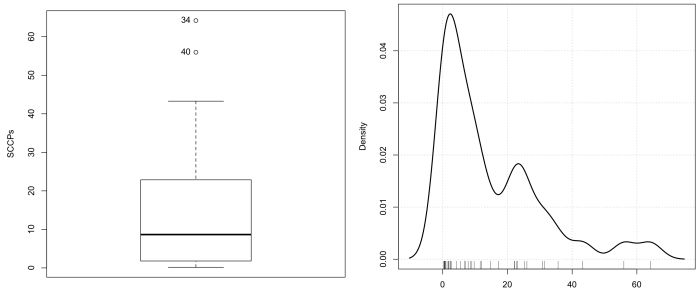

Figure B.2.1.6: Box- (left) and density (right) plots for SCCPs. The numbers indicated: 34 and 40 are: 44 (Furumset), and 50 (Solheimsfjell).

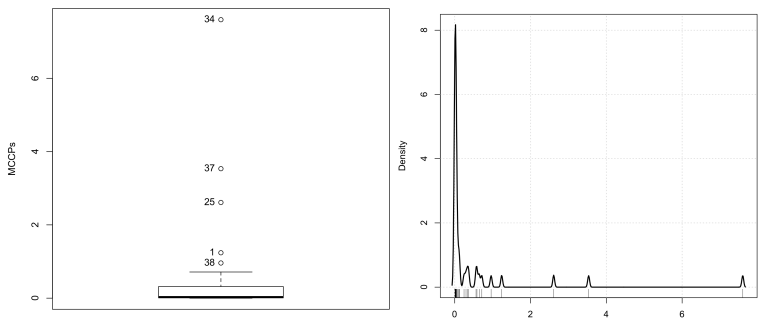

Figure B.2.1.7: Box- (left) and density (right) plots for MCCPs. The numbers indicated: 34, 37, and 25 are: 44 (Furumset), 47 (Utboja), and 35 (Aglen).

B.3 Statistical analysis

B.3.1 The difference between background and urban concentration levels.

```
        Wilcoxon signed rank test with continuity correction

data:  Background and Urban
V = 17, p-value = 0.05009
alternative hypothesis: true location shift is not equal to 0
```

B.3.2 The difference between north and south concentration levels

```
        Two Sample t-test

 data:  PCBslog$logPCBsS and PCBslog$logPCBsN
 t = 1.9066, df = 42, p-value = 0.03172
 alternative hypothesis: true difference in means is greater than 0
 95 percent confidence interval:
  0.03234779       Inf
 sample estimates:
       mean of x        mean of y  pooled std.dev.
       3.3342250        3.0596469        0.4776515
```

Diagramområde

```
        Two Sample t-test

data:  NordSorlog$logDDxS and NordSorlog$logDDxN
t = 2.3437, df = 40, p-value = 0.01207
alternative hypothesis: true difference in means is greater than 0
95 percent confidence interval:
 0.1240308       Inf
sample estimates:
       mean of x        mean of y  pooled std.dev.
       3.6201775        3.1796511        0.6090582
```

```
        Two Sample t-test

data:  NordSorlog$logDPS and NordSorlog$logDPN
t = 6.2797, df = 42, p-value = 7.862e-08
alternative hypothesis: true difference in means is greater than 0
95 percent confidence interval:
 1.545999      Inf
sample estimates:
       mean of x        mean of y  pooled std.dev.
       2.7272267        0.6156635        1.1152303
```

```
        Two Sample t-test

data:  NordSorlog$logMCCPsS and NordSorlog$logMCCPsN
t = 0.09167, df = 42, p-value = 0.4637
alternative hypothesis: true difference in means is greater than 0
95 percent confidence interval:
 -0.4075663        Inf
sample estimates:
       mean of x        mean of y  pooled std.dev.
      -0.7339132       -0.7574069        0.8500028
```

```
        Two Sample t-test

data:  NordSorlog$logSCCPsS and NordSorlog$logSCCPsN
t = 1.7469, df = 42, p-value = 0.04398
alternative hypothesis: true difference in means is greater than 0
95 percent confidence interval:
 0.01387689        Inf
sample estimates:
       mean of x        mean of y  pooled std.dev.
       1.0354330        0.6623803        0.7082552
```

```
        Two Sample t-test

data:  NordSorlog$logNBFRsS and NordSorlog$logNBFRsN
t = 1.5092, df = 42, p-value = 0.06937
alternative hypothesis: true difference in means is greater than 0
95 percent confidence interval:
 -0.06939563         Inf
sample estimates:
       mean of x        mean of y  pooled std.dev.
        2.424146         1.817866         1.332359
```

B.3.2 Correlation test for SOM and concentration levels

```
        Pearson's product-moment correlation

data:  SOM and sumPCBs.logpg.dw.
t = 3.6711, df = 42, p-value = 0.0003381
alternative hypothesis: true correlation is greater than 0
95 percent confidence interval:
 0.2756548 1.0000000
sample estimates:
      cor
0.4928793
```

```
        Pearson's product-moment correlation

data:  SOM and sumDDX.logpg.dw
t = 3.3421, df = 40, p-value = 0.000906
alternative hypothesis: true correlation is greater than 0
95 percent confidence interval:
 0.2384295 1.0000000
sample estimates:
      cor
0.4672103
```

```
        Pearson's product-moment correlation

data:  SOM and logDEC.pg.dw.
t = 6.605, df = 20, p-value = 9.823e-07
alternative hypothesis: true correlation is greater than 0
95 percent confidence interval:
 0.6665644 1.0000000
sample estimates:
      cor
0.8280467
```

```
        Pearson's product-moment correlation

data:  SOM and logDP.pg.dw.
t = 6.0348, df = 18, p-value = 5.248e-06
alternative hypothesis: true correlation is greater than 0
95 percent confidence interval:
 0.6363437 1.0000000
sample estimates:
      cor
0.8180655


        Pearson's product-moment correlation

data:  SOM and logHCB.pg.dw.
t = 5.2931, df = 42, p-value = 2.046e-06
alternative hypothesis: true correlation is greater than 0
95 percent confidence interval:
 0.4532675 1.0000000
sample estimates:
      cor
0.6325694


        Pearson's product-moment correlation

data:  SOM and logHCH.pg.dw.
t = 2.0449, df = 38, p-value = 0.02392
alternative hypothesis: true correlation is greater than 0
95 percent confidence interval:
 0.05545099 1.00000000
sample estimates:
      cor
0.3148501


        Pearson's product-moment correlation

data:  SOM and logMCCPs.pg.dw.
t = 1.1868, df = 38, p-value = 0.1213
alternative hypothesis: true correlation is greater than 0
95 percent confidence interval:
 -0.07888868  1.00000000
sample estimates:
      cor
0.1890573


        Pearson's product-moment correlation

data:  SOM and logNBFRs.pg.dw.
t = 1.76, df = 26, p-value = 0.04509
alternative hypothesis: true correlation is greater than 0
95 percent confidence interval:
 0.00967992 1.00000000
sample estimates:
      cor
0.3262725


        Pearson's product-moment correlation

data:  SOM and logPeCB.pg.dw.
t = 3.4924, df = 32, p-value = 0.0007109
alternative hypothesis: true correlation is greater than 0
95 percent confidence interval:
 0.2805129 1.0000000
sample estimates:
      cor
0.5253228


        Pearson's product-moment correlation

data:  SOM and logSCCPs.pg.dw.
t = 2.0099, df = 33, p-value = 0.02634
alternative hypothesis: true correlation is greater than 0
95 percent confidence interval:
 0.05229506 1.00000000
sample estimates:
      cor
0.3302551
```

B.3.4 Correlation test for latitude and concentration levels

```
        Pearson's product-moment correlation

data:  latitude. and logDDx
t = -2.7822, df = 40, p-value = 0.004099
alternative hypothesis: true correlation is less than 0
95 percent confidence interval:
 -1.0000000 -0.1620037
sample estimates:
       cor
-0.4026696

        Pearson's product-moment correlation

data:  latitude. and logDP.syn.anti
t = -2.4829, df = 23, p-value = 0.01038
alternative hypothesis: true correlation is less than 0
95 percent confidence interval:
 -1.0000000 -0.1452897
sample estimates:
       cor
-0.4597617


        Pearson's product-moment correlation

data:  latitude. and log.MCCPs
t = -1.6573, df = 38, p-value = 0.05285
alternative hypothesis: true correlation is less than 0
95 percent confidence interval:
 -1.000000000  0.004704202
sample estimates:
       cor
-0.2596267



        Pearson's product-moment correlation

data:  latitude. and logDEC601.4
t = -1.1324, df = 20, p-value = 0.1354
alternative hypothesis: true correlation is less than 0
95 percent confidence interval:
 -1.0000000  0.1260949
sample estimates:
       cor
-0.2454691


        Pearson's product-moment correlation

data:  latitude. and logPCBs
t = -3.4541, df = 42, p-value = 0.000637
alternative hypothesis: true correlation is less than 0
95 percent confidence interval:
 -1.0000000 -0.2483329
sample estimates:
      cor
-0.470349


        Pearson's product-moment correlation

data:  latitude. and logNBFRs
t = -2.5513, df = 33, p-value = 0.007775
alternative hypothesis: true correlation is less than 0
95 percent confidence interval:
 -1.0000000 -0.1390156
sample estimates:
       cor
-0.4059007

        Pearson's product-moment correlation

data:  latitude. and logPBDEs
t = -1.3777, df = 26, p-value = 0.09002
alternative hypothesis: true correlation is less than 0
95 percent confidence interval:
 -1.00000000  0.06188401
sample estimates:
       cor
-0.2608382
```

```
        Pearson's product-moment correlation

data:  latitude. and logSCCPs
t = -2.414, df = 32, p-value = 0.01084
alternative hypothesis: true correlation is less than 0
95 percent confidence interval:
 -1.0000000 -0.1187643
sample estimates:
    cor
-0.3925
```

B.3.5 Air- to soil exchange of PCBs

Table B.3.5.1 PCB-28 and 180 t-Test: Two variables with assumed equal variance.

	Variabel 1	*Variabel 2*
Average	7,3	9,7
Variance	0,16	0,16
Observations	55	55
Groupvariance	0,16	
Assumed deviation		
between the averages	0	
df	108	
t-Stat	-30,67	
P(T<=t) one-sided	1,9997E-55	
T-critical, one-sided	1,65908514	
P(T<=t) two-sided	3,9995E-55	
T-critical, two-sided	1,98217348	

Table B.3.5.2 PCB-28 and 52 t-Test: two variables with assumed equal variance.

	Variabel 1	*Variabel 2*
Average	7,3	7,7
Variance	0,16	0,16
Observations	55	55
Groupvariance	0,16	
Assumed deviation between the averages	0	
df	108	
t-Stat	-4,88966157	
P(T<=t) one-sided	1,7694E-06	
T-critical, one-sided	1,65908514	
P(T<=t) two-sided	3,5389E-06	
T-critical, two-sided	1,98217348	

Table B.3.5.3 PCB-52 and 101 t-Test: two variables with assumed equal variance.

	Variabel 1	*Variabel 2*
Average	7,7	8,2
Variance	0,16	0,16
Observations	55	55
Groupvariance	0,16	
Assumed deviation between the averages	0	
df	108	
t-Stat	-6,79634522	
P(T<=t) one-sided	3,0616E-10	
T-critical, one-sided	1,65908514	
P(T<=t) two-sided	6,1233E-10	
T-critical, two-sided	1,98217348	

Table B.3.5.4 PCB-101 and 180 t-Test: two variables with assumed equal variance.

	Variabel 1	*Variabel 2*
Average	8,2	9,7
Variance	0,16	0,16
Observations	55	55
Groupvariance	0,16	
Assumed deviation between the averages	0	
df	108	
t-Stat	-18,9812434	
P(T<=t) one-sided	1,7225E-36	
T-critical, one-sided	1,65908514	
P(T<=t) two-sided	3,4449E-36	
T-critical, two-sided	1,98217348	

B.3.6 Population density

Table 3.6.1 Population density between urban and background soils, t-test: two variables with assumed different variance.

	Variabel 1	*Variabel 2*
Average	3,4	1,1
Variance	0,038	0,29
Observations	10	45
Assumed deviation between the averages	2,5	
df	42	
t-Stat	-1,70184	
P(T<=t) one-sided	0,048089	
T-critical, one-sided	1,681952	
P(T<=t) two-sided	0,096178	
T-critical, two-sided	2,018082	

Table 3.6.2 The relationship between latitude and population density for urban and background soils combined.

Regresjonsstatistikk	
Multippel R	0,518129
R-square	0,268458
Adjusted R-square	0,254655
Standarddeviation	0,890882
Observations	55

Variance analyze

	df	*SK*	*GK*	*F*	*Signifcance-F*
Regression	1	15,43664	15,43664	19,44967	5,08E-05
Residuuales	53	42,06458	0,793671		
Total	54	57,50122			

	Coefficent	*Standarddeviation*	*t-Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95,0%*	*Upper 95,0%*
Intersection	9,34805	1,782866	5,243273	2,8E-06	5,772074	12,92403	5,772074	12,92403
X-variabel 1	-0,12225	0,027721	-4,41018	5,08E-05	-0,17785	-0,06665	-0,17785	-0,06665

Table 3.6.2 The relationship between latitude and population density for urban and background soils combined.

Regresjonsstatistikk	
Multippel R	0,271518
R-square	0,073722
Adjusted R-square	0,052181
Standarddeviation	0,525457
Observations	45

Variance analyze

	df	*SK*	*GK*	*F*	*Signifcance-F*
Regression	1	0,944928	0,944928	3,422345	0,071199
Residuuales	43	11,87253	0,276105		
Total	44	12,81746			

	Coefficent	*Standarddeviation*	*t-Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95,0%*	*Upper 95,0%*
Intersection	3,298174	1,201673	2,744653	0,008803	0,874771	5,721578	0,874771	5,721578
X-variabel 1	-0,03407	0,018417	-1,84996	0,071199	-0,07121	0,003071	-0,07121	0,003071

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