

LANGTRANSPORT OG AVSETNING AV ORGANISKE MILJØGIFTER I NORDVESTLIGE EUROPA

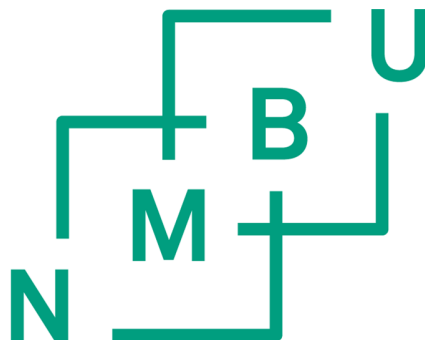
*Long-range atmospheric transport and deposition of
organic pollutants (POPs) in North Western Europe*

Philosophiae doctor (ph.d.) avhandling

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Ås/Adamstuen 2014



Avhandling nr 2014:90
ISSN 1894-6402
ISBN 978-82-575-1248-4

Herren gir og herren tar!

Master Yoda

Acknowledgements

I have reached the point where it is time to reflect on what has filled days, evenings, and nights the last 7 years. The PhD-study, better known as “dannelsesprosess” has taken its time.

It has been a journey topped with frustrations, happiness, tonnes of laughter, tears (from both laughter and sadness), panic sweat, running from polar bears, an occasional broken arm, love and infinitely wonderful friendships.

The “adventure” began in 2007. I had been walking around in the NILU corridors joyful and childlike since the autumn of 2006, and thought to be safe when I ran into my now dear friend and after a while koala-office companion: Marianne H. I have often said that you tricked me into the PhD-“tvangstrøya” (tight shirt with long arms). However, I have to admit that I am grateful as well.

The PhD has been financially feasible through a series of funding projects from the Research Council of Norway (183437, 173428 and 196191). Further, I would give a HUGE thank YOU to my supervisors Knut, Martin and Roland. Firstly Knut, aka Master Yoda. I am truly sorry if I have caused you occasionally headaches due to excessive head shaking over disturbing texts and thoughts. Contrasting us in the metric system (height), I would be the vegetation by the foot of the Everest, which would be you. Thank you for endless hours of patience and guidance. In order to explain the journey of “dannelse”, I have included a handful of comments. Our collaboration started out nicely with comments like this: «*Det var for så vidt en del interessant her, men det blir for mye*» (**Paper I**). Yet, at the same time: “...*min hovedbekymring er likevel at du ikke ser ut til å operere med et "consistent approach" mellom kapitlet ovenfor og den statistiske analysedelen...*” (**Paper II**), consequently, more hours in front of the computer was needed. From **Paper IV**, expressions like: “*her er det forbedringspotensiale*”, “*om det er korrekt...*”, “... *i den grad det er interessant å nevne...*” was frequently used. From draft synopsis: “*Jeg vet ikke hva jeg skal si... SAMTLIGE artikler (EMEP, Birkenes, Kyst og Jord) handler på en eller annen måte om langtransport av POPs, og det er virkelig den røde tråd i avhandlingen din. Hjelp og trøst, la oss si at den handler om kniplinger fra Hardanger på 1800-tallet, hva er da vitsen med å gjøre et poeng av hva den ikke handler om?*” After what I recall, you needed to search for inner peace crosscountry skiing after that one? It is appropriate to mention that the first read-through of the synopsis resulted in 1322 revisions, and it continued...! From this it is clear that I needed assistance regarding writing and I have to thank you for words of wisdom such as “*skrive, skrive, skrive*” and “*do or do not, there is no try*”. Your innumerable effort resulted in this PhD-thesis. THANK YOU! I also have to thank Martin, excellent supervisor, but if possible less patient than Knut. I remember, we had an argument concerning the coordinates in the fourth study (soil sampling). After some discussion, regarding how it is essential to present exact coordinates to avoid ending up collecting soil in the sea, I asked a fairly critical question: what if I do not have better coordinates? Hai dios mio! You replied somewhat upset: this was neither the time or place to be negative! Nevertheless, the coordinates now refers to places in Europe and Norway it should be easy to locate, so thank you, in addition to all the help in regarding lab related questions and in writing. Last but not least, I have to thank good old SVK (Store Vennlige Kjempe), synonymous with Svalbard. You are the closest a human form can be to polarbears! You are constantly traveling, but you have a high involvement for the environment and pollutants. Furthermore, I would also like to thank my co-authors, Kevin, Jasmin, Sabine, Andreas, Eiliv and Andrew for constructive effort, assistance and feedback.

Moreover, I would also like to thank colleagues at NILU which have contributed to increase not only the graphical but also the academic work during the PhD. First, Sabine, for the model calculations and patience and Anne Gunn for a series of figures of levels of pollutant in Europe and also a synoptic figure included in the thesis. Thirdly, Pernilla for her highly appreciated contribution on the theory of the passive air

sampler. THANKS. I would further honor and thank Anders, Hans, Stein, Helene (Narvestad), Mebrat for all the analytical results, and also a gigantic thank to all colleagues and friends at NILU. More detailed I would like to thank Anders and Hans for their effort in trying to explain the meaning of internal standards, and the mystery of EI, ECNI, and GC-MS.

And to my friends and family, you are the ones which have given me hope through the PhD process against the constant feeling of sinking. You are many, and I will from the bottom of my heart thank you for your endless optimism, indomitable believe that everything is going to be fine, and that it is perfectly normal to do the same work several times. Specifically, I would thank Marianne H, comrade, friend and allay at our former campground KOALA office. You have taught me about life, to be tough and to embrace possibilities that stand in front of you (ref this PhD). You embrace a unique mixture of realism, honesty, toughness, stubbornness and love, which you now need more than ever. I am deeply grateful for knowing you, and thank you for being my friend. Furthermore, I thank (P)Ingerd (started her PhD after me, and finished before me...) for her enormous professional competence, which you have nicely shared with me under our daily intake of “WASA knekkebrød” and “makrell i tomat”. Over meters of “knekkebrød”, a fishing quota of mackerel in tomato and also a small lake of tea and coffee, mutual frustrations and philosophical considerations was often concluded with “PhD-livet er ikke så verst, bare man jamför”. Secondly, I would also like to thank, Cille, Bjørn Atle, Berit, Linda x 2, Linn Cecilie, Henriette, Camilla, SvalbardPernilla, Helene (aka Narvestad), Therese (voluntary reader of synopsis), and all you other near and dear ones for infinite goood times preferably in combination of intake of fluid other than tea and coffee...

Finally, I would like to thank my dearest family, and my son Jonas specifically. I have been studying since you were three years old. Now you are 20, have completed the army, spend more time away from home than home and you are ready for your own adventures. I am immensely proud of you, and I love you very much! I would also thank your father, Pål, as he through the earlier years made it possible for me to spend so much time studying. THANK YOU! And mom, I have you for life (pure biologically) but also for your life long tireless staying power and for always believing in me, which has inspired me to never give up. And then to my three brothers, for the everlasting long-lived debates concerning where to buy light bulbs, one-way traffic, and general high pitched discussions about the smallest things. Since I will always be your little sister I have learned to raise my voice, stand against general sarcasm, but always feel the inner strength which I believe has helped me through a number of obstacles during the years of PhD.

Very last, but far from least important: Thanks to Radioresepsjonen, DJ Friendly, Svalbard, polar bears, koalas. Randoneeski and snow, to remind me that there is a life outside the Windows Office package, deadlines and strict supervisors ☺

Hagan, Nittedal, September 2014



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List of abbreviations

AAS = active air sampler (or active air sampling)
B = bioaccumulation
BC = black carbon
BCF = bioconcentration factor
CI = confidence interval
CLRTAP = The 1979 Geneva Convention on Long-range Transboundary Air Pollution
 C_{AIR} = concentration in air
 C_{PAS} = concentration in passive sampling media
DDD = dichlorodiphenyldichloroethane
DDE = dichlorodiphenyldichloroethylene
DDT = dichlorodiphenyltrichloroethane
DE = diatomaceous earth
EC = emission contribution
ECNI = electron capture negative ion
EI = electron impact
EMEP = The Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe
ES = emission sensitivity
EVA = thin film of ethylene vinyl acetate
GMP = Global Monitoring Plan
HCB = hexachlorobenzene
HCHs = hexachlorocyclohexane isomers
 K_{AW} = air-water partition coefficient
 k_A = mass transfer coefficient
 K_{OW} = octanol-water partition coefficient
 K_{OA} = octanol-air partition coefficient
 $K_{PAS-AIR}$ = passive sampling media-air partition coefficient
LOI = loss of ignition
LS = local source
LPDS = low-density polyethylene sheets
LRT = long-range transport
LRAT = long-range atmospheric transport
MDL = method detection limit
MMR = ratio between the maximum and minimum air concentrations
P = persistence (or vapour pressure)
PC = physical-chemical
PDMS = poly(dimethylsiloxane)
PAS = passive air sampler (or passive air sampling)
PAHs = polycyclic aromatic hydrocarbons
PCBs = polychlorinated biphenyls
PeCB = pentachlorobenzene
POG = polymer-coated glass cylinders
PRCs = performance reference compounds
PSM = passive sampling media
PUF = polyurethane foam

Rs = uptake rate
SC = Stockholm Convention
SCCPs = short-chain chlorinated paraffins
So = octanol solubility
SPMD = semi permeable membrane devices
Sw = aqueous solubility
SIP = sorbent-impregnated polyurethane foam
SOM = soil organic matter
SVOC = semi-volatile organic compounds
T = toxicity
V_{PAS} = volume of passive sampling media
XAD = polystyrene divinylbenzene copolymeric resin

List of papers

Paper I Halse, A. K.; Schlabach, M.; Eckhardt, S.; Sweetman, A.; Jones, K. C.; Breivik, K. Spatial variability of POPs in European background air. *Atmospheric Chemistry and Physics*, 2011, *11*, 1549-1564.

Paper II Halse, A.K.; Schlabach, M.; Sweetman, A.; Jones, K. C.; Breivik, K. Using passive air samplers to assess local sources *versus* long range atmospheric transport of POPs. *Journal of Environmental Monitoring*, 2012, *14*, 2580-2590.

Paper III Halse, A. K.; Eckhardt, S.; Schlabach, M.; Stohl, A.; Breivik, K. Forecasting long-range atmospheric transport episodes of polychlorinated biphenyls using FLEXPART. *Atmospheric Environment*, 2013, *71*, 335-339.

Paper IV Halse, A. K.; Schlabach, M.; Jones, K. C.; Schuster, J.; Steinnes, E.; Breivik, K. Endosulfan, pentachlorobenzene and short-chain chlorinated paraffins in background soils from Western Europe. *Environmental Pollution*, In press.

Abstract

Persistent organic pollutant (POPs) are toxic compounds which typically consist of one or more groups of hydrocarbons that are aromatic or aliphatic as well as halogenated (chlorine, bromine, fluorine). POPs are normally characterized by low water-solubility and a lipophilic nature, hence they are susceptible for accumulation in fatty tissues. Usually, POPs are semi-volatile and persistent in both air as well as in other environmental media and therefore able to undergo long-range atmospheric transport. POPs may therefore deposit in remote and pristine environments (i.e. the Arctic), far away from any point sources. The focus of this thesis is on selected POPs, which are regulated by international agreements.

A specific aim of this thesis was to increase the understanding of the distribution of some legacy POPs in air, by use of a passive air sampling technique, active air samplers (AAS), and an atmospheric transport model (FLEXPART). Passive air samplers (PAS) were deployed at 86 European background stations in 34 countries, mainly utilizing the established EMEP measurement network. The results document spatial variability of legacy POPs and their distribution largely reflects historical and contemporary source regions in Europe. Parallel to the European background site campaign, passive air samples were collected in rural Norwegian coastal zones with dietary advisories on seafood because of elevated levels of POPs. By combining results from these two campaigns, it was possible to evaluate whether local sources or long-range atmospheric transport mainly control the atmospheric POP burdens in contaminated coastal zones. The results documented that some Norwegian coastal zones are strongly influenced by local emission sources of regulated POPs. Furthermore, a model-based forecast system has been developed and evaluated, attempting to predict long-range atmospheric transport (LRAT) episodes to background areas. The forecast system was evaluated for PCBs (polychlorinated biphenyls) at Birkenes by carrying out targeted sampling under predicted LRAT episodes throughout a year (events with expected high concentrations). Measured concentrations in air from the targeted sampling revealed that the model system was largely able to predict LRAT episodes, in addition to identifying the main source areas affecting the site. The study illustrates that a model based forecast system has the potential to complement existing monitoring programmes for POPs in air. The thesis also assesses the occurrence and distribution of “newly regulated” POPs (i.e. pentachlorobenzene (PeCB), endosulfans and short-chain chlorinated paraffins (SCCPs)) in

environmental surface media. Soil samples were collected from background areas along a transect from England to Norway. The highest concentrations were found for SCCPs, followed by endosulfans and PeCB. The concentrations of SCCPs were highest near assumed source regions in southern areas, whereas endosulfans and PeCB were more evenly distributed along the transect. Furthermore, endosulfans and PeCB showed many similarities in their spatial pattern, and also with other legacy POPs as previously reported. Endosulfans often peaked in areas with elevated precipitation rates, whereas endosulfan sulfate was the predominant component within the group. PeCB correlated with black carbon in soils, and we therefore believe combustion processes is a key source of PeCB to the atmosphere. The soil survey furthermore illustrated how simple distribution and mobility maps may provide additional mechanistic information to assess the environmental fate and distribution in soils beyond the statistical analyses performed.

Norsk sammendrag

Persistente organiske miljøgifter (POPs) er giftige forbindelser som typisk består av en eller flere grupper av hydrokarboner som ofte er både aromatiske samt halogenerte (klor, brom, fluor). POPs kombinerer gjerne lav vannløselighet med høy fettløselighet, og kan dermed akkumulere i fettrikt vev. Vanligvis er de også delvis flyktige og har lang levetid i både luft og andre medier, noe som medfører at de kan transporteres over lange avstander fra kildeområder til avsidesliggende områder, som for eksempel Arktis. Denne avhandlingen fokuserer i hovedsak på POPs som allerede er regulert gjennom internasjonale avtaleverk.

Denne avhandlingen bidrar med å øke forståelsen rundt fordelingsmønstre av regulerte POPs i luft, ved bruk av både passive og aktive luftprøvetakingsteknikker (AAS), samt anvendelse av en atmosfærisk transportmodell (FLEXPART). Passive luftprøvetakere (PAS) ble utplassert på 86 europeiske bakgrunnsstasjoner i 34 land, hovedsakelig basert på det etablerte målenettverket til EMEP. Resultatene dokumenterte romlig variasjon av POPs og utbredelsesmønsteret reflekterer både pågående og tidligere kilderegioner i Europa av POPs. Parallelt med den europeiske kampanjen ble det også tatt luftprøver i norske kystsoner som har kostholdsråd på sjømat, noe som gjorde det mulig å vurdere om det er lokale kilder eller langtransport som hovedsakelig kontrollerer den atmosfæriske belastningen av POPs på disse stedene. Resultatene fra kystsonundersøkelsen dokumenterte at enkelte norske kystsoner er sterkt påvirket av lokale utslippskilder når det gjelder regulerte POPs. Videre ble et modellbasert varslingsystem utviklet for å evaluere hvorvidt det er mulig å forutsi langtransportepisoder til et bakgrunnsområde i Sør-Norge. Varslingssystemet ble evaluert for PCB (polyklorerte bifenyler) på Birkenes ved å samle inn ekstra prøver under varslede episoder (forventede høye konsentrasjoner av PCB i luft) gjennom ett år. Resultatene viste at modellen i stor grad er i stand til å forutsi langtransportepisoder, samt identifisere kildeområdene til målestasjonen. Studien illustrerer også at et modellbasert varslingsystem har potensiale til å komplementere eksisterende overvåkningsprogrammer for POPs i luft.

Avhandlingen omhandler også feltstudier av langtransportpotensiale samt fordeling av enkelte «nyere» regulerte POPs (PeCB, endosulfaner og kortkjedede klorparafiner). Jordprøver ble innsamlet fra bakgrunnsområder langs et transekt fra England til Norge. Klorparafiner ble funnet i de høyeste konsentrasjonene, etterfulgt av endosulfaner og PeCB. Konsentrasjonen av

klorparafiner var høyest nær antatte kildeområder i sør. Endosulfaner og PeCB utviste derimot større likheter i deres romlige fordeling, herunder tidligere regulerte POPs hvis forekomst har blitt rapportert tidligere. Endosulfaner viste seg å ha høyere konsentrasjoner i nedbørsrike områder, og endosulfansulfat dominerte innad i denne gruppen. Konsentrasjoner av PeCB i jord var korrelert med sot, og vi antar derfor at forbrenningsprosesser er en vesentlig utslippskilde til PeCB. Jordundersøkelsen illustrerte videre hvordan enkle fordelings- og mobilitetskart kan bidra med mekanistisk tilleggsinformasjon om miljøskjebne og fordeling i jord utover de statistiske analysene som ble utført.

1. Introduction

1.1. Historical perspective

Throughout history of mankind, air pollution has likely caused potential harmful effects on the environment. More than a century ago, Fridjof Nansen noted dark stains on the snow during his walk over the Polar Basin, questioning the effects this may have on the melting snow (Nansen, 1924). During the sixties to eighties of the last century, acidic precipitation was of high concern in our Nordic region. During the 1970's, a monitoring programme was therefore established to examine suspected long-range transport of air pollution in north-western Europe (Ottar, 1976, 1977, 1978). By combining air and deposition measurements with emission inventories (Semb, 1978) and calculated trajectory plots (Eliassen, 1978), transboundary air pollution was confirmed. Along with the historical emissions of inorganic compounds (e.g. sulphur dioxides, nitrogen oxides, and metals), an increasing number of organic chemicals have been intentionally produced and released to the environment over the last century. The book *Silent Spring* (Carson, 1962) was an alarming reminder of how the environment has been affected by some of these organic pollutants, notably selected organochlorine pesticides. DDTs (trichlorodiphenyltrichloroethanes and related compounds) is one group of these man-made chemicals which was documented to have caused harmful effects on the environment. The use of DDTs to mitigate diseases such as malaria and typhus (Ogata et al., 2009; Somerville and Liebens, 2011) was also proven to have damaging effects for wildlife and in particular birds, due to the thinning of the eggshells (Bouwman et al., 2013). Increasing concerns about the potential negative effects of POPs like DDTs on environmental and human health resulted in various national and international regulatory measures in the decades to come. The DDTs is just one example of a compound group classified as persistent organic pollutants (POPs) today (see section 1.2).

Figure 1 presents the timetable for relevant international and regional regulatory agreements. The 1979 Convention (CLRTAP) is one of the regulatory agreements, which later came to include POPs, and which entered into force in 1983 (UNECE, 2004). The fundamental principle under the CLRTAP was to “*limit and, as far possible, gradually reduce and prevent air pollution including long range trans-boundary air pollution*“. In 1998, the Aarhus protocol on Persistent Organic Pollutants was established under CLRTAP (UNECE, 1998) and entered into force in October

2003. By September 2014 the Aarhus Protocol has been ratified by 33 parties, and signed by 36 (UN, 2014) (see Fig. 1).

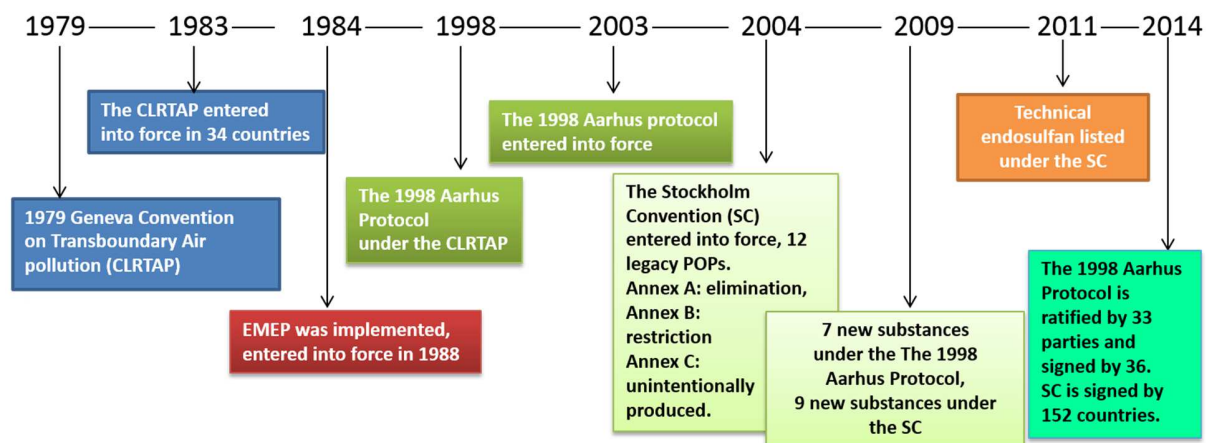


Figure 1: Timeline for regulatory agreements on POPs.

Under the CLRTAP, a long-term measurement programme, the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP), which now also include POPs, has also been initiated (UNECE, 2010b) (Fig. 1). In addition to the CLRTAP, a global treaty on POPs was agreed upon in Stockholm in May 2001, i.e. the Stockholm Convention (SC) on Persistent Organic Pollutants, which entered into force in 2004 (UNEP, 2009b). By September 2014, the SC has been signed by 152 countries and include 179 parties (UNEP, 2004). Under the SC a global monitoring plan (GMP) (UNEP, 2007) has been established in order to evaluate the effectiveness of this global agreement. Common for both the Aarhus Protocol and SC is the focus on organic chemicals which fulfil all four POPs criteria (persistent (P), bioaccumulative (B), toxic (T) and long-range transport (LRT) potential) (UNECE, 1998; UNEP, 2003), see section 1.2. Substances which are regulated under one or both of these two agreements, are referred to as (legacy) POPs in this thesis (see Table 1). Nonetheless, some POPs (e.g. DDTs for control of malaria) are still in use in some countries (Bogdal et al., 2013; Huang et al., 2014; Nyarango et al., 2006). Both conventions are continually revised, and the list of regulated POPs is growing (UNECE, 2010a; UNEP, 2009b) (see Fig. 1 and Table 1).

Table 1: Regulated compounds (legacy POPs) under the Stockholm Convention and the 1998 Aarhus Protocol

Regulated compounds	The Stockholm Convention	The 1998 Aarhus Protocol	Included in this study
<i>Aldrin</i> ^{1,5}	X	X	-
<i>Chlordane</i> ^{1,5}	X	X	X
<i>Trichlorodiphenyltrichloroethane (DDT)</i> ^{1,5}	X	X	X
<i>Dieldrin</i> ^{1,5}	X	X	-
<i>Endrin</i> ^{1,5}	X	X	-
<i>Heptachlor</i> ^{1,5}	X	X	-
<i>Hexachlorbenzene (HCB)</i> ^{1,5}	X	X	X
<i>Mirex</i> ^{1,5}	X	X	-
<i>Toxaphene</i> ^{1,5}	X	X	-
<i>Polychlorinated biphenyls (PCBs)</i> ^{1,5}	X	X	X
<i>Polychlorinated dibenzo-p-dioxins</i> ^{1,5}	X	X	-
<i>Polychlorinated dibenzofurans</i> ^{1,5}	X	X	-
<i>α-hexachlorocyclohexane (α-HCH)</i> ^{2,5}	X	X	X
<i>β-hexachlorocyclohexane (β-HCH)</i> ^{2,5}	X	X	X
<i>Chlordecone</i> ^{2,5}	X	X	-
<i>Hexabromobiphenyl</i> ^{2,5}	X	X	-
<i>Hexabromodiphenyl ether and heptabromodiphenyl ether (octabromobiphenyl)</i> ^{2,6}	X	X	-
<i>γ-hexachlorocyclohexane (Lindane) (γ-HCH)</i> ^{2,6}	X	X	X
<i>Pentachlorobenzene (PeCB)</i> ^{2,6}	X	X	X
<i>Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride</i> ^{2,6}	X	X	-
<i>Technical endosulfan (α- and β-endosulfan)</i> ³	X	-	X
<i>Tetrabromodiphenyl ether</i> ²	X	-	-
<i>Pentabromodiphenyl ether</i> ^{2,6}	X	X	-
<i>Hexabromocyclododecane (HBCD)</i> ^{4,6}	X	X	-
<i>Short-chain chlorinated paraffins (SCCPs)</i> ^{6,7}	-	X	X
<i>Chlorinated naphthalenes</i> ^{4,6}	-	X	-
<i>Hexachlorobutadiene</i> ⁴	-	-	-
<i>Pentachlorophenol</i> ⁴	-	-	-
<i>Polycyclic aromatic hydrocarbons (PAHs)</i> ⁵	-	X	X

¹⁾ Regulated under the SC in 2004, “dirty dozen” (UNEP, 2003)

²⁾ Regulated under the SC in 2009, “nasty nine” (UNEP, 2009a)

³⁾ Regulated under the SC in 2011, “evil endo” (UNEP, 2011)

⁴⁾ Under review for listing under the SC by the Persistent Organic Pollutants Review Committee (POPRC) (UNEP, 2012)

⁵⁾ Listed under the 1998 Aarhus Protocol (UNECE, 1998)

⁶⁾ Listed under 1998 Aarhus Protocol in 2009 (UNECE, 2010a)

⁷⁾ HBCD enter into force under the SC, 26 November 2014 (UNEP, 2013)

While Table 1 lists regulated compounds within the SC and the Aarhus protocol, this dissertation focuses on selected polychlorinated biphenyls (PCBs), DDTs, hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB) and chlordanes. This thesis also include studies of polycyclic aromatic hydrocarbons (PAHs) which are regulated under the 1998 Aarhus Protocol only. Furthermore, the following newly regulated POPs have been studied; i.e. endosulfans, pentachlorobenzene (PeCB) and short-chain chlorinated paraffins (SCCPs). Table A1 provides more detailed information (name, CAS and IUPAC number, physical-chemical properties and structural formula) on the individual compound and compound groups investigated. Past and contemporary sources of investigated compounds are discussed in section 1.4.

1.2. POPs criteria

1.2.1. Persistence (P)

Persistence is media-specific and typically reported as the time required for the concentration of a substance to be reduced to half of its original value with absence of additional inputs (UNECE, 2010a; UNEP, 2009b). According to both the 1998 Aarhus protocol and SC, the persistence criterion is fulfilled when the half-lives of POPs in water is \geq two months, and in soil and sediment \geq six months (UNECE, 2010a; UNEP, 2011). It should be noted that half-life is temperature dependent, and chemicals with shorter half-lives may exhibit extended persistence when entering the cold polar environments. An alleged indicator of persistence is the presence of a contaminant in remote areas such as the Arctic and the Antarctic (Riget et al., 2010; Webster et al., 1998). Additionally, the overall environmental persistence in a multimedia environment is dependent on mode of entry and environmental partitioning properties of the compounds of interest. Because overall persistence is difficult to determine empirically, overall multimedia half-lives are often estimated using modelling approaches (Webster et al., 1998).

1.2.2. Bioaccumulation (B)

POPs are typically both lipophilic and hydrophobic, i.e. fat-loving and water-hating, as reflected by a high octanol-water partition coefficient (K_{ow}) (Mackay, 1991). Hence, they tend to favour organic matter at the expense of the aqueous phase (Jones and de Voogt, 1999), resulting in accumulation of POPs in lipid tissues within aquatic organisms. POPs are said to be potentially bio accumulative when the bioconcentration factor (BCF) is > 5000 or $\log K_{ow} > 5$ (McLachlan et al., 2011).

1.2.3. Toxicity (T)

Toxic effects of POPs can be either (i) acute and/or (ii) chronic. A measurement of the toxicity is the lethal dose (LD), and is the level of concentration that will eliminate 50 % of a population either acute (LD₅₀) or chronic (LC₅₀). Several POPs are proven to have carcinogenic properties, immunological, hormonal and reproductive disrupting properties (e.g. AMAP, 1998; Consonni et al., 2008; Langer et al., 2008; Routti et al., 2010).

1.2.4. Long range transport (LRT) potential

POPs are finally characterized by their potential for long-range transport (LRT) (Vallack et al., 1998). Although different definitions of long range transport (LRT) potential are debated, a half-life in air of more than 2 days or monitoring data from a remote area would indicate that this criterion is fulfilled (UNEP, 2009b). The combination of persistence and favourable physical-chemical properties may thus make POPs prone to LRT by air, water or through a combination of both. LRT of POPs by air is discussed in further detail in section 1.3.2.

1.3. POPs behaviour

The fate and behaviour of POPs in the environment will largely be dictated by persistence, the physical-chemical (PC) properties and reactivity of individual POPs. Of key significance are those PC properties which control their distribution between air, water and octanol, whereby the latter serve as a surrogate for organic carbon / lipids (Gouin and Wania, 2007).

1.3.1. Physical-chemical properties

Reliable and accurate PC properties are essential for sound estimation and evaluation of the environmental distribution and transport potential of a chemical (Gouin et al., 2000). The aqueous solubility (S_w), octanol solubility (S_o), vapour pressure (P), Henry's law constant (H), partition coefficient between octanol and water (K_{OW}), partition coefficient between octanol and air (K_{OA}) and partition coefficient between the air and water (K_{AW}) for each compound in question all offer useful information for a complete characterisation of environmental behaviour and fate (Li et al., 2003; Ma et al., 2010; Shen and Wania, 2005; Xiao et al., 2004). The phase distribution of POPs can be plotted in a 2-dimensional chemical partitioning space map (Wong and Wania, 2011) like in Figure 2. Here, the relationship $\log K_{OW} = \log K_{OA} + \log K_{AW}$ is used, whereby $\log K_{OW}$ appear as diagonal bands of constant $\log K_{OW}$. The figure illustrates the phase partitioning of selected POPs included in this thesis, and further how POPs often have the ability to be present in several

environmental compartments. Therefore, they are often referred to as multimedia pollutants (see also **Paper IV**).

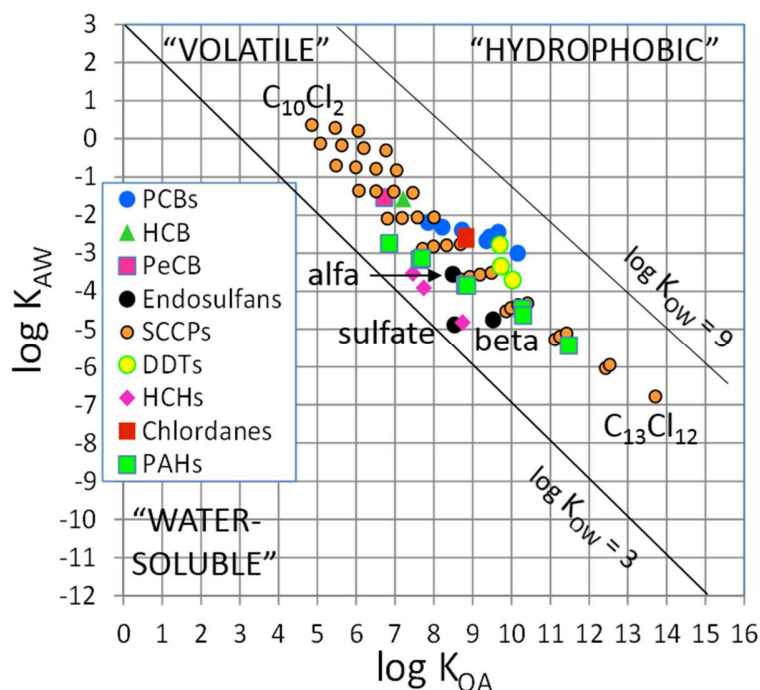


Figure 2: Chemical partitioning space map, showing the equilibrium phase distribution for studied POPs. Data on physical-chemical properties for individual POPs (PCBs, HCB, HCHs, chlordanes, PAHs, DDTs, individual endosulfans, PeCB and SCCPs) were adapted from the literature (Gawor and Wania, 2013; Li et al., 2003; Ma et al., 2010; Shen et al., 2005; U.S. EPA, 2011; Xiao et al., 2004).

POPs located in the upper left region are volatile (low K_{OA} and high K_{AW}) and have large potential to evaporate from environmental surface compartments like e.g. soil (**Paper IV**). Compounds located in upper right corner have strong affinity for octanol at the expense of water and are therefore hydrophobic. If present in soil, these compounds tend to sorb strongly to organic solids and are hence prone to erosion rather than leaching or evaporation (**Paper IV**). Substances with a high K_{OA} , if present in the atmosphere, furthermore tend to attach strongly to particles. Compounds located in the lower left are more water-soluble and may be found in dissolved state if present in the water phase (low K_{OA} , low K_{AW}), and are more prone to leaching if present in soils.

While Figure 2 displays PC properties determined at 25°C, it is important to note that PC properties typically are temperature dependent. Of particular note is the temperature dependency of vapour pressure, which increases at higher temperatures. Consequently, the partition coefficients between

air and water (K_{AW}) and air and octanol (K_{OA}) will be affected by a reduction in the temperature. While K_{OW} is typically less temperature-dependent than K_{AW} and K_{OA} . The net result of a reduction in temperature from 25°C is that a specific chemical plotted in Figure 2 will move diagonally towards the lower right corner (i.e. become less “volatile”). As temperature is a significant parameter in order to evaluate the distribution of POPs in the environment, reliable estimates of temperature-dependent PC properties are needed for more realistic evaluations. However, available data on PC properties reported in the literature are often in conflict and uncertainties for specific parameters may range over several orders of magnitude (Shen and Wania, 2005). Great care is therefore required when selecting PC properties for various environmental assessments and modelling studies (Renner, 2002). Recognizing the often haphazard selection of PC properties seen in earlier studies, a number of more recent studies have attempted to provide more reliable, consistent and accurate data sets by exploiting the thermodynamic constraints to which organic chemicals are subject (Beyer et al., 2002). The data used to construct Figure 2 are reflecting so-called final adjusted values from authoritative studies published over the last decade, taking into account all reliable empirical data published to date as well as adjusted to be in accordance with thermodynamic constraints.

1.3.2. Long range atmospheric transport (LRAT)

From the 1980s onwards, it was increasingly recognized that POPs also exhibited potential for long-range atmospheric transport (LRAT) to remote regions such as Nordic and Arctic regions (Oehme and Manø, 1984; Ottar, 1981; Pacyna and Oehme, 1988). A number of pioneering studies on the occurrence and LRAT behaviour of POPs in air were carried out in Scandinavia (Bidleman et al., 1981; Bidleman et al., 2004; Brorström-Lundén, 1996; Haugen et al., 1998; Wania and Haugen, 1999). These studies were often carried out at EMEP stations, contributing with data to national and international monitoring programs. The number of measurement sites for POPs has gradually increased in recent years, improving the spatial coverage in Europe. Through LRAT, POPs may also enter and exchange with surface media in various ecosystems, such as water, soil and vegetation (Armitage et al., 2009; Breivik and Wania, 2002; Hornbuckle et al., 2006; Sundqvist et al., 2010). Examples of field studies of POPs in this area, which have targeted multiple environmental compartments include, latitudinal transect studies from Southern UK to Northern Norway (Meijer et al., 2003a; Ockenden et al., 1998; Schuster et al., 2010).

Some POPs may be transported to higher latitudes by a series of evaporation and deposition steps, also called “grasshopping” (Wania and Mackay, 1996). Warmer regions will favour evaporation from environmental surface media, with subsequent transport/hopping to higher latitudes (Mackay and Wania, 1995). At lower temperatures, the vapour pressure of the substance will decrease and by this, the substance will obtain a higher affinity for sorption onto atmospheric particles (Bidleman, 1999). When absorbed onto particles, POPs become more prone to be removed from the atmosphere by dry particulate or wet deposition. Once deposited to a surface media (soil, water, snow or ice), POPs may either become retained or re-volatilized (**Paper IV**). The potential for re-emission will be dependent on various factors, such as the affinity of the environmental surface medium for the chemical, its potential to degrade the chemical, the vapour-pressure of the compound and temperature (van Pul et al., 1998). Differences in PC-properties of a contaminant mixture during atmospheric transport may lead to global fractionation (Ockenden et al., 1998).

Theoretical evaluations of LRT potential of POPs have more recently been carried out by modelling their characteristic travel distance (CTD) (analogue to half-life). CTD refers to the distance a compound may travel before the concentration is reduced to $1/e$ (37 %) of the original concentration and considers the concerted action of mode of emissions, degrading reactions and net atmospheric exchange with environmental surface media (“stickiness”) (Bennett et al., 1998; Beyer et al., 2000; Scheringer, 1997). In other words, LRAT of POPs is mitigated by atmospheric reaction and net atmospheric deposition, i.e. loss processes.

The predominant degrading loss process of gaseous POPs in air is through chemical reaction with the highly reactive hydroxyl (OH) radicals (Atkinson, 1990), while major transformation processes in other environmental compartments like soil, sediment and water are photolysis and microbiological degradation (Sinkkonen and Paasivirta, 2000). Degrading reactions will typically be slower at lower temperatures, leading to prolonged environmental half-lives in cold environments (enhanced persistence). Typically, photolysis is reduced due to lower solar angle and biodegradation by microorganisms will also be reduced (Wania and Mackay, 1993).

LRAT of POPs is also moderated by (net) atmospheric deposition to environmental surface media such as soils. Soils are considered to be important reservoirs and potential sinks for POPs (Meijer et al., 2003b). Boreal soils are of particular interest, due to the low ambient temperatures and high soil organic matter (SOM) content which enhance the storage capacity of POPs (Moeckel et al.,

2008). Previous studies have reported data on the occurrence and distribution of many legacy POPs along expected pollution gradients for empirical evaluation of LRAT (e.g. Hassanin et al., 2004; Hassanin et al., 2005; Meijer et al., 2002; Schuster et al., 2011). Consequently, by assessing concentration gradients in soils from possible major source regions to more remote areas, empirical evaluation of the occurrence, distribution, fate and LRAT behaviour is feasible, which may complement and evaluate theoretical predictions (e.g. CTDs).

1.3.2.1. Atmospheric transport models

Several existing long-term monitoring programs are based on AAS techniques, such as EMEP (Aas and Breivik, 2009; Aas, 2008; Tørseth et al., 2012). In contrast to PAS, AAS is often non-continuous and takes place at fixed time intervals (e.g. one day per week), hence current measurement strategies may overlook LRAT episodes with elevated concentrations (e.g. Yao et al., 2007) (**Paper III**). However, data from AAS may be particularly useful to evaluate predictions from atmospheric POP models, aiming to study source-receptor relationships for POPs.

Atmospheric transport-oriented models for POPs can mainly be divided into two main categories; Eulerian models and Lagrangian models, which both typically have been adapted from classical air pollution dispersion models. Eulerian models simulate chemical transport and fate using a gridded structure (Hansen et al., 2006; Malanichev et al., 2004). In contrast, Lagrangian dispersion models rather follows plume parcels through the atmosphere (e.g. Eckhardt et al., 2009). Additionally, there are a number of multimedia box models, usually fugacity-based (Mackay, 1991), which typically aim to describe the transport and fate of POPs within and across different environmental media. Fugacity-based models often contain simplified descriptions of chemical transport in air (and/or water), but they add complexity by targeting multiple environmental compartments.

In this work, the Lagrangian particle dispersion model FLEXPART has been used (Stohl et al., 2005; Stohl et al., 1998) (**Papers I and III**). FLEXPART calculates the movement of an air mass parcel over certain distances, which gives a more realistic understanding of the accompanying meteorology. The flows and reaction of POPs in the air masses are subjected to specific processes in the atmosphere, such as turbulence, convection, deposition and atmospheric reaction with hydroxyl (OH) radicals (Eckhardt et al., 2009; 2007). An advantage of the FLEXPART model in

the context of this work is the possibility to estimate trajectories of an air mass and trace it backward as well as forward in time (Eckhardt et al., 2007; Stohl et al., 1998) (**Paper III**).

1.4. Sources and emissions

Primary emissions of POPs can be divided into two main categories (i) primary emissions occurring as a result of the production, use and disposal of intentionally produced POPs, or (ii) primary emissions because of unintentionally formed POP by-products originating from various combustion or chemical/industrial processes. Intentionally produced POPs are often divided into two sub-groups; pesticides and industrial chemicals (Breivik et al., 2004). Some POPs belong to more than one category, e.g. HCB and PCBs. HCB has been used as a pesticide, in the chemical industry (e.g. paints, solvents), and may also be formed unintentionally as a by-product from the chemical industry or through combustion processes (Bailey, 2001; Lohmann et al., 2000). PCBs have been extensively used as an industrial chemical (Harrad et al., 1994), but may additionally be formed in various combustion processes (Lohmann et al., 2000). In addition to primary emissions, POPs may also be re-emitted from environmental reservoirs that have been contaminated in the past. These are called secondary emissions (Bidleman, 1999; Harrad et al., 1994).

1.4.1. Pesticides

Environmental emissions of pesticides today may occur as results of primary emissions (e.g. remaining agricultural use of stockpiles) as well as secondary sources. Several pesticides are regulated under the 1998 Aarhus Protocol (UNECE, 1998) and the SC (UNEP, 2002) (Table 1). The 1998 Aarhus Protocol listed 11 pesticides among the initial 16 POPs, while the SC listed 9 pesticides among the initial 12 legacy POPs, also known as the “dirty dozen” (UNEP, 2002) (Table 1). The current study includes the following pesticides: chlordanes, DDTs, HCB, HCHs, PeCB and endosulfan (see Table 1). The chlordanes are listed as compounds for elimination under both conventions, while DDTs are listed as a substance with restrictions on emissions under both conventions. HCB has been used as a fungicide and is listed under elimination and restriction under the Aarhus protocol (UNECE, 1998) and the SC (UNEP, 2002). HCHs are insecticides which have been extensively used around the world (Breivik et al., 1999; Li, 1999). HCHs originate ultimately from production and usage of technical HCH (various HCH-isomers) or Lindane (> 99% γ -HCH) (Breivik et al., 1999). The major constituents in the technical mixtures of HCHs are α -, β - and γ -HCH. While only γ -HCH inhibits insecticide properties, all three isomers in the technical mixture

have toxic effects (Li, 1999). Technical mixtures of HCHs are listed under elimination under the 1998 Aarhus Protocol, while Lindane is listed under restricted use (UNECE, 2010a). Technical HCHs and production of Lindane are listed for elimination as one of nine new POPs under the SC in 2009 whereas use of Lindane is restricted (UNEP, 2009a). The technical endosulfan mixture contains two isomers (α - and β - endosulfan) (Weber et al., 2010) and was listed under the SC in 2011 (UNEP, 2011). PeCB has been listed under the SC (UNEP, 2009b) and adopted under the Aarhus protocol (UNECE, 2010a). In addition to being a pesticide, PeCB is also emitted as an industrial chemical (Bailey et al., 2009).

1.4.2. Industrial chemicals

Industrial POPs have been produced for various uses, such as di-electrical and cutting fluids lubricants (Wang et al., 2010), flame retardants (Haukas et al., 2009), plasticizers (Kohler et al., 2005). PCBs were first synthesised in the end of the 1920s, and the production peaked in the 1970s (Breivik et al., 2002). PCBs were produced as technical mixtures (U.S. EPA, 2013; Yum et al., 2010), and have been used in a broad range of electrical equipment (e.g. transformers and capacitors) (Breivik et al., 2011), in paints (Ruus et al., 2006) and building materials (Andersson et al., 2004). PCBs are listed for elimination and reduction under the 1998 Aarhus protocol (UNECE, 1998) and the SC (UNEP, 2002). PeCB and SCCPs have been used as industrial chemicals for many decades. PeCB can be found in electrical fluids (UNECE, 2007). SCCPs are a complex mixture of polychlorinated *n*-alkanes (PCAs), and have been used in a broad range of materials such as paints, sealants and as flame retardants (UNECE ad hoc expert group on POPs, 2003). SCCPs are still produced extensively in China (Zeng et al., 2011), while they are increasingly phased out in Europe.

1.4.3. Unintentionally formed by-products

Examples of emission sources of unintentionally formed POP by-products include waste incinerators, open burning of waste, industrial processes (e.g. metallurgic or chemical) (Mazur et al., 2010; Morf et al., 2007), and incomplete burning of fossil fuel (Halsall et al., 1994). Unintentionally formed POPs include dioxins and furans (PCDD/Fs) (Altarawneh et al., 2009; Lavric et al., 2004), PAHs (Kulik et al., 2006; Ravindra et al., 2008), HCB (Bailey, 2001; Barber et al., 2005), PeCB (Bailey et al., 2009) and PCBs (Liu et al., 2009). Emissions from major stationary sources of PAHs and PCDD/Fs, may be mitigated using best available techniques (BAT) (UNECE, 2009).

1.5. Active air samplers (AAS)

Air measurements of semi-volatile organic contaminants (SVOCs) have historically been carried out using active air samplers (AAS). The air is drawn through a sampler module which consists of a filter (to collect particles and particle associated compounds) and a sorbent (to collect gas phase compounds) or occasionally only one of these two, reflecting sampling constraints and/or the target compound(s) considered. The sorbent varies depending on target compounds but common for semi-volatile organic compounds are polyurethane foam (PUF) or polystyrene divinylbenzene copolymer (XAD)-resin. Air is drawn through the sampler by a pump working at a controlled flow rate. This gives a known sample volume, which in turn enables concentrations in air to be obtained. A key advantage of AAS in the context of LRAT is the short time of sampling which in combination with appropriate modelling tools (e.g. trajectories) offers possibilities to study specific episodes (**Paper III**). Further, the large sample volume usually allows for excellent sensitivity and low detection limits. However, the need of electricity, trained field personnel and the high costs associated with these types of air samplers, limits their spatial coverage (Aas and Breivik, 2009; Hung et al., 2013).

1.6. Passive air samplers (PAS)

A complementary alternative to AAS is passive air sampling, which does not require a pump and electricity. This, in combination with their low cost and ease of handling, allows for both increased spatial and temporal coverage, both in indoor and outdoor environments (Bohlin et al., 2008). This work has further applied and evaluated the performance of one of the most commonly used passive air sampling technique for semi-volatile POPs (or SVOCs), i.e. PUF disks (**Paper I, II**).

Different passive air sampling strategies are available. An example of a natural PAS is plant foliage. Needles and leaves have a large surface area and the waxy cuticle has high affinity for many organic pollutants (Muir et al., 1993), which means that SVOCs can be taken up from the atmosphere by the foliage. However, difficulties with reliable measurements due to environmental variability such as age, season, and species limit their utility (McLachlan et al., 1995). As a result, man-made PAS have been developed as an alternative. Examples include, but are not limited to, PUF disks (Harner et al., 2006; Jaward et al., 2004; Pozo et al., 2006), semi-permeable membrane devices (SPMDs) (Huckins et al., 2002), XAD-resin based samplers (Krogseth et al., 2013; Wania

et al., 2003), polymer coated glass (POG) (Harner et al., 2003), and solid phase micro extraction (SPME) (Wang et al., 2009).

In order to collect measureable amounts, the PAS typically requires deployment for weeks/months or up to years, and as a result, PAS provide long-term time-averaged concentrations. Information on spatial and long-term temporal trends is achieved and thus appropriately complements AAS strategies. Passive air sampling is a semi-quantitative method since the sampled air volume is not known with a similar accuracy as for AAS. Instead, a fictive flow rate (i.e. the uptake rate) and sampling volume can be estimated from calibration studies against AAS, or by the use of performance reference compounds (PRCs). The concentrations in air are then calculated based on the estimated uptake rates and the amount of POPs accumulated in the sampling material.

1.6.1. Introduction to theory of passive air sampling

PAS techniques are based on free flow and molecular diffusion of pollutants from the air to a sampling medium (i.e. the PAS) which has a high retention capacity for the target pollutants. Differences in chemical potentials between the air and the sampling medium of the pollutant create a net flow into the PAS until equilibrium between the two phases has established. More detailed, the mass transfer of pollutants from the air to the PAS is described by individual transport processes across several boundary layers. If the PAS is deployed inside a chamber (e.g. PUF in a flying saucer/UFO design (Fig. 3)), the transport to the sampling material follows a three-step process; i) from outer air to the air inside the chamber, ii) from inside-air to the air-side boundary layer of the PAS, and iii) from the air-side boundary layer into the passive sampling medium (PSM) (Bartkow et al., 2005).



Figure 3: Deployed PAS on the Norwegian coast (Photo: Marianne Haukås) and fixed to a pole at the Zeppelin station, Ny-Ålesund (Photo: Anne Karine Halse)

In theory, the transport into the sampler medium is mainly due to molecular diffusion, and the movement is described as a gradient flux (F) by Fick's First Law (Bartkow et al., 2005). F is a function of the overall air-side mass transfer coefficient (k_A) (which is the velocity of the pollutants across each boundary layer), the area of the passive sampling medium (A_{PAS} , m²) as well as the difference between the concentration in air (C_{AIR} , pg/m³) and the concentration in the PAS (C_{PAS} , pg/m³) (Mackay, 1991), together with the PAS-air partition coefficient ($K_{PAS-AIR}$). $K_{PAS-AIR}$ is the ratio of the concentration in the air and the concentration in the PAS when the two are in equilibrium and describes the extent to which compounds are enriched in the PAS relative to in air (Bartkow et al., 2005). The final flux (F) or accumulation rate (pg/time unit) of pollutants can be described according to eq. 1.

$$F = k_A A_{PAS} \left(C_{AIR} - \frac{C_{PAS}}{K_{PAS-AIR}} \right) \quad (1)$$

The accumulation of pollutants in the PAS is a balance of the rate of uptake minus the rate of loss. The compounds accumulate in the PAS through a linear, curvilinear and equilibrium phase as shown in Figure 4. At the beginning, the uptake is linear, airside controlled and a function of k_A and C_{AIR} , while the loss rate is negligible since $\left(\frac{C_{PAS}}{K_{PAS-AIR}} \right)$ is small, and the uptake is larger than the loss. The flux/transport is mainly directed into the PAS, illustrated by the bigger arrow downwards in Figure 4. This condition is ideal in field because under these conditions there is a direct relationship between number of days deployed and volume sampled, which represents the uptake rate (m³/day) (Shoeib and Harner, 2002). Along with the increased exposure time (number of days

or weeks) the levels of target compounds in the PAS increase and the loss fraction ($\frac{C_{PAS}}{K_{PAS-AIR}}$) becomes larger, consequently the uptake is reduced and enters a curvilinear phase. As exposure time increases, the ($\frac{C_{PAS}}{K_{PAS-AIR}}$) further increases and eventually becomes equal to C_{AIR} , and the curve enters into equilibrium phase where uptake and loss rates are thought to be equal (i.e. no net-flux into the PUF) (Shoeib and Harner, 2002).

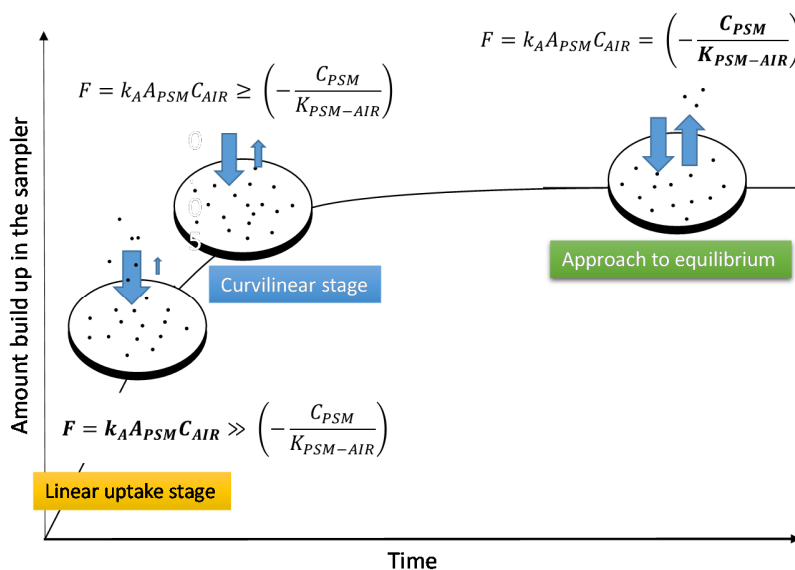


Figure 4: Theoretical uptake curve for PAS, illustrating linear, curvilinear uptake phase, and approach to equilibrium (Bartkow et al., 2005; Shoeib and Harner, 2002).

The time to reach equilibrium is dependent on sampler design as well as the $K_{PAS-AIR}$. $K_{PAS-AIR}$ is compound- and sampler-specific, correlated to the K_{OA} (see 1.3.1) of the compound, and thereby a function of temperature. As shown in Figure 5, the uptake (volume sampled) is linear within a longer time period for compounds with higher K_{OA} values, and consequently higher $K_{PAS-AIR}$ values, while compounds with lower K_{OA} will approach equilibrium faster (Pozo et al., 2004). See Table A1 for more information regarding K_{OA} values for the selected compounds within this study. Further, Table A2 presents temperature-adjusted K_{OA} values and theoretically estimated number of days until 25% (t_{25}) and 95% (t_{95}) of the equilibrium stage in the PUF-PAS has been reached (Shoeib and Harner, 2002).

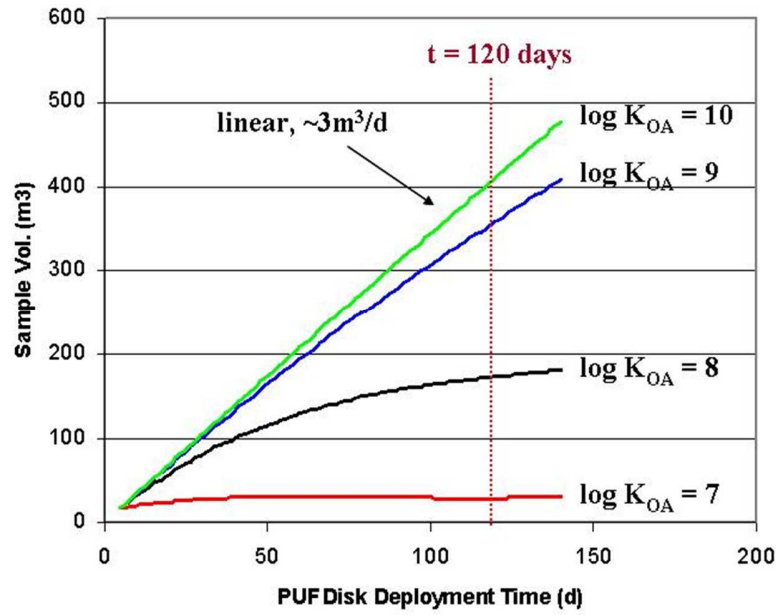


Figure 5: Uptake curves for a range of octanol-air partition coefficients (K_{OA}) (Farrar et al., 2005a).

In order to estimate the volume of air sampled during the deployment period, the following relationship can be drawn (eq.2),

$$V_{PAS} = k_A A_{PAS} \Delta t \quad (2)$$

and where $V_{PAS} = \frac{M_{PAS}}{C_A}$

From this, $k_A A_{PAS}$ represents the passive air uptake rate R_s (m^3/day), i.e. the volume of air passed through PAS per time period, and Δt is the exposure period of the sample (Shoeib and Harner, 2002). The uptake rate is obtained through i) calibration studies against AAS from the slope of the linear uptake phase (Fig. 5) or from Equation 3, ii) by using PRCs or by iii) modelling exercises.

$$R = \frac{M_{PAS}}{C_A \Delta t} \quad (3)$$

Air concentrations are then estimated according to

$$C_A = \frac{M_{PAS}}{R \Delta t} \quad (4)$$

In this thesis (**Paper I** and **II**), the sample volumes and the concentrations of gas phase compounds were estimated by use of PRCs. The PRCs consist of isotope labelled or unlabelled non-native compounds exhibiting limited concentrations in the air. Ideally, the PRCs should cover a wide

range of physical-chemical properties (e.g. partition coefficients/volatilities) corresponding to the range for the native target SVOCs (Huckins et al., 2002). The loss of PRCs during the exposure period depends on the physical-chemical properties of the PRCs, the exposure time, and environmental conditions (such as wind speed) just as the uptake of target pollutants. The loss rate of the PRCs from the PAS is believed to be correlated to the uptake rate (R_s) of target compounds in the same PAS. For example, the thicker the boundary layer the slower the loss and the uptake, and vice versa. Consequently, site-specific environmental factors, such as wind-speed effects, can be accounted for in the estimates of air concentrations (Moeckel et al., 2009). In reality, PRCs do not cover the full-range of target SVOCs, and they are not applicable for particle-associated compounds and can therefore only be used to assess air concentrations of gas phase SVOCs. By use of PRCs, individual uptake rates can be calculated based on concentrations of each PRC (Eq. 5),

$$R_s = \ln \left(\frac{C_{PRC,t}}{C_{PRC,0}} \right) A_{PAS} \delta_{FILM} K_{PAS-AIR} \rho_{PAS} / t \quad (5)$$

Where ($C_{PRC,t}/C_{PRC,0}$) is the recovery of individual PRCs, A_{PAS} is the area of the PUF-disk, δ_{FILM} is the effective film thickness, ρ_{PAS} is the density of the PAS material (g/m^3). $K_{PAS-AIR}$ is a function of K_{OA} (i.e. $\log K_{PAS-AIR} = 0.6366 \cdot \log K_{OA} - 3.1774$ (Shoeib and Harner, 2002)) and is also temperature dependent, while t is the deployment time in days. An average R_s , based on the individual R_s , is then ultimately used. In order to back-calculate the volume of air sampled, it has been recommended to only use R_s based on PRCs where the loss (C/C_0) ≥ 40 % during deployment (Pozo et al., 2009), but PRCs with losses in the range of 20-80 % may alternatively be applied (Huckins et al., 2002; Moeckel et al., 2009).

1.6.1.1. Linear/kinetic passive air samplers

PAS strategies usually target sampling during either the linear uptake phase or the equilibrium stage (Fig. 4). An important factor common for both is the challenge to sample adequately, i.e. sample quantifiable amounts while staying within the same uptake phase for all target compounds. As described above, compounds with low K_{OA} will bypass the linear uptake phase faster than those with higher K_{OA} (Fig. 5, Table A2) and it is important to make sure that the exposure time corresponds to the maximum length of the linear uptake phase or the minimum of the equilibrium phase.

Ideally, PAS targeting the linear uptake phase should therefore have large uptake capacity and fast uptake rates (Wania et al., 2003). The PUF-PAS design used in this thesis (**Paper I, II**) work as a linear/kinetic sampler. The PUF disks have high affinity and uptake capacity for SVOCs, including many POPs. The use of PUF as a PAS has already been explored in numerous studies on a local, regional and a global scale (Chaemfa et al., 2008; Harner et al., 2006; Harner et al., 2004; Jaward et al., 2004; Klanova et al., 2006; Motelay-Massei et al., 2005; Pozo et al., 2004; Pozo et al., 2006; Shoeib and Harner, 2002). The sampling material (PUF) is shielded by a stainless steel chamber (Fig. 3), where the PUF disk is centred in the middle on a metal rod. PUF-PAS in the field are often deployed at some distance above the ground, e.g. in a tree (Fig. 3), fence or lamppost. At exceptionally windy places, PAS may have to be placed in a fixed position using a support pole. However, deployment in a fixed position may reduce the dampening effect of the bowls and a higher uptake rate could be expected.

Besides the PUF-disks, other linear uptake samplers are also available, e.g. the XAD-PAS and the triolein (lipid) containing semi permeable membrane device (SPMD). In the XAD-PAS, XAD-resin is placed inside a wind-protecting chamber (Krogseth et al., 2013; Wania et al., 2003; Zhang et al., 2012). The sorbent has a higher sorption capacity to retain SVOCs in comparison to the PUF-disk and can therefore be deployed for longer periods before equilibrium is reached (i.e. months to years). Recently, XAD sorbent-impregnated polyurethane foam (SIP) disks (Koblizkova et al., 2012) have been developed and tested in order to increase the sorption capacity of the PUF-disks and thereby to expand the sampling domain towards more volatile chemicals while still operating in the linear uptake phase.

SPMDs consist of a solvent-filled polyethylene tube (Bartkow et al., 2005; Huckins et al., 2002; Ockenden et al., 2001; Ockenden et al., 1998), which can be used for both water and air sampling. SPMDs may also be used as equilibrium samplers (1.4.3.2). The solvent/sorbent inside the SPMDs can be switched to another organic sorbent such as a silicone or poly(dimethylsiloxane) (PDMS) material (Wennrich et al., 2002). Another linear passive air sampler using polyethylene is the low-density polyethylene sheets (LPDS) (Bartkow et al., 2004; Khairy and Lohmann, 2013).

1.6.1.2. Equilibrium passive air samplers

An ideal equilibrium sampler has fast uptake rate and limited uptake capacity in order to achieve equilibrium without requiring extensive exposure times. However, the uptake capacity must also

be sufficiently high to accumulate enough chemical for analytical detection. An example of equilibrium PAS include polymer-coated glass cylinders (POG) which consist of a thin film of ethylene vinyl acetate (EVA) deployed on glass (Harner et al., 2003). Here, the compounds diffuse into the sampler media until equilibrium is reached (Farrar et al., 2005b; Wilcockson and Gobas, 2001).

1.6.1.3. Sampling artefacts

The PUF-PAS technique is a semi-quantitative method. Uncertainties related to the uptake rates, whether the sampling occurs during the linear uptake phase, and the performance for PAS to sample particle-associated compounds may all introduce potential errors or lower the accuracy in estimated air concentrations. The performance of the PUF-PAS, and thereby also the end-point results, may also be affected by site specific environmental conditions such as wind speed, temperature and air concentrations (Chaemfa et al., 2009b; Harner et al., 2004; Klanova et al., 2008; Tuduri et al., 2006).

The uptake rate should, in theory, not vary by compound (Fig. 5) and a generic uptake rate is therefore often used to estimate air concentrations. Some studies have, however, shown large variations of uptake rates between individual SVOCs (Bohlin et al., 2014; Klanova et al., 2008; Melymuk et al., 2011). Hence, applying a generic uptake rate may introduce errors for some SVOCs, and applying various uptake rates to individual or grouped SVOCs may help to increase the accuracy. Whether one generic or various uptake rates should be used is still debated by the users of PUF-PAS.

Most PAS designs are suspected to mainly sample gaseous volatile compounds, but the PUF-PAS has been shown to also accumulate particle-associated compounds to some extent (Klanova et al., 2008). Its performance for particle-associated compounds is dubious. The particle fraction seems to be collected with lower uptake rates and accuracy and the accumulation may not follow the theoretical framework of the PUF-PAS (Klanova et al., 2008). This is a challenge for the use of PUF-PAS for SVOCs with high K_{OA} . PRCs are not applicable for particle-associated compounds and can therefore only be used to assess air concentrations of gas phase SVOCs.

Wind speed may influence the thickness of the boundary layer surrounding the PUF-PAS and thereby both the uptake rate and the duration of the linear uptake phase (i.e. time to equilibrium). High wind speeds reduce the thickness of the boundary layer, increase the uptake rate and shorten

the length of the linear uptake phase. Correspondingly, low wind speeds cause stagnant air around the PUF-disk and thereby reduce the uptake rate. Hence, in order to minimize wind speed effects, the PUF-disk is protected by a housing consisting of two stainless steel metal domes (i.e. flying saucer or UFO design, Fig. 3) (Tuduri et al., 2006). Additionally, by using PRCs, site-specific uptake rates can be achieved and wind-speed effects accounted for.

Surrounding temperatures may affect the sampling by the PUF-disk, but the effect is complex and varies by compound. Generally, at higher temperature, the duration of the linear uptake phase may be shortened and the uptake rate is consequently affected (see Table A2), while at lower temperatures the semi-volatile compounds may be increasingly sorbed to airborne particles, which in turn may reduce the uptake in PUF-disk. These effects may not be captured by the use of PRCs. The PRCs and their temperature-dependent partition coefficients (K_{OA} , $K_{PSM-AIR}$) (Bartkow et al., 2006; Melymuk et al., 2011) are based on meteorological modelled air temperatures and not on measured temperatures. Ambient conditions in the field may therefore not be captured.

Another issue regarding PUF-PAS is the potential resistance within the sampling material, which may influence the R_s (eq.5). Recent studies suggest that compounds accumulate in the outer parts of the sampler in close contact to the air, resulting in higher R_s for shorter exposure times (e.g. 1-3 weeks). This may be due to possible kinetic resistance within the PUF-disk (Bohlin et al., 2014; Zhang et al., 2012).

Nevertheless, ongoing work with the PUF-PAS aim to quantify and control the sampling artifacts by detailed calibration studies, evaluation of sampler housing designs, and the use of PRCs. From a clear recognition of their major weaknesses and strengths, PAS is regarded to be a complimentary and useful method for air sampling in comparison to AAS (**Paper I and II**), see also (Chaemfa et al., 2009a; Gouin et al., 2008; Harner et al., 2013; Pozo et al., 2009).

1.6.2. Application of passive samplers/spatial mapping

The global monitoring plan (GMP) within the SC, as well as other international monitoring programmes for POPs in air, calls for comparable and consistent monitoring data to evaluate whether international agreements are efficient in terms of reducing environmental exposures (UNEP, 2007). For policy-makers interested in evaluation of potential future control strategies, it is furthermore vital to discriminate between emissions from primary and secondary sources (1.4). Finally, it is also beneficial for national authorities to be able to discriminate between LRAT from

neighbouring countries and domestic local sources (LS). PAS has the potential to contribute with useful data to address many relevant aspects in this regard. In this thesis, PAS are used to obtain a consistent and comprehensive dataset for evaluation of spatial patterns of POPs in European background air (**Paper I**) and this dataset is later explored with regard to its potential to discriminate between LRAT and LS in controlling atmospheric POPs burdens in Norway (**Paper II**).

Paper I thus complements the current measurement programme for POPs in background air within EMEP, which is based on a limited station network based on conventional AAS, mainly located in the Central and North-Western part of Europe (Aas and Breivik, 2009; Nizzetto et al., 2014). The application of PAS thus has a significant potential in terms of providing a more complete picture of spatial distribution patterns e.g. (Pozo et al., 2009). Regions with higher population density (Jartun et al., 2009; Ruus et al., 2006) or industrial activity (Ishaq et al., 2009; Næs, 1998) are, in contrast to background areas, considered to be potential source regions for many POPs. Atmospheric burdens of selected POPs in contaminated areas is a key topic in **Paper II**, while **Papers I** and **II** both offer insights into the importance of LS vs LRAT and primary versus secondary sources in controlling concentrations in air.

2. OBJECTIVES

The main objective of this doctoral thesis has been to study the occurrence, distribution and long-range atmospheric transport of selected POPs, mainly in North Western Europe, by field studies of air and soil in combination with various modelling techniques. Specific objectives for the four papers that form the backbone of the thesis are as follows:

Objective I (Paper I): The main goal is to improve the understanding of the occurrence and spatial patterns of POPs in background air across Europe, using passive air samplers in combination with an existing model (FLEXPART).

Objective II (Paper II): The main goal is to assess the potential influence of local sources versus long-range atmospheric transport in controlling atmospheric burdens of selected POPs in Norwegian coastal zones with consumption advisories on seafood, using passive air samplers.

Objective III (Paper III): The main goal is to develop, evaluate and apply a forecast system for predicting long-range atmospheric transport of selected PCBs to a monitoring site in southern Norway (Birkenes), using active air sampling in concert with an existing model (FLEXPART).

Objective IV (Paper IV): The main goal of the final study is to obtain a mechanistic and quantitative understanding of the occurrence, fate and distribution of newly regulated POPs in background soils from UK and Norway by combining empirical data, statistical analysis and chemical space/mobility plots.

3. MATERIALS AND METHODS

3.1. Field studies

The two first studies (**Paper I and II**) utilized PAS, and sampling was coordinated to occur at the same time to facilitate comparison of results. In **Paper I**, PAS were deployed at background sites in a number of European countries, mainly using established EMEP measurement sites (Aas and Breivik, 2008). The samplers were exposed in the field for about 3 months during late summer of 2006. The study region included 34 countries and 86 sites, located from Spitsbergen (78°N) in the north to Cyprus (33°N) in the south, and from Greenland (38°W) in the west to Kazakhstan (75°E) in the east (**Paper I**) (Fig. 6, blue dots). In the second study (**Paper II**), contaminated coastal zones were monitored using PAS in order to evaluate the contribution of possible LS versus LRAT in controlling concentrations of POPs in air. Similar to **Paper I**, PAS were deployed along the Norwegian coast for 3 months during late summer of 2006 (Fig. 6, red dots). The locations were selected on the basis of existing advisories on the consumption of seafood, caused by elevated levels of POPs (Økland, 2005). To achieve representative “background” concentrations in each coastal zone, areas close to major roads and industrial activities were avoided, while preference was given to parks and private properties to avoid interference. Moreover, in order to evaluate spatial variability within a coastal zone, two PAS devices were deployed at different sites in some selected coastal areas (N=5) (**Paper II**).

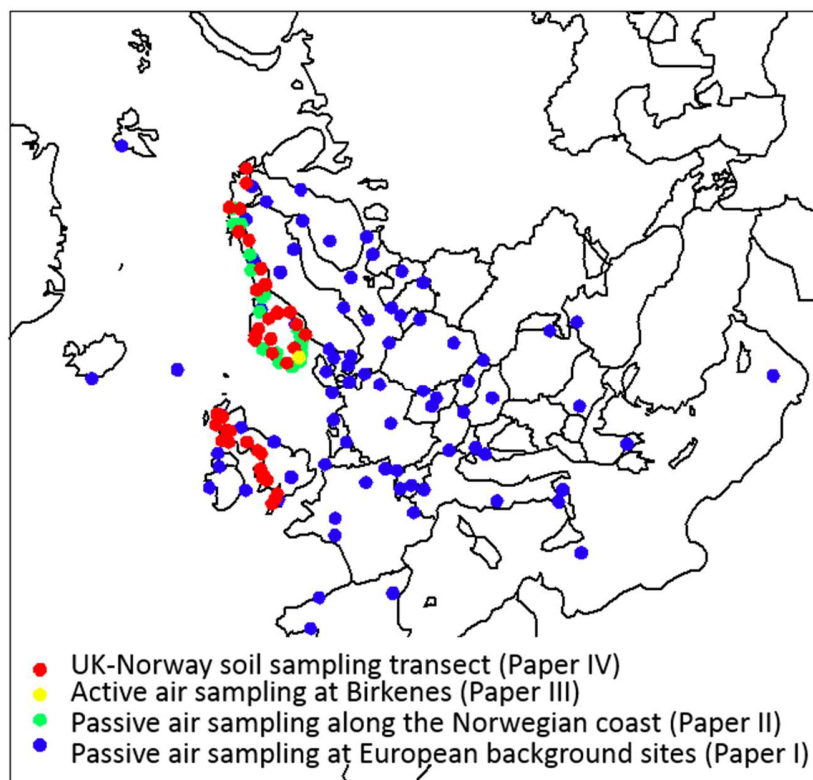


Figure 6: Overview over sampling sites included in the thesis.

In order to identify major source regions and to monitor possible LRAT events to a specific site, the third study (**Paper III**) targeted one Norwegian EMEP background station, i.e. the Birkenes observatory in Southern Norway (N 58°23, E 08°15, 190 m.a.s.l) (Eckhardt et al., 2009). For this study, a model based forecast system was developed and evaluated using targeted atmospheric monitoring (AAS) under predicted LRAT events (Fig. 6, yellow dot).

The fourth study (**Paper IV**) focused on deposition of newly regulated POPs to the terrestrial environment. Background surface soils along a UK-Norway transect, ranging from N 50°35, W 4°31 to N 70°31, E 28°1, were collected in 2008 (Schuster et al., 2011). The 59 soil samples, collected from 39 sites, represented two different types of background soil, i.e. woodland (coniferous/deciduous) (WL) soil and grassland (GL) soil (Fig. 6).

3.2. Sampling (air and soil)

Air sampling was mainly based on passive air sampling, using PUF-PAS. These campaigns were carried out using PAS alone (**Paper II**), or in combination with AAS at selected EMEP sites (**Paper I**).

The PUF-disks were spiked with a PRC mixture (Huckins et al., 2002) prior to deployment. The loss rates of PRCs during deployment were used to back-calculate the air concentrations (**Paper I and II**) (sect. 1.6). In the field, the PUF-disks were placed between two stainless steel metal domes as sheltering device (Fig.3) (Wilford et al., 2004).

Targeted air samples were collected by use of a high-volume active air sampling device (AAS) (Eckhardt et al., 2009), utilizing a modified pump (**Paper III**). This included both an on-line control of the sampling system and the possibility to apply a higher flow rate to achieve shorter sampling periods in order to better capture specific LRAT episodes.

Soil samples, woodland (WL) and grassland (GL) soil were collected by use of a stainless steel hand-held corer and the targeted sampling depth was the upper layer (0-5 cm). Ten individual cores were taken within a plot of approximately 1 x 1 square meter and pooled as a composite sample from each site (Meijer et al., 2002). The pooled samples were stored in a freezer at ~-18 °C until further sample preparation (**Paper IV**).

3.3. Modelling

Modelling tools were applied for fate and transport assessments. In **Paper I** we utilized FLEXPART in order to evaluate source-receptor relationship for selected measurement sites. In **Paper III**, the FLEXPART model was run daily using meteorological forecast data to predict the concentration of PCB-28 one day ahead over a time period of about two years, starting in 2008. Based on these initial predictions, a threshold (> 95% percentile) for targeted sampling of predicted LRAT events was defined (**Paper III**). Targeted air sampling was carried out when the predicted concentrations exceeded the threshold. After completed targeted sampling, FLEXPART was run backward in time with meteorological analysed data for the targeted episodes, resulting in more accurate predictions of source-receptor relationships during specific episodes.

3.4. Sample extraction and clean-up

The extraction, clean-up and sample analysis was carried out as described in **Paper I to IV**, and references therein, and only a brief introduction will be given here. After exposure, the air

samples/PUF-disks (field blank and deployed samples) from the first and second study, together with the PUF-plugs and glass fibre filters for the third study (**Paper III**), and the soil samples (**Paper IV**) were stored in a freezer (at ~ - 18°C) until extraction and clean-up. The air samples were Soxhlet extracted, and the extracts were divided into two aliquots. One aliquot was treated with concentrated sulfuric acid (**Paper I, II and III**) prior to further clean-up by fractionation with a silica column. The other aliquot (PAH part) (**Paper I and II**) of the extract was cleaned on a silica column without any acid treatment.

Soil samples (**Paper IV**) were dried, sieved and stored cold until extraction and clean-up. Extraction of the soil samples was carried out by using a Dionex, Accelerated Solvent Extraction (ASE) extraction unit. The soil organic matter (SOM) content was determined with loss of ignition (LOI) at 550 °C. In the same way as for the air samples, the soil extracts were also divided into two aliquots, i.e. one for the endosulfan fraction (α -endosulfan, β -endosulfan and endosulfan sulfate), and one for the PeCB and SCCPs, prior to the clean-up procedures. The aliquot for the determination of endosulfans was cleaned using a silica column only, while the aliquot for the determination of the PeCB and SCCPs was treated with sulfuric acid followed by a fractionation using a silica column (**Paper IV**).

All extracts were reduced to 0.5 mL and solvent-changed. Further, the extracts were reduced to ~ 100 μ L by nitrogen blow-down and recovery standard was added.

3.4.1. Selected target compounds

While 209 PCB congeners exist, this study focuses on the 7 indicator PCBs, i.e. PCB-28,-52, -101,-118,-153, and -180, collectively referred to as Σ_7 PCBs (**Papers I-III**). Regarding the HCHs, α -, β - and γ -HCH (Σ_3 HCHs) were included (**Papers I, II**), and *trans*-/ *cis*-chlordanes and *trans*-/ *cis*-nonachlor (Σ_4 chlordanes) represent the group of cyclodiene pesticides (**Papers I, II**). The DDTs include dichlorodiphenyltrichloroethane (*o,p'*- and *p,p'*-DDTs), dichlorodiphenyldichloroethylene (*p,p'*-DDE) and dichlorodiphenyldichloroethane (*p,p'*-DDD), collectively referred to as Σ_4 DDTs (**Papers I, II**). The individual PAHs studied were fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene and benzo(a)pyrene, referred to as Σ_8 PAHs (**Papers I, II**). For the endosulfans, the study focused on α -endosulfan, β -endosulfan and endosulfan sulfate (Σ endosulfans) (**Paper IV**). A mixture of short-chain chlorinated paraffins (SCCPs, C₁₀-C₁₃) were studied in **Paper IV**. Additionally, both HCB (**Papers**

I, II, IV) and PeCB (**IV**) were studied. More information about the selected compounds is available in Table A1.

3.5. Chemical analysis

The final extracts were analysed on an Agilent 6890N gas chromatograph coupled to a Waters AutoSpec mass spectrometer (GC/HRMS) in electron impact (EI) mode. The different PCB congeners (PCB-28, -52, -101, -118, -138, -153, -180) and some PRCs (non-native PCBs: PCB-23,-30,-32,-107,-198) (**Paper I** and **II**) were separated using a HT-8 fused silica capillary column (50 m length, 0.22 mm I.D., 0.15 μ m film thickness). Separation of α -HCH, β -HCH, γ -HCH, *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT, together with the PRCs (PCB-12,-14, $^2\text{H}_6$ - γ -HCH) compounds were done by use of a HP-1 (J&W Scientific) fused silica column (25 m length, 0.2 mm I.D., 0.33 μ m film thickness). Analysis of PAHs was carried out by a GC/LRMS on an Agilent 6890N gas chromatograph coupled to an Agilent 5973 mass spectrometer in electron impact (EI) mode. Separation was carried out by use of fused silica capillary column from Zebron (ZB-5) (30 m length, 0.25 mm I.D., 0.10 μ m film thickness). Analysis of the pesticides (*trans*-chlordane, *cis*-chlordan, *trans*-nonachlor, *cis*-nonachlor) was carried out by a low resolution Agilent 6890N gas chromatograph coupled to an Agilent 5973 mass spectrometer (GC/LRMS) in electron capture negative ion (ECNI) mode. Separation was done by an Ultra-2 (25 m length, 0.2 mm I.D., 0.11 μ m film thickness) fused silica capillary column (**Papers I, II, III**).

Analysis of the endosulfans and SCCPs was carried out by a high resolution Agilent 6890N and HP 6890 gas chromatograph, respectively, coupled to an Agilent 5973 mass spectrometer (GC/HRMS) in ECNI mode. The endosulfan isomers were separated using an Ultra 2 (J&W Scientific) fused silica capillary column (25 m length, 0.2 mm I.D., 0.11 μ m film thickness), while separation of the SCCPs were done by use of a Rxi[®]-5ms (Restek) fused silica capillary column (25 m length, 0.11 mm I.D., 0.11 μ m film thickness). The PeCB was analysed with an Agilent 6890N gas chromatograph coupled to high resolution mass spectrometry (Autospec-Ultima) (GC/HRMS) in electron impact (EI) mode. The column used was an Ultra 2 (J&W Scientific) fused silica capillary column (15 m length, 0.25 mm I.D., 0.25 μ m film thickness) (**Paper IV**). All analyses were carried out by use of ^{13}C labelled internal standards, and more information concerning the individual standards is given in the individual studies (**Paper I-IV**).

4. DISCUSSION OF FINDINGS

4.1. Introductory remarks concerning the methods

4.1.1. Quality assurance and uncertainty of analytical results

Generally, for quality assurance and quality control, all analytical procedures were monitored by use of accredited routines (ISO/IEC 17025) together with regular analysis of a standard reference material (SRM). Uncertainty in chemical analysis can be influenced by various factors, e.g. loss of analyte during sample extraction and clean-up, possible contamination of samples, accuracy in the standards and instrumental parameters. To compensate for potential loss during clean-up and extraction procedures, the samples were initially added a mixture of ^{13}C -labeled compounds (internal standard) which were quantified by a recovery standard added as the final step in the clean-up procedure (**Papers I-IV**). The recoveries of internal standards added to the air and soil samples prior to extraction, were generally lower for the more volatile compounds and higher for the less volatile POPs (**Paper I, II, and IV**). To monitor for possible contamination of the air samples, field and method blanks were prepared and analysed along with the exposed samples. Regarding the soil samples, diatomaceous earth (DE) was used as method blanks, while for the air samples unexposed PUF-disks were analysed in parallel to the exposed samples. Results from the blank samples showed minimal contamination for both air and soil samples. The overall estimate of the expanded uncertainty (95% confidence interval (CI)) in the chemical analysis is believed to accumulate up to $\pm 20\text{-}35\%$ (**Papers I-IV**), depending on the compound of interest. The uncertainty in results for SCCPs is assumed to be higher (about $\pm 50\%$) due to the complexity of the group and incomplete peak separation, as well as the lack of a suitable ^{13}C -labeled internal standard (Sverko et al., 2012).

4.1.2. Uncertainties in back-calculated air concentrations

For some of the passive air sampling sites, loss of PRCs during deployment was too small to estimate a site-specific uptake rate, and it was necessary to use a default value for the uptake rate (**Paper II**). The reason for the limited loss of PRCs may be due to low temperatures at these sites, as the number of individual PRCs experiencing a sufficient loss tended to decrease towards the Northern sites. This could indicate that the volatility range of our selected PRCs were less suitable at sites experiencing colder temperatures. In contrast, for sites experiencing higher temperatures, there is an increasing risk that the sampling bypassed the linear uptake phase for several compounds of interest. From theoretical assumptions (see Table A2), we therefore caution that

some of the more volatile substances (fluorene > HCB > α -HCH > phenanthrene \approx γ -HCH \approx anthracene > PCB-28 and to some extent PCB-52) may have started to approach equilibrium during the 3-month deployment period (**Papers I and II**).

4.2. Spatial and temporal variability of POPs in air

4.2.1. POPs in European background air

The overall results from the European campaign are presented in Table 2. Within the group of target pesticides included in the study, the most abundant compounds/groups was HCB, followed by HCHs, DDTs and chlordanes (**Paper I**).

HCB was detected in all samples and showed limited spatial variability across European background sites (**Paper I**). Overall, the lowest levels of the HCHs were found in Scandinavia and in the Arctic, while the highest levels were found in Central and Eastern parts of Europe (**Paper I**). α - and γ -HCH were the most abundant within the group of HCHs, while β -HCH was sometimes below MDL. The large spatial variability of the β -isomer may be partly attributed to enhanced water solubility in comparison to α - and γ -HCH (Li et al., 2002) (**Paper I**). α - and β -HCH were occasionally elevated in the south-eastern part of Europe, possibly reflecting a large historical usage of technical HCH which, unlike Lindane, contained significant amounts of these isomers (**Paper I**). α -HCH was more homogeneously distributed compared to γ - and β -HCH. The α -HCH isomer has also been shown to have a high LRAT potential (Beyer et al., 2000; Wania and Mackay, 1996), and relatively high levels were found in the Arctic (**Paper I**) which mirrors findings from other remote environments, e.g. the Antarctica (Kallenborn et al., 2013). γ -HCH in European background air is assumed to originate from usage of either Lindane or technical HCHs (**Paper I**). Highest concentrations of γ -HCH were found in air across central parts of Europe, and may reflect historical usage of Lindane (Breivik et al., 1999).

1 Table 2: Concentrations of selected PCBs, HCHs, DDTs, chlordanes and HCB (pg/m³) and selected PAHs (ng/m³) at European
2 background sites.

Compounds	Average±S.D.	Median	% above MDL	Max/min ratio (MMR)
PCB-28	5±4	4	100	34
PCB-52	5±4	4	100	25
PCB-101	4±5	3	100	84
PCB-118	1.5±1.5	1.0	95	>55
PCB-138	2.0±2.4	1.2	95	>102
PCB-153	3±4	2	94	>87
PCB-180	0.8±0.9	0.6	98	>122
Σ ₇ PCB	21±19	17		>55
α-HCH	26±24	21	100	33
β-HCH	2±7	1	85	>380
γ-HCH	35±38	19	100	94
Σ ₃ HCHs	64±59	46		>36
<i>p,p'</i> -DDE	21±47	6	74	>177
<i>p,p'</i> -DDD	0.5±1.1	0.2	79	>169
<i>o,p'</i> -DDT	4±7	2	87	>143
<i>p,p'</i> -DDT	6±9	2	86	>240
Σ ₄ DDTs	32±62	10		>312
Fluorene	1.7±1.8	1.0	98	>83
Phenanthrene	3±3	2	95	>147
Anthracene	0.07±0.1	0.03	88	>130
Fluoranthene	0.7±0.8	0.4	95	>117
Pyrene	0.4±0.4	0.2	99	>153
Benz[a]anthracene	0.02±0.03	0.01	68	>49
Chrysene	0.07±0.07	0.03	95	>58
Benzo[a]pyrene	0.008±0.01	0.002	43	>15
Σ ₆ PAH	6±6	4		>205
HCB	49±18	45	100	5
trans-Chlordane	0.8±1.1	0.4	95	>104
cis-Chlordane	1.2±0.7	1.2	98	>46
trans-Nonachlor	1.3±1.0	1.2	98	>77
cis-Nonachlor	0.16±0.1	0.15	87	>11
Σchlordanes	3.5±2.7	3.2		>114

3

Within the group of DDTs (sect. 3.4.1., Table A1), *p,p'*-DDE was most abundant followed by *p,p'*-DDT, *o,p'*-DDT and *p,p'*-DDD (**Paper I**). The highest concentrations of Σ_4 DDTs were found in the Central and Eastern part of Europe, while the lowest levels were detected in the Northern part of Europe (**Paper I**). In order to evaluate possible recent use of technical DDTs, the *p,p'*-DDE/*p,p'*-DDT ratio was estimated whereby a value < 1 may indicate fresh use of technical DDT (Pozo et al., 2006). For most sites, the signal was found to be weathered (>1), indicating old sources of DDTs. Another ratio, i.e. *o,p'*-DDT/*p,p'*-DDT was determined in order to evaluate possible influence of dicofol. The latter is a miticide and contains ~10% of the *o,p'*-DDT isomer (Becker, 2008; Gillespie et al., 1994). Several European countries utilize dicofol for agricultural usage (Gillespie et al., 1994; Turgut et al., 2009). The present study showed that one or more sites in 14 European countries experienced a ratio >1, which may indicate fresh usage of dicofol (**Paper I**).

The chlordanes were detected at lower concentrations compared to HCHs and DDTs. The predominant components within Σ_4 chlordanes were *cis*-chlordane and *trans*-nonachlor (**Paper I**). The highest concentrations of Σ_4 chlordanes were found in Central Europe (**Paper I**). The technical mixture of chlordane consists mostly of *trans*-chlordane, *cis*-chlordane and *trans*-nonachlor (Sovocool et al., 1977), with a *trans*-chlordane/*cis*-chlordane ratio 1.56 (Bidleman et al., 2002). The *trans*-chlordane isomer is more easily degraded in comparison to *cis*-chlordane, and a ratio > 1.56 imply new input of technical chlordane. Some sites (n=4) with elevated ratio were found in Eastern and Central parts of Europe (**Paper I**). Lower levels of the Σ_4 chlordanes were found in the northern part of Europe.

PCBs were detected at most background sites in Europe (**Paper I**). The more abundant PCBs within Σ_7 PCBs were PCB-28, -52, -101 and -153, of which 28, 52 and 101 were detected in all samples. The max/min ratio (MMR) of Σ_7 PCBs (Table 2) within the European background sites (**Paper I**) indicate that levels are not homogenous, which suggests that there may still be ongoing primary or secondary emissions influencing the various measurement sites. Further, the MMR tends to increase with the degree of chlorination, suggesting that lighter PCBs are more evenly distributed in European background air compared to the heavier PCBs. The LRAT potential of heavier PCBs may be more limited compared to lighter PCBs, causing larger variability in the air concentrations for the heavier substances (Wania and Daly, 2002) (**Paper I**). The spatial pattern

for Σ_7 PCBs clearly shows that the highest concentrations were related to more densely populated regions in central parts of Europe.

The spatial distribution of PAHs revealed that the lighter compounds (phenanthrene, fluorene, fluoranthene) were most abundant within Σ_8 PAHs (**Paper I**). Concentrations of heavier PAHs, such as benzo(a)pyrene, benz(a)anthrene and chrysene were often below MDL. The latter may be caused by their temperature dependent partition coefficient (K_{OA}). Substances with high K_{OA} may be more easily sorbed to particles which the passive air sampler is not designed to capture (Klanova et al., 2008). The spatial pattern for PAHs revealed no clear trend across Europe.

4.2.2. Local sources (LS) versus LRAT in contaminated coastal zones

In the second study (**Paper II**), we wanted to carry out an assessment of the contribution of LS versus LRAT in controlling POP burdens in air within various contaminated coastal areas in Norway. This was performed by dividing the observed concentration found at individual coastal sites by the anticipated background concentration attributed to LRAT alone (Eq. 6).

$$R = \frac{C(\text{coastal site})}{C(\text{background})} \quad (6)$$

Three corresponding ratios (R_n) were estimated, each based on three different background scenarios, i.e. $n = R_{NW}$ (Norwegian, $N=5$), R_{ND} (Nordic, $N=12$), R_{EU} (European, $N=86$). The uncertainty in these ratios (R_{NWmin} , R_{NWmax} , R_{NDmin} , R_{NDmax}) were furthermore estimated as detailed in **Paper II**. From these ratios, the coastal sites may be classified as either predominantly influenced by LS ($R \geq 2$), influenced by LS ($R \geq 1$) or predominantly influenced by LRAT ($R \leq 1$). Figure 7 presents the ratios based on the Norwegian background scenario for selected substances (**Paper II**). Typically, more sites were classified as being affected by LS when the ratios were derived on the basis of either R_{NW} or R_{ND} , compared with R_{EU} (**Paper II**). The latter implies locally elevated levels even when seen in a European background context.

LS largely influenced the observed air concentration of Σ_7 PCBs in most coastal sites as $R_{NW} \geq 2$ for 21 out of 24 sites (Fig.7A). However, only about half of the coastal sites were considered as elevated due to LS when evaluated in a Nordic background context ($R_{ND} \geq 2$). Yet, five sites located in major urban areas (Bergen I, Kristiansand II, Oslo, Tromsø I and Stavanger) remained as predominantly influenced by LS even when evaluated in a European context ($R_{EU} \geq 2$). From a more

detailed analysis of results for individual PCB congeners, it appeared that heavier PCBs are more prone to lead to locally elevated levels, presumably because lighter PCBs are more prone to LRAT.

For PAHs, the analysis was restricted to Σ_6 PAHs (**Paper II**). Applying R_{NW} , 23 out of 26 sites were recognized with $R_{NW} \geq 2$. Using R_{NWmax} , the number of sites ≥ 2 was reduced to 2 (see Fig. 7B). This implies that it was difficult to obtain a reliable estimate of the anticipated background concentration of PAHs in air (**Paper II**). An interesting feature was the marked difference within the Σ_6 PAHs. For example, some of the more industrial sites experienced elevated concentrations by anthracene, fluoroanthene, pyrene and chrysene. A site known to have been polluted by creosote in the past showed elevated levels of anthracene and fluorene (**Paper II**) (Fig. 7B).

The concentration of α -HCH was fairly uniform in these coastal sites. 15 out of 27 sites were recognized with $R_{NW} \geq 2$, suggesting LS was dominating the measured levels (Fig. 7C). However, extensive emissions of technical HCH in about half of these coastal areas seems unlikely. Rather, we believe that the fairly homogeneous concentrations and the apparent influence by LS may be explained by the location of the samplers. They were all deployed close to the coast, and the locally elevated concentrations may have been due to secondary re-emission from the ocean (Dalla Valle et al., 2005; Shen et al., 2004). The background stations used to estimate contribution from LRAT, in contrast, were mainly located inland and far away from the ocean. γ -HCH was also found to be locally elevated at many coastal sites (Fig. 7D) (**Paper II**). However, γ -HCH is less prone to re-volatilisation in comparison to α -HCH and some sites may have been affected by recent usage of Lindane.

Results for the other substances that not included in Figure 7, i.e. HCB, DDTs and chlordanes are discussed in more detail in **Paper II**. Of note, strongly elevated levels of HCB was found at Kristiansand II, indicating that the sampler had been located close to a major hot spot. Likewise, elevated levels of both *o,p'*-DDT and *p,p'*-DDT was detected at a site in Bergen. When comparing results for duplicated PAS deployed at different sites within the same coastal zone, it was clear that the potential influence of LS within a given coastal zone may differ significantly. Any inferences made about the likely influence of LS in a specific coastal zone are therefore restricted to the specific site where the sample was collected as well as when it was exposed (**Paper II**)

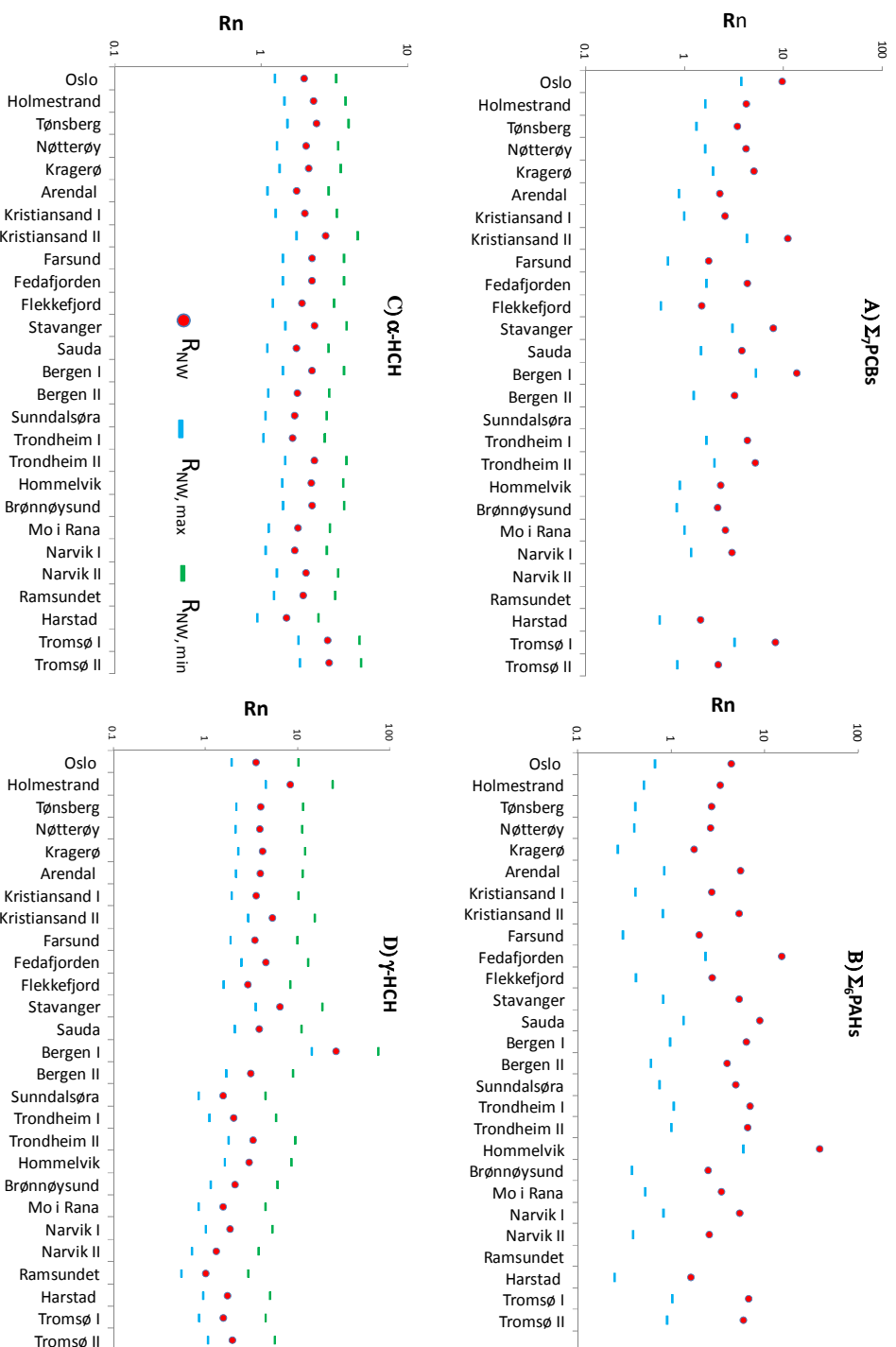


Figure 7(a-d): Estimated contribution from local sources, expressed as the ratio (R_{NW}) of measured air concentrations divided by the anticipated contribution from long-range atmospheric transport alone (Norwegian background scenario). The uncertainty in this ratio ($R_{NW,max}$, $R_{NW,min}$) is estimated as detailed in Paper II.

4.2.3. PAS as a complementary technique to AAS

An important goal of Paper I was to assess the potential of PAS to serve as a complimentary technique to AAS within the EMEP monitoring program. Duplicates of PAS were therefore co-deployed with AAS at selected EMEP sites (Košetice (CZ), Pallas (FI), Råö (S), Birkenes (NO), Stórhöfði (IS), Spitsbergen (NO) and Aspvreten (S)), in order to further evaluate the performance of the PAS technique (**Paper I**). However, the AAS strategies within EMEP vary both in terms of sampling duration and frequencies. Only Stórhöfði and Råö stations are sampling continuously, while Košetice, Birkenes, Aspvreten, Pallas and Spitsbergen have sampling coverage less than 30 % of the time (**Paper I**). Moreover, most of the AAS results were obtained from sampling and quantitative analysis done by different laboratories, except for the samples from Spitsbergen (Zeppelin station, Ny-Ålesund, Svalbard) and Birkenes, where preparation and analysis were done at NILU. Thus, differences in sample treatment and analytical procedures in different laboratories introduce additional uncertainty into the obtained results. Possible differences between PAS and AAS were estimated as $(C_{PAS}-C_{AAS})/C_{AAS}$. A positive deviation shows higher concentration in the PAS relative to the AAS. Results for the AAS were averaged over the same period of time (i.e. 3 months) as the PAS to achieve comparability. The overall results for the various compound groups (PCBs, DDTs, HCHs, PAHs and HCB) revealed that the key factors leading to discrepancies were the sampling frequencies as well as the effect of analysis in different laboratories (**Paper I**). The latter effect could introduce variances of up to a factor of 2 (Su and Hung, 2010).

For the Σ_7 PCBs, the ratio $(C_{PAS}-C_{AAS})/C_{AAS}$ varied from negative to positive relative deviation. The largest positive deviation was found for Košetice which operates the AAS one day per week. This means that the AAS was exposed to different air masses compared to the PAS (**Paper I**). As Košetice is also located close to major source regions in Europe, the effect of sampling different air masses could therefore be particularly significant.

The comparison was also carried out for α -HCH and γ -HCH for all EMEP POPs sites mentioned above. Overall, both positive and negative deviations were observed (**Paper I**). A relatively high positive deviation of +318% was seen for α -HCH at Stórhöfði, where air is sampled continuously. For Birkenes (air sampling one day/week) the relative deviation for both isomers was negative ($C_{PAS} < C_{AAS}$). As both AAS and PAS from Birkenes were analysed at the same laboratory, the more plausible explanation could be the differences in the sampling coverage between AAS and PAS.

For the Σ_4 DDTs, several results were below MDL for PAS and not reported for the AAS, and as a result only three sites were compared (**Paper I**). Similarly, comparison was only feasible for some PAHs at four sites (**Paper I**). The highest positive deviation for Σ_4 DDTs and PAHs was again seen for Košetice. For PAHs, the best agreement between PAS and AAS was found for Pallas and Råö. At the latter site, sampling is performed continuously, which means that both PAS and AAS were exposed to similar air masses.

For HCB, data from four sites were available for comparison. The relative deviation was similar at all sites except for Stórhöfði where C_{PAS} exceeded C_{AAS} by several orders of magnitude. The most plausible explanation is that AAS experienced loss of HCB due to breakthrough effects, which means that the more volatile POPs (e.g. HCB) have potential to be drawn through the sampling material and thereby to not be fully retained by the AAS sampling material.

In summary, **Paper I** illustrates how coordinated PAS sampling campaigns may illuminate strengths and weaknesses with both PAS and AAS sampling techniques. The results also illustrate the inherent disadvantages of using inconsistent approaches (sampling frequencies and duration, analytical techniques) in monitoring programmes aiming to establish comparable and consistent measurement data. Nevertheless, the comparison was generally more favourable when both AAS and PAS were exposed to the “same” air masses and analysed in the same laboratory.

4.2.4. Utilizing an atmospheric transport model (FLEXPART)

The atmospheric transport model FLEXPART has been used in this thesis to explore differences in source-receptor relationships for PCB-28 at selected European PAS sites (**Paper I**) as well as to develop, apply and evaluate a forecast system for LRAT episodes of PCBs, using Birkenes as a case study (**Paper III**) (sect. 1.3.2.1). In the first study, we also wanted to evaluate whether the obtained PAS results were comparable with modelled air concentrations. In the third study, measured concentrations using AAS were compared to predicted concentrations. For both studies, PCB-28 was used as a tracer compound, since it has *i*) high potential for LRAT, and is solely present in the gaseous phase and *ii*) spatially resolved emission inventories are available for PCB-28 (Breivik et al., 2007) which is a key input to the model.

In the first study, PAS-derived concentrations were compared to modelled concentrations at 17 selected EMEP stations (**Paper I**), and Figure 8 presents the main results. The agreement between the measured concentrations using PAS and the modelled results was within a factor of three for

16 out of 17 sites (solid lines) and mostly within a factor of two (dashed lines). The model-derived results also compared favourably with data obtained on the basis of AAS (**Paper I**). However, the predicted concentrations were often higher than measured (both AAS and PAS), which may be due to overestimation in the emission inventory used to drive the model (**Paper I**). The FLEXPART model also considers primary emissions only, and caution should be applied for the comparison with empirically derived data, since possible secondary emissions of PCB-28 are not included. Nevertheless, it has been proposed that the occurrence of PCBs in background air is mainly dictated by primary emissions (Schuster et al., 2010).

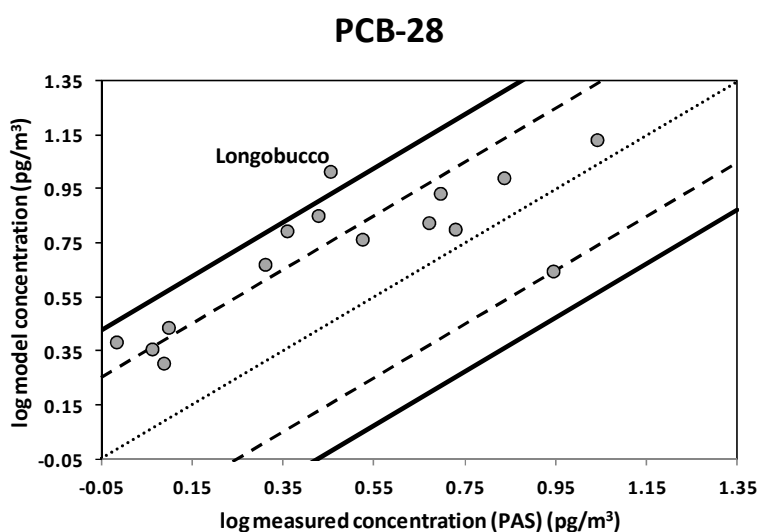


Figure 8: Modelled versus observed (PAS) air concentration for PCB-28 at selected sites. The dashed and solid lines represent agreement within a factor of 2 and 3, respectively. (**Paper I**).

In the third study (**Paper III**) we evaluated the capability of the FLEXPART model to predict LRAT episodes to a specific measurement site employing AAS (Birkenes), as well as to trace the major source regions of PCBs which affect specific LRAT episodes. The predicted concentrations of PCB-28 from the targeted episodes were compared to results from 24-hour samples collected weekly as part of the regular monitoring programme (n=52) (Aas and Breivik, 2012). The results show that FLEXPART was able to single out LRAT episodes for PCBs as the measured concentrations in all targeted samples (E1-E3e, Fig. 9) exceeded the 75th percentile of the concentrations derived from the regular monitoring program. The targeted samples also included the highest measured concentrations of all samples collected. Overall, this indicates that we have a good understanding of the major source regions affecting concentrations in air of PCB-28 at this

measurement site (**Paper III**). Additionally, the results showed that the forecast system as developed for PCB-28 may also serve as a surrogate for individual PCBs within Σ_7 PCBs (see Fig. 9). This finding implies that the major source regions for the seven individual PCBs are likely to be similar to PCB-28 (**Paper III**).

However, the highest measured and modelled concentrations did not completely agree (**Paper III**). This indicates possible uncertainty in the spatial distribution of PCB emissions. Alternatively, the study illustrates how modelling and monitoring approaches combined may increase our understanding of POP sources.

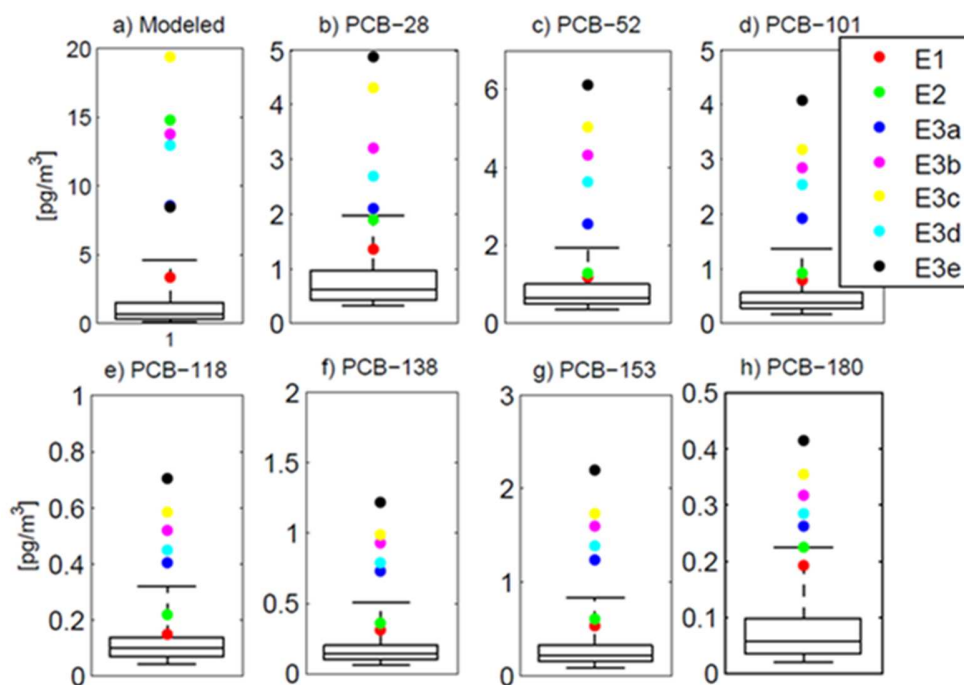


Figure 9: Modelled (FLEXPART-r) PCB-28 (a) and measured PCB concentrations (b-h) in units of pg/m^3 , for both the annual sampling program and the targeted samples. The box and whisker plots show the annual results (2011) for Birkenes, Southern Norway based on weekly samples. The line shows the median, while the box and whiskers delineates the 25 and 75 percentiles and the 5 and 95 percentiles, respectively. Targeted samples are additionally represented by colored dots.

4.3. Newly regulated POPs in background soils

While the first studies evaluated the occurrence, spatial (**Papers I and II**), and temporal (**Paper III**) patterns of legacy POPs in air, the fourth study reports on environmental levels and distribution of selected newly regulated POPs in background soils along an expected pollution gradient (**Paper IV**). The fourth study thereby expands on the studies of air by targeting contaminant patterns in an environmental surface compartment impacted by atmospheric deposition, and by targeting newly regulated POPs.

4.3.1. Endosulfans

The average concentration of Σ endosulfans in all soil samples was 2.6 ± 3.2 ng/g SOM. The predominant compound within the Σ endosulfan group in background soils was endosulfan sulfate, the major transformation product of the parent endosulfan compound in soil (Antonious et al., 1998; Walse et al., 2003). α -endosulfan is more volatile in comparison to both β -endosulfan and endosulfan sulfate in soils (Fig. 2), and was detected at lower concentrations in the soil samples. Both α - and β -endosulfan were often below MDL, and the remaining discussion is therefore restricted to Σ endosulfans.

The average concentration of Σ endosulfans in woodland (WL) soil was about three times higher than grassland (GL) soil, which may be explained by the forest filter effect (Wania and McLachlan, 2001) combined with the higher content of soil organic matter (SOM) in forest soil compared to GL soil (**Paper IV**). A high and significant correlation was found between SOM and Σ endosulfans in soils ($r=0.80$, $p<0.001$). The latitudinal distribution of Σ endosulfans peaked in regions typically experiencing elevated precipitation rates (Aamot et al., 1996; Becker et al., 2011).

Data on newly regulated POPs was compared with previously reported data on several legacy POPs (Schuster et al., 2011). For all soils combined, significant correlations were found between the Σ endosulfans and HCB ($r=0.82$, $p<0.001$), Σ endosulfans and Σ_{31} PCBs ($r=0.73$, $p<0.001$) as well as between Σ endosulfans and PeCB ($r=0.58$, $p<0.001$) (**Paper IV**).

4.3.2. Pentachlorobenzene

The average concentration of PeCB in all soils was 1.1 ± 1.1 ng/g SOM. PeCB also correlated with HCB ($r=0.63$, $p<0.001$) and Σ_{31} PCBs ($r=0.62$, $p<0.001$). A high correlation was found between PeCB and SOM ($r=0.70$, $p<0.001$), and PeCB and black carbon (BC) ($r=0.57$, $p<0.001$). The latter correlation indicates that PeCB and BC may to some extent be co-emitted

from various combustion processes (Liu et al., 2013; Nie et al., 2011). The average concentration of PeCB in UK soil was about twice as high as in Norwegian soil (**Paper IV**).

The average concentrations of PeCB in GL and WL soils were comparable. However, PeCB was significant correlated with BC for GL soil ($r=0.66$, $p<0.01$), but only to a smaller extent with BC in WL soil ($r=0.41$, $p<0.05$). The reason for this may be the lower and weaker correlation between BC and SOM in WL soil ($r=0.42$, $p<0.05$) compared to GL soil ($r=0.79$, $p<0.001$). We therefore suspect that BC in WL soils may be more easily diluted than in GL soils because of elevated inputs of organic matter to WL soils. SOM was furthermore found to be somehow more important in explaining the occurrence of PeCB in Norwegian soils compared with UK soils (**Paper IV**).

4.3.3. Short-chain chlorinated paraffins

The average concentration of SCCPs in all soil samples was 35 ± 100 ng/g SOM. The highest concentrations of SCCPs were found in soil at lower latitudes, while several sites at higher latitudes experienced concentrations below MDL (**Paper IV**). SCCPs did not correlate with any POPs nor any site variables included in the soil study, which altogether indicate that SCCPs are comparatively less prone to LRAT. SCCPs thus appear to be more influenced by proximity to sources than by soil characteristics (**Paper IV**). Nevertheless, the results for SCCPs should be considered with a healthy scepticism as they are associated with large analytical uncertainties (section 4.1.1).

Conclusions

A comprehensive picture of spatial variability of POPs in European background air have been obtained based on passive air sampling (PAS).

- Generally, higher concentrations of PCBs were found in more densely populated parts of Europe.
- The levels of γ -HCH were elevated in central parts of Europe, while concentrations of α -, β -HCH and DDTs were highest in the south-eastern part.
- There was no clear spatial pattern for PAHs, suggesting that local sources rather than long range atmospheric transport (LRAT) affected their distribution.
- Levels of HCB were evenly distributed across Europe, and concentrations of chlordanes were low.
- Predicted concentrations of PCB-28, using FLEXPART, agreed within a factor of 3 with PAS measurements for 16 out of 17 sites.

A nested PAS monitoring approach has been explored to assess the occurrence as well as the potential influence of local sources (LS) versus LRAT in controlling concentrations of POPs in Norwegian coastal zones with consumption advisories on seafood.

- Concentrations of PCBs were typically elevated at sites in larger cities and up to ten times higher than anticipated from LRAT alone.
- HCB and PAHs were occasionally locally elevated at sites in coastal zones with former or current industrial activities.
- An urban site in Bergen was influenced by legacy organochlorine pesticides (technical DDTs and Lindane).
- α -HCH was consistently elevated at coastal sites, attributed to volatilization from the sea.
- While significant influence from LS was frequently detected, the extent of this influence was largely dependent on the scenario explored for the anticipated background concentration and restricted to the site in question.

A forecast system for predicting long-range atmospheric transport of PCB-28 to a background monitoring site in southern Norway has been developed, evaluated and applied.

- The FLEXPART model was successful in predicting LRAT events of PCB-28.

- Concentrations in targeted samples included the highest measured levels throughout the year, and all exceeded the 75th percentile of the concentrations obtained from the regular monitoring program.
- The forecast system complements existing monitoring strategies, occurring at fixed intervals, and has potential to enhance our understanding of POP sources.

Key factors affecting the occurrence and distribution of selected newly regulated POPs (Σ endosulfans, PeCB and short-chain chlorinated paraffins (SCCPs)) in background soils from UK and Norway were identified and discussed.

- The highest average concentration was found for SCCPs, followed by Σ endosulfans and PeCB.
- Unlike the SCCPs, Σ endosulfans and PeCB exhibited many similarities with each other as well as with other legacy POPs previously reported.
- Soil organic matter (SOM) and black carbon (BC) were important parameters explaining the distribution of Σ endosulfans and PeCB in soils, respectively.
- Concentrations of Σ endosulfans peaked in areas experiencing elevated precipitation rates.
- PeCB appears to be partly co-emitted with BC from combustion processes and partly retained in soils closer to source regions.
- The occurrence and distribution of SCCPs in background soils seems largely controlled by proximity to source regions.

Future perspectives

Based on the aim of this thesis and the conclusions drawn, the following key suggestions and recommendations are identified:

Further use of passive air samples (PAS) in existing monitoring programmes, such as EMEP, is encouraged, both to improve spatial and temporal coverage. Future coordinated PAS campaigns are encouraged as they may serve as an inter-comparison exercise both within and across existing monitoring networks, also complementing inter-laboratory comparison studies. However, PAS remain to be a semi-quantitative method for determining concentrations of POPs in air. Confidence in back-calculated concentrations based on PUF-PAS may increase in future studies by increasing the number and volatility range of depuration compounds beyond those used herein. The performance of other cost-efficient PAS strategies (e.g. equilibrium-based samplers, or XAD-samplers) require further evaluation in terms of their applicability to support relevant monitoring programmes like the EMEP programme.

PAS also proved useful to screen for potential influence from local sources of legacy POPs in controlling atmospheric burdens in contaminated coastal areas. However, the current study was restricted to specific sites sampled during summer. Future studies expanding on this work should address potential seasonal and spatial variability within zones implicated as being affected by local sources of POPs in order to (i) evaluate potential seasonal differences in local sources versus LRAT, and (ii) verify and track the local emission source(s) using a denser network of samplers close to hot-spots. Future air sampling strategies should also be combined with sampling and analysis of additional environmental surface media to better assess contaminant pathways (influence from primary versus secondary emissions in controlling environmental burdens).

The FLEXPART model proved to be a versatile and useful tool for attempts to forecast long-range atmospheric transport of PCBs to a specific site. The targeted sampling strategy which proved to be a success for selected PCBs, may therefore add value to relevant air monitoring programmes, whereby sampling occurs at fixed intervals in a non-continuous fashion. Future work may want to try to expand these efforts towards other sites as well as other POPs. An interesting future application would be to evaluate the forecast system by targeting transport of POPs from a specific source region with highly uncertain or suspected emissions.

Factors affecting levels of newly regulated POPs in background soils were identified. However, analytical results presented for SCCPs remain uncertain and further efforts to improve

analytical methods are needed. The soil study demonstrated that simple, yet mechanistically-oriented, chemical distribution and mobility plots (chemical space maps) are useful as complementary tools to assess whether any inferences made from statistical analysis of observations are reasonable from a mechanistic standpoint. Further exploration of similar techniques, also for other environmental media, are therefore encouraged to assess whether correlations seen from empirical observations are fortuitous, rather than an indication of a causal relationship.

References

- Aamot, E., Steinnes, E., and Schmid, R. (1996). Polycyclic aromatic hydrocarbons in Norwegian forest soils: Impact of long range atmospheric transport. *Environmental Pollution* **92**, 275-280.
- Aas, W., and Breivik, K. (2008). *Heavy metals and POPs measurements, 2006 Co-operative programme for monitoring and evaluation of long range transmission of air pollutants in Europe (EMEP)*, Rep. No. NILU, Kjeller.
- Aas, W., and Breivik, K. (2009). *Heavy metals and POP measurements 2007, Co-operative programme for monitoring and evaluation of long-range transmissions of air pollutants in Europe*, Rep. No. O-95038/O-99050. NILU, Kjeller.
- Aas, W., and Breivik, K. (2012). *Heavy metals and POP measurements, 2010.* , Rep. No. NILU (Norwegian Institute of Air Research), Kjeller.
- Aas, W., Breivik, Knut (2008). *Heavy metals and POPs measurements, 2006*, Rep. No. Norsk Institutt for luftforskning, Kjeller.
- Altarawneh, M., Dlugogorski, B. Z., Kennedy, E. M., and Mackie, J. C. (2009). Mechanisms for formation, chlorination, dechlorination and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). *Progress in Energy and Combustion Science* **35**, 245-274.
- AMAP (1998). *AMAP Assessment Report, Arctic Pollution Issues*, Rep. No. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway.
- Andersson, M., Ottesen, R., and Volden, I. (2004). Building materials as a source of PCB pollution in Bergen, Norway. *Science of the Total Environment* **325**, 139-144.
- Antonious, G. F., Byers, M. E., and Snyder, J. C. (1998). Residues and fate of endosulfan on field-grown pepper and tomato. *Pesticide Science* **54**, 61-67.
- Armitage, J. M., McLachlan, M. S., Wiberg, K., and Jonsson, P. (2009). A model assessment of polychlorinated dibenzo-p-dioxin and dibenzofuran sources and fate in the Baltic Sea. *Science of the Total Environment* **407**, 3784-3792.
- Atkinson, R. (1990). Gas-phase tropospheric chemistry of organic-compounds-A review. *Atmospheric Environment Part a-General Topics* **24**, 1-41.
- Bailey, R. E. (2001). Global hexachlorobenzene emissions. *Chemosphere* **43**, 167-182.
- Bailey, R. E., van Wijk, D., and Thomas, P. C. (2009). Sources and prevalence of pentachlorobenzene in the environment. *Chemosphere* **75**, 555-564.
- Barber, J. L., Sweetman, A. J., van Wijk, D., and Jones, K. C. (2005). Hexachlorobenzene in the global environment: Emissions, levels, distribution, trends and processes. *Science of the Total Environment* **349**, 1-44.
- Bartkow, M. E., Booij, K., Kennedy, K. E., Muller, J. F., and Hawker, D. W. (2005). Passive air sampling theory for semivolatile organic compounds. *Chemosphere* **60**, 170-176.
- Bartkow, M. E., Hawker, D. W., Kennedy, K. E., and Muller, J. F. (2004). Characterizing uptake kinetics of PAHs from the air using polyethylene-based passive air samplers of multiple surface area-to-volume ratios. *Environmental Science & Technology* **38**, 2701-2706.
- Bartkow, M. E., Jones, K. C., Kennedy, K. E., Holling, N., Hawker, D. W., and Muller, J. F. (2006). Evaluation of performance reference compounds in polyethylene-based passive air samplers. *Environmental Pollution* **144**, 365-370.
- Becker, L., Scheringer, M., Schenker, U., and Hungerbuhler, K. (2011). Assessment of the environmental persistence and long-range transport of endosulfan. *Environmental Pollution* **159**, 1737-1743.
- Becker, S. (2008). Trends and behaviour of semi-volatile organic compounds in the Arctic Atmosphere, Lancaster University, Lancaster.
- Bennett, D. H., McKone, T. E., Matthies, M., and Kastenber, W. E. (1998). General formulation of characteristic travel distance for semivolatile organic chemicals in a multimedia environment. *Environmental Science & Technology* **32**, 4023-4030.

- Beyer, A., Mackay, D., Matthies, M., Wania, F., and Webster, E. (2000). Assessing long-range transport potential of persistent organic pollutants. *Environmental Science & Technology* **34**, 699-703.
- Beyer, A., Wania, F., Gouin, T., Mackay, D., and Matthies, M. (2002). Selecting internally consistent physicochemical properties of organic compounds. pp. 941-953.
- Bidleman, T. F. (1999). Atmospheric transport and air-surface exchange of pesticides. *Water Air and Soil Pollution* **115**, 115-166.
- Bidleman, T. F., Christensen, E. J., Billings, W. N., and Leonard, R. (1981). Atmospheric transport of organochlorines in the North-Atlantic gyre. *Journal of Marine Research* **39**, 443-464.
- Bidleman, T. F., Jantunen, L. M. M., Helm, P. A., Brorstrom-Lunden, E., and Juntto, S. (2002). Chlordane enantiomers and temporal trends of chlordane isomers in arctic air. *Environmental Science & Technology* **36**, 539-544.
- Bidleman, T. F., Wong, F., Backe, C., Sodergren, A., Brorstrom-Lunden, E., Helm, P. A., and Stern, G. A. (2004). Chiral signatures of chlordanes indicate changing sources to the atmosphere over the past 30 years. *Atmospheric Environment* **38**, 5963-5970.
- Bogdal, C., Abad, E., Abalos, M., van Bavel, B., Hagberg, J., Scheringer, M., and Fiedler, H. (2013). Worldwide distribution of persistent organic pollutants in air, including results of air monitoring by passive air sampling in five continents. *Trac-Trends in Analytical Chemistry* **46**, 150-161.
- Bohlin, P., Audy, O., Skrdlikova, L., Kukucka, P., Pribylova, P., Prokes, R., Vojta, S., and Klanova, J. (2014). Outdoor passive air monitoring of semi volatile organic compounds (SVOCs): a critical evaluation of performance and limitations of polyurethane foam (PUF) disks. *Environmental Science-Processes & Impacts* **16**, 433-444.
- Bohlin, P., Jones, K. C., Tovalin, H., and Strandberg, B. (2008). Observations on persistent organic pollutants in indoor and outdoor air using passive polyurethane foam samplers. *Atmospheric Environment* **42**, 7234-7241.
- Bouwman, H., Viljoen, I. M., Quinn, L. P., and Polder, A. (2013). Halogenated pollutants terrestrial and aquatic bird eggs: Converging patterns of pollutant profiles, and impacts and risks from high levels. *Environmental Research* **126**, 240-253.
- Breivik, K., Alcock, R., Li, Y. F., Bailey, R. E., Fiedler, H., and Pacyna, J. M. (2004). Primary sources of selected POPs: regional and global scale emission inventories. *Environmental Pollution* **128**, 3-16.
- Breivik, K., Gioia, R., Chakraborty, P., Zhang, G., and Jones, K. C. (2011). Are Reductions in Industrial Organic Contaminants Emissions in Rich Countries Achieved Partly by Export of Toxic Wastes? *Environmental Science & Technology* **45**, 9154-9160.
- Breivik, K., Pacyna, J. M., and Munch, J. (1999). Use of alpha-, beta- and gamma-hexachlorocyclohexane in Europe, 1970-1996. *Science of the Total Environment* **239**, 151-163.
- Breivik, K., Sweetman, A., Pacyna, J. M., and Jones, K. C. (2002). Towards a global historical emission inventory for selected PCB congeners - a mass balance approach 1. Global production and consumption. *Science of the Total Environment* **290**, 181-198.
- Breivik, K., Sweetman, A., Pacyna, J. M., and Jones, K. C. (2007). Towards a global historical emission inventory for selected PCB congeners - A mass balance approach-3. An update. *Science of the Total Environment* **377**, 296-307.
- Breivik, K., and Wania, F. (2002). Mass budgets, pathways, and equilibrium states of two hexachlorocyclohexanes in the Baltic Sea environment. *Environmental Science & Technology* **36**, 1024-1032.
- Brorström-Lundén, E. (1996). Atmospheric deposition of persistent organic compounds to the sea surface. *Journal of Sea Research* **35**, 81-90.
- Carson, R. (1962). *Silent Spring*, Houghton Mifflin Company, New York.

- Chaemfa, C., Barber, J. L., Gocht, T., Harner, T., Holoubek, I., Klanova, J., and Jones, K. C. (2008). Field calibration of polyurethane foam (PUF) disk passive air samplers for PCBs and OC pesticides. *Environmental Pollution* **156**, 1290-1297.
- Chaemfa, C., Barber, J. L., Kim, K. S., Harner, T., and Jones, K. C. (2009a). Further studies on the uptake of persistent organic pollutants (POPs) by polyurethane foam disk passive air samplers. *Atmospheric Environment* **43**, 3843-3849.
- Chaemfa, C., Wild, E., Davison, B., Barber, J. L., and Jones, K. C. (2009b). A study of aerosol entrapment and the influence of wind speed, chamber design and foam density on polyurethane foam passive air samplers used for persistent organic pollutants. *Journal of Environmental Monitoring* **11**, 1135-1139.
- Consonni, D., Pesatori, A. C., Zocchetti, C., Sindaco, R., D'Oro, L. C., Rubagotti, M., and Bertazzi, P. A. (2008). Mortality in a population exposed to dioxin after the Seveso, Italy, accident in 1976 : 25 years of follow-up. *American Journal of Epidemiology* **167**, 847-858.
- Dalla Valle, M., Jurado, E., Dachs, J., Sweetman, A. J., and Jones, K. C. (2005). The maximum reservoir capacity of soils for persistent organic pollutants: implications for global cycling. *Environmental Pollution* **134**, 153-164.
- Eckhardt, S., Breivik, K., Li, Y. F., Mano, S., and Stohl, A. (2009). Source regions of some persistent organic pollutants measured in the atmosphere at Birkenes, Norway. *Atmospheric Chemistry and Physics* **9**, 6597-6610.
- Eckhardt, S., Breivik, K., Mano, S., and Stohl, A. (2007). Record high peaks in PCB concentrations in the Arctic atmosphere due to long-range transport of biomass burning emissions. *Atmospheric Chemistry and Physics* **7**, 4527-4536.
- Eliassen, A. (1978). OECD study of long-range transport of air-pollutants - long-range transport modeling. *Atmospheric Environment* **12**, 479-487.
- European Chemicals Bureau (2008). *European Union Risk Assessment Report: Alkanes, C10-13, chloro, updated version*, Rep. No. European Chemicals Bureau, Luxemburg.
- Farrar, N. J., Harner, T., Shoeib, M., Sweetman, A., and Jones, K. C. (2005a). Field deployment of thin film passive air samplers for persistent organic pollutants: A study in the urban atmospheric boundary layer. *Environmental Science & Technology* **39**, 42-48.
- Farrar, N. J., Harner, T. J., Sweetman, A. J., and Jones, K. C. (2005b). Field calibration of rapidly equilibrating thin-film passive air samplers and their potential application for low-volume air sampling studies. *Environmental Science & Technology* **39**, 261-267.
- Gawor, A., and Wania, F. (2013). Using quantitative structural property relationships, chemical fate models, and the chemical partitioning space to investigate the potential for long range transport and bioaccumulation of complex halogenated chemical mixtures. *Environmental Science-Processes & Impacts* **15**, 1671-1684.
- Gillespie, M. J., Lythgo, C. M., Plumb, A. D., and Wilkins, J. P. G. (1994). A survey comparing the chemical composition of dicofol formulations sold in the UK before and after the introduction of the EC prohibition directive 79/117/EEC. *Pesticide Science* **42**, 305-314.
- Gouin, T., Mackay, D., Webster, E., and Wania, F. (2000). Screening chemicals for persistence in the environment. *Environmental Science & Technology* **34**, 881-884.
- Gouin, T., and Wania, F. (2007). Time trends of arctic contamination in relation to emission history and chemical persistence and partitioning properties. *Environmental Science & Technology* **41**, 5986-5992.
- Gouin, T., Wania, F., Ruepert, C., and Castillo, L. E. (2008). Field testing passive air samplers for current use pesticides in a tropical environment. *Environmental Science & Technology* **42**, 6625-6630.
- Halsall, C. J., Coleman, P. J., Davis, B. J., Burnett, V., Waterhouse, K. S., Hardingjones, P., and Jones, K. C. (1994). Polycyclic aromatic-hydrocarbons in UK urban air. *Environmental Science & Technology* **28**, 2380-2386.
- Hansen, K. M., Prevedouros, K., Sweetman, A. J., Jones, K. C., and Christensen, J. H. (2006). A process-oriented inter-comparison of a box model and an atmospheric chemistry transport model:

- Insights into model structure using alpha-HCH as the modelled substance. *Atmospheric Environment* **40**, 2089-2104.
- Harner, T., Farrar, N. J., Shoeib, M., Jones, K. C., and Gobas, F. (2003). Characterization of polymer-coated glass as a passive air sampler for persistent organic pollutants. *Environmental Science & Technology* **37**, 2486-2493.
- Harner, T., Pozo, K., Gouin, T., Macdonald, A. M., Hung, H., Caine, J., and Peters, A. (2006). Global pilot study for persistent organic pollutants (POPs) using PUF disk passive air samplers. *Environmental Pollution* **144**, 445-452.
- Harner, T., Shoeib, M., Diamond, M., Stern, G., and Rosenberg, B. (2004). Using passive air samplers to assess urban - Rural trends for persistent organic pollutants. 1. Polychlorinated biphenyls and organochlorine pesticides. *Environmental Science & Technology* **38**, 4474-4483.
- Harner, T., Su, K., Genualdi, S., Karpowicz, J., Ahrens, L., Mihele, C., Schuster, J., Charland, J. P., and Narayan, J. (2013). Calibration and application of PUF disk passive air samplers for tracking polycyclic aromatic compounds (PACs). *Atmospheric Environment* **75**, 123-128.
- Harrad, S. J., Sewart, A. P., Alcock, R., Boumphrey, R., Burnett, V., Duartedavidson, R., Halsall, C., Sanders, G., Waterhouse, K., Wild, S. R., and Jones, K. C. (1994). Polychlorinated-biphenyls (PCBs) in the British environment - sinks, sources and temporal trends. *Environmental Pollution* **85**, 131-146.
- Hassanin, A., Breivik, K., Meijer, S. N., Steinnes, E., Thomas, G. O., and Jones, K. C. (2004). PBDEs in European background soils: Levels and factors controlling their distribution. *Environmental Science & Technology* **38**, 738-745.
- Hassanin, A., Lee, R. G. M., Steinnes, E., and Jones, K. C. (2005). PCDD/Fs in Norwegian and UK soils: Implications for sources and environmental cycling. *Environmental Science & Technology* **39**, 4784-4792.
- Haugen, J. E., Wania, F., Ritter, N., and Schlabach, M. (1998). Hexachlorocyclohexanes in air in southern Norway. Temporal variation, source allocation, and temperature dependence. *Environmental Science & Technology* **32**, 217-224.
- Haukas, M., Hylland, K., Berge, J. A., Nygard, T., and Mariussen, E. (2009). Spatial diastereomer patterns of hexabromocyclododecane (HBCD) in a Norwegian fjord. *Science of the Total Environment* **407**, 5907-5913.
- Hornbuckle, K., Carlson, D., Swackhamer, D., Baker, J., and Eisenreich, S. (2006). Polychlorinated Biphenyls in the Great Lakes. In *Persistent Organic Pollutants in the Great Lakes* (R. Hites, ed.), Vol. 5N, pp. 13-70. Springer Berlin / Heidelberg.
- Huang, T., Guo, Q., Tian, H., Mao, X. X., Ding, Z. Y., Zhang, G., Li, J., Ma, J. M., and Gao, H. (2014). Assessing spatial distribution, sources, and human health risk of organochlorine pesticide residues in the soils of arid and semiarid areas of northwest China. *Environmental Science and Pollution Research* **21**, 6124-6135.
- Huckins, J. N., Petty, J. D., Lebo, J. A., Almeida, F. V., Booij, K., Alvarez, D. A., Clark, R. C., and Mogenssen, B. B. (2002). Development of the permeability/performance reference compound approach for in situ calibration of semipermeable membrane devices. *Environmental Science & Technology* **36**, 85-91.
- Hung, H., MacLeod, M., Guardans, R., Scheringer, M., Barra, R., Hamer, T., and Zhang, G. (2013). Toward the next generation of air quality monitoring: Persistent organic pollutants. *Atmospheric Environment* **80**, 591-598.
- Ishaq, R., Persson, N. J., Zebuhr, Y., Broman, D., and Naes, K. (2009). PCNs, PCDD/Fs, and Non-orthoPCBs, in Water and Bottom Sediments from the Industrialized Norwegian Grenlandsfjords. *Environmental Science & Technology* **43**, 3442-3447.
- Jartun, M., Ottesen, R. T., Steinnes, E., and Volden, T. (2009). Painted surfaces - important sources of polychlorinated biphenyls (PCBs) contamination to the urban and marine environment. *Environmental Pollution* **157**, 295-302.

- Jaward, F. M., Farrar, N. J., Harner, T., Sweetman, A. J., and Jones, K. C. (2004). Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environmental Science & Technology* **38**, 34-41.
- Jones, K. C., and de Voogt, P. (1999). Persistent organic pollutants (POPs): state of the science. *Environmental Pollution* **100**, 209-221.
- Kallenborn, R., Breivik, K., Eckhardt, S., Lunder, C. R., Mano, S., Schlabach, M., and Stohl, A. (2013). Long-term monitoring of persistent organic pollutants (POPs) at the Norwegian Troll station in Dronning Maud Land, Antarctica. *Atmospheric Chemistry and Physics* **13**, 6983-6992.
- Khairy, M. A., and Lohmann, R. (2013). Feasibility of using low density polyethylene sheets to detect atmospheric organochlorine pesticides in Alexandria, Egypt. *Environmental Pollution* **181**, 151-158.
- Klanova, J., Eupr, P., Kohoutek, J., and Harner, T. (2008). Assessing the influence of meteorological parameters on the performance of polyurethane foam-based passive air samplers. *Environmental Science & Technology* **42**, 550-555.
- Klanova, J., Kohoutek, J., Hamplova, L., Urbanova, P., and Holoubek, I. (2006). Passive air sampler as a tool for long-term air pollution monitoring: Part 1. Performance assessment for seasonal and spatial variations. *Environmental Pollution* **144**, 393-405.
- Koblizkova, M., Genualdi, S., Lee, S. C., and Harner, T. (2012). Application of Sorbent Impregnated Polyurethane Foam (SIP) Disk Passive Air Samplers for Investigating Organochlorine Pesticides and Polybrominated Diphenyl Ethers at the Global Scale. *Environmental Science & Technology* **46**, 391-396.
- Kohler, M., Tremp, J., Zennegg, M., Seiler, C., Minder-Kohler, S., Beck, M., Lienemann, P., Wegmann, L., and Schmidt, P. (2005). Joint sealants: An overlooked diffuse source of polychlorinated biphenyls in buildings. *Environmental Science & Technology* **39**, 1967-1973.
- Krogseth, I. S., Zhang, X. M., Lei, Y. D., Wania, F., and Breivik, K. (2013). Calibration and Application of a Passive Air Sampler (XAD-PAS) for Volatile Methyl Siloxanes. *Environmental Science & Technology* **47**, 4463-4470.
- Kulik, N., Goi, A., Trapido, M., and Tuhkanen, T. (2006). Degradation of polycyclic aromatic hydrocarbons by combined chemical pre-oxidation and bioremediation in creosote contaminated soil. *Journal of Environmental Management* **78**, 382-391.
- Langer, P., Kocan, A., Tajtakova, M., Koska, J., Radikova, Z., Ksinantova, L., Imrich, R., Huckova, M., Drobna, B., Gasperikova, D., Sebokova, E., and Klimes, I. (2008). Increased thyroid volume, prevalence of thyroid antibodies and impaired fasting glucose in young adults from organochlorine cocktail polluted area: Outcome of transgenerational transmission? *Chemosphere* **73**, 1145-1150.
- Lavric, E. D., Konnov, A. A., and De Ruyck, J. (2004). Dioxin levels in wood combustion - a review. *Biomass & Bioenergy* **26**, 115-145.
- Li, N. Q., Wania, F., Lei, Y. D., and Daly, G. L. (2003). A comprehensive and critical compilation, evaluation, and selection of physical-chemical property data for selected polychlorinated biphenyls. *Journal of Physical and Chemical Reference Data* **32**, 1545-1590.
- Li, Y. F. (1999). Global technical hexachlorocyclohexane usage and its contamination consequences in the environment: from 1948 to 1997. *Science of the Total Environment* **232**, 121-158.
- Li, Y. F., Macdonald, R. W., Jantunen, L. M. M., Harner, T., Bidleman, T. F., and Strachan, W. M. J. (2002). The transport of beta-hexachlorocyclohexane to the western Arctic Ocean: a contrast to alpha-HCH. *Science of the Total Environment* **291**, 229-246.
- Liu, G. R., Liu, W. B., Cai, Z. W., and Zheng, M. H. (2013). Concentrations, profiles, and emission factors of unintentionally produced persistent organic pollutants in fly ash from coking processes. *Journal of Hazardous Materials* **261**, 421-426.
- Liu, G. R., Zheng, M. H., Liu, W. B., Wang, C. Z., Zhang, B., Gao, L. R., Su, G. J., Xiao, K., and Lv, P. (2009). Atmospheric Emission of PCDD/Fs, PCBs, Hexachlorobenzene, and Pentachlorobenzene from the Coking Industry. *Environmental Science & Technology* **43**, 9196-9201.

- Lohmann, R., Northcott, G. L., and Jones, K. C. (2000). Assessing the contribution of diffuse domestic burning as a source of PCDD/Fs, PCBs, and PAHs to the UK atmosphere. *Environmental Science & Technology* **34**, 2892-2899.
- Ma, Y. G., Lei, Y. D., Xiao, H., Wania, F., and Wang, W. H. (2010). Critical Review and Recommended Values for the Physical-Chemical Property Data of 15 Polycyclic Aromatic Hydrocarbons at 25 degrees C. *Journal of Chemical and Engineering Data* **55**, 819-825.
- Mackay, D. (1991). *Multimedia Environmental Models; the Fugacity Approach*, Lewis Publishing Company, Chelsea, MI.
- Mackay, D., and Wania, F. (1995). Transport of contaminants to the Arctic-partitioning, processes and models. *Science of the Total Environment* **160-61**, 25-38.
- Malanichev, A., Mantseva, E., Shatalov, V., Strukov, B., and Vulykh, N. (2004). Numerical evaluation of the PCBs transport over the Northern Hemisphere. *Environmental Pollution* **128**, 279-289.
- Mazur, M., Oleniacz, R., Bogacki, M., and Szczyglowski, P. (2010). *Emission of polycyclic aromatic hydrocarbons (PAHs) during the production of carbon and graphite electrodes*, Crc Press-Taylor & Francis Group, Boca Raton.
- McLachlan, M. S., Czub, G., MacLeod, M., and Arnot, J. A. (2011). Bioaccumulation of Organic Contaminants in Humans: A Multimedia Perspective and the Importance of Biotransformation. *Environmental Science & Technology* **45**, 197-202.
- McLachlan, M. S., Welschpausch, K., and Tolls, J. (1995). Field validation of a model of the uptake of gaseous SOC in LOLIUM-MULTIFLORUM (rye grass). *Environmental Science & Technology* **29**, 1998-2004.
- Meijer, S. N., Ockenden, W. A., Steinnes, E., Corrigan, B. P., and Jones, K. C. (2003a). Spatial and temporal trends of POPs in Norwegian and UK background air: Implications for global cycling. *Environmental Science & Technology* **37**, 454-461.
- Meijer, S. N., Ockenden, W. A., Sweetman, A., Breivik, K., Grimalt, J. O., and Jones, K. C. (2003b). Global distribution and budget of PCBs and HCB in background surface soils: Implications or sources and environmental processes. *Environmental Science & Technology* **37**, 667-672.
- Meijer, S. N., Steinnes, E., Ockenden, W. A., and Jones, K. C. (2002). Influence of environmental variables on the spatial distribution of PCBs in Norwegian and UK soils: Implications for global cycling. *Environmental Science & Technology* **36**, 2146-2153.
- Melymuk, L., Robson, M., Helm, P. A., and Diamond, M. L. (2011). Evaluation of passive air sampler calibrations: Selection of sampling rates and implications for the measurement of persistent organic pollutants in air. *Atmospheric Environment* **45**, 1867-1875.
- Moeckel, C., Harner, T., Nizzetto, L., Strandberg, B., Lindroth, A., and Jones, K. C. (2009). Use of Depuration Compounds in Passive Air Samplers: Results from Active Sampling-Supported Field Deployment, Potential Uses, and Recommendations. *Environmental Science & Technology* **43**, 3227-3232.
- Moeckel, C., Nizzetto, L., Di Guardo, A., Steinnes, E., Freppaz, M., Filippa, G., Camporini, P., Benner, J., and Jones, K. C. (2008). Persistent Organic Pollutants in Boreal and Montane Soil Profiles: Distribution, Evidence of Processes and Implications for Global Cycling. *Environmental Science & Technology* **42**, 8374-8380.
- Morf, L. S., Tremp, J., Gloor, R., Schuppisser, F., Stengele, M., and Taverna, R. (2007). Metals, non-metals and PCB in electrical and electronic waste Actual levels in Switzerland. *Waste Management* **27**, 1306-1316.
- Motelay-Massei, A., Harner, T., Shoeib, M., Diamond, M., Stern, G., and Rosenberg, B. (2005). Using passive air samplers to assess urban-rural trends for persistent organic pollutants and polycyclic aromatic hydrocarbons. 2. Seasonal trends for PAHs, PCBs, and organochlorine pesticides. *Environmental Science & Technology* **39**, 5763-5773.
- Muir, D. C. G., Segstro, M. D., Welbourn, P. M., Toom, D., Eisenreich, S. J., Macdonald, C. R., and Whelpdale, D. M. (1993). Patterns of accumulation of airborne organochlorine contaminants in Lichens from the Upper Great-Lakes region of Ontario. *Environmental Science & Technology* **27**, 1201-1210.

- Nansen, F. (1924). *Blant sel og bjørn*, Dybwad.
- Nie, Z. Q., Zheng, M. H., Liu, W. B., Zhang, B., Liu, G. R., Su, G. J., Lv, P., and Xiao, K. (2011). Estimation and characterization of PCDD/Fs, dl-PCBs, PCNs, HxCBz and PeCBz emissions from magnesium metallurgy facilities in China. *Chemosphere* **85**, 1707-1712.
- Nizzetto, L., Aas, W., and Krogseth, I. S. (2014). *Monitoring of environmental contaminants in air and precipitation, annual report 2013*, Rep. No. 20/2014. NILU, Kjeller.
- Nyarango, P. M., Gebremeskel, T., Mebrahtu, G., Mufunda, J., Abdulmumini, U., Ogbamariam, A., Kosia, A., Gebremichael, A., Gunawardena, D., Ghebrat, Y., and Okbaldet, Y. (2006). A steep decline of malaria morbidity and mortality trends in Eritrea between 2000 and 2004: the effect of combination of control methods. *Malaria Journal* **5**.
- Næs, K. (1998). The distribution and effects on Norwegian fjord and coastal ecosystems of polycyclic aromatic hydrocarbons (PAHs) generated by the production of primary aluminium and manganese alloys. Thesis, University of Oslo.
- Ockenden, W. A., Corrigan, B. P., Howsam, M., and Jones, K. C. (2001). Further developments in the use of semipermeable membrane devices as passive air samplers: Application to PCBs. *Environmental Science & Technology* **35**, 4536-4543.
- Ockenden, W. A., Sweetman, A. J., Prest, H. F., Steinnes, E., and Jones, K. C. (1998). Toward an understanding of the global atmospheric distribution of persistent organic pollutants: The use of semipermeable membrane devices as time-integrated passive samplers. *Environmental Science & Technology* **32**, 2795-2803.
- Oehme, M., and Manø, S. (1984). The long-range transport of organic pollutants to the Arctic. *Fresenius Zeitschrift Fur Analytische Chemie* **319**, 141-146.
- Ogata, Y., Takada, H., Mizukawa, K., Hirai, H., Iwasa, S., Endo, S., Mato, Y., Saha, M., Okuda, K., Nakashima, A., Murakami, M., Zurcher, N., Booyatumanondo, R., Zakaria, M. P., Dung, L. Q., Gordon, M., Miguez, C., Suzuki, S., Moore, C., Karapanagioti, H. K., Weerts, S., McClurg, T., Burres, E., Smith, W., Van Velkenburg, M., Lang, J. S., Lang, R. C., Laursen, D., Danner, B., Stewardson, N., and Thompson, R. C. (2009). International Pellet Watch: Global monitoring of persistent organic pollutants (POPs) in coastal Waters. 1. Initial phase data on PCBs, DDTs, and HCHs. *Marine Pollution Bulletin* **58**, 1437-1446.
- Ottar, B. (1976). Organization of long-range transport of air-pollution of monitoring in Europe. *Water Air and Soil Pollution* **6**, 219-229.
- Ottar, B. (1977). International agreement needed to reduce long-range transport of air-pollutants in Europe. *Ambio* **6**, 262-269.
- Ottar, B. (1978). Assessment of OECD study on long-range transport of air-pollutants (LRTAP). *Atmospheric Environment* **12**, 445-454.
- Ottar, B. (1981). The transfer of airborne pollutants to the Arctic region. *Atmospheric Environment* **15**, 1439-1445.
- Pacyna, J. M., and Oehme, M. (1988). Long-range transport of some organic-compounds to the Norwegian Arctic. . *Atmospheric Environment* **22**, 243-257.
- Pozo, K., Harner, T., Lee, S. C., Wania, F., Muir, D. C. G., and Jones, K. C. (2009). Seasonally Resolved Concentrations of Persistent Organic Pollutants in the Global Atmosphere from the First Year of the GAPS Study. *Environmental Science & Technology* **43**, 796-803.
- Pozo, K., Harner, T., Shoeib, M., Urrutia, R., Barra, R., Parra, O., and Focardi, S. (2004). Passive-sampler derived air concentrations of persistent organic pollutants on a north-south transect in Chile. *Environmental Science & Technology* **38**, 6529-6537.
- Pozo, K., Harner, T., Wania, F., Muir, D. C. G., Jones, K. C., and Barrie, L. A. (2006). Toward a global network for persistent organic pollutants in air: Results from the GAPS study. *Environmental Science & Technology* **40**, 4867-4873.
- Ravindra, K., Sokhi, R., and Van Grieken, R. (2008). Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. *Atmospheric Environment* **42**, 2895-2921.
- Renner, R. (2002). The K-ow controversy. *Environmental Science & Technology* **36**, 410A-413A.

- Riget, F., Bignert, A., Braune, B., Stow, J., and Wilson, S. (2010). Temporal trends of legacy POPs in Arctic biota, an update. *Science of the Total Environment* **408**, 2874-2884.
- Routti, H., Arukwe, A., Jenssen, B. M., Letcher, R. J., Nyman, M., Backman, C., and Gabrielsen, G. W. (2010). Comparative endocrine disruptive effects of contaminants in ringed seals (*Phoca hispida*) from Svalbard and the Baltic Sea. *Comparative Biochemistry and Physiology C-Toxicology & Pharmacology* **152**, 306-312.
- Ruus, A., Green, N. W., Maage, A., and Skei, J. (2006). PCB-containing paint and plaster caused extreme PCB-concentrations in biota from the Sorfjord (Western Norway) - A case study. *Marine Pollution Bulletin* **52**, 100-103.
- Scheringer, M. (1997). Characterization of the environmental distribution behavior of organic chemicals by means of persistence and spatial range. *Environmental Science & Technology* **31**, 2891-2897.
- Schuster, J. K., Gioia, R., Breivik, K., Steinnes, E., Scheringer, M., and Jones, K. C. (2010). Trends in European Background Air Reflect Reductions in Primary Emissions of PCBs and PBDEs. *Environmental Science & Technology* **44**, 6760-6766.
- Schuster, J. K., Gioia, R., Moeckel, C., Agarwal, T., Bucheli, T. D., Breivik, K., Steinnes, E., and Jones, K. C. (2011). Has the Burden and Distribution of PCBs and PBDEs Changed in European Background Soils between 1998 and 2008? Implications for Sources and Processes. *Environmental Science & Technology* **45**, 7291-7297.
- Semb, A. (1978). SULFUR EMISSIONS IN EUROPE. *Atmospheric Environment* **12**, 455-460.
- Shen, L., and Wania, F. (2005). Compilation, evaluation, and selection of physical-chemical property data for organochlorine pesticides. *Journal of Chemical and Engineering Data* **50**, 742-768.
- Shen, L., Wania, F., Lei, Y. D., Teixeira, C., Muir, D. C. G., and Bidleman, T. F. (2004). Hexachlorocyclohexanes in the north American atmosphere. *Environmental Science & Technology* **38**, 965-975.
- Shen, L., Wania, F., Lei, Y. D., Teixeira, C., Muir, D. C. G., and Bidleman, T. F. (2005). Atmospheric distribution and long-range transport behavior of organochlorine pesticides in north America. *Environmental Science & Technology* **39**, 409-420.
- Shoeib, M., and Harner, T. (2002). Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environmental Science & Technology* **36**, 4142-4151.
- Sinkkonen, S., and Paasivirta, J. (2000). Degradation half-life times of PCDDs, PCDFs and PCBs for environmental fate modeling. *Chemosphere* **40**, 943-949.
- Somerville, M. F., and Liebens, J. (2011). DDTs in Soils Affected by Mosquito Fumigation in Belize. *Soil & Sediment Contamination* **20**, 289-305.
- Sovocool, G. W., Lewis, R. G., Harless, R. L., Wilson, N. K., and Zehr, R. D. (1977). Analysis of technical chlordane by gas chromatography mass spectrometry. *Analytical Chemistry* **49**, 734-740.
- Stohl, A., Forster, C., Frank, A., Seibert, P., and Wotawa, G. (2005). Technical note: The Lagrangian particle dispersion model FLEXPART version 6.2. *Atmospheric Chemistry and Physics* **5**, 2461-2474.
- Stohl, A., Hittenberger, M., and Wotawa, G. (1998). Validation of the Lagrangian particle dispersion model FLEXPART against large-scale tracer experiment data. *Atmospheric Environment* **32**, 4245-4264.
- Su, Y. S., and Hung, H. L. (2010). Inter-laboratory comparison study on measuring semi-volatile organic chemicals in standards and air samples. *Environmental Pollution* **158**, 3365-3371.
- Sundqvist, K. L., Tysklind, M., Geladi, P., Hopke, P. K., and Wiberg, K. (2010). PCDD/F Source Apportionment in the Baltic Sea Using Positive Matrix Factorization. *Environmental Science & Technology* **44**, 1690-1697.
- Sverko, E., Tomy, G. T., Marvin, C. H., and Muir, D. C. G. (2012). Improving the Quality of Environmental Measurements on Short Chain Chlorinated Paraffins to Support Global Regulatory Efforts. *Environmental Science & Technology* **46**, 4697-4698.
- Tuduri, L., Harner, T., and Hung, H. (2006). Polyurethane foam (PUF) disks passive air samplers: Wind effect on sampling rates. *Environmental Pollution* **144**, 377-383.

- Turgut, C., Gokbulut, C., and Cutright, T. J. (2009). Contents and sources of DDT impurities in dicofol formulations in Turkey. *Environmental Science and Pollution Research* **16**, 214-217.
- Tørseth, K., Aas, W., Breivik, K., Fjæraa, A. M., Fiebig, M., Hjellbrekke, A. G., Lund Myhre, C., Solberg, S., and Yttri, K. E. (2012). Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972-2009. *Atmospheric Chemistry and Physics* **12**, 5447-5481.
- U.S. EPA. *Estimation Programs Interface Suite(TM) for Microsoft Windows*, v 4.1. http://www.epa.gov/oppt/exposure/pubs/updates_episuite_v4.10.revised.htm. 2013. Accessed Desember 15
- U.S. EPA. *Aroclor and Other PCB Mixtures*. <http://www.epa.gov/osw/hazard/tsd/pcbs/pubs/aroclor.htm>. 2014. Accessed February 27
- UN. *Treaty Collection, Chapter XXVII Environment*. https://treaties.un.org/Pages/ViewDetails.aspx?src=TREATY&mtdsg_no=XXVII-1-g&chapter=27&lang=en. 2014. Accessed September 12
- UNECE. *The 1998 Aarhus Protocol on persistent organic pollutants (POPs)*. . <http://www.unece.org/env/lrtap/welcome.html>. 2014. Accessed September 30
- UNECE (2004). *Handbook for the 1979 Convention on long-range transboundary air pollution and its protocols*, Rep. No. United Nations Economics Commission for Europe, New York, Geneva. <http://www.unece.org/fileadmin/DAM/env/lrtap/BIBLE.E.pdf>.
- UNECE (2007). *Exploration of management options for Pentachlorobenzene (PeCB), Paper for the 6th meeting of the UNECE CLRTAP Task Force on Persistent Organic Pollutants*, Rep. No. United Nations Economics Commission for Europe, Vienna. <http://www.unece.org/fileadmin/DAM/env/lrtap/TaskForce/popsxg/2007/6thmeeting/Exploration%20of%20management%20options%20for%20PeCB%20Final.doc.pdf>.
- UNECE (2009). *Guidance document on best available techniques to control emissions of persistent organic pollutants from major stationary sources*, Rep. No. ECE/EB.AIR/2009/14. United Nations Economics Commission for Europe <http://www.unece.org/fileadmin/DAM/env/documents/2009/EB/eb/POPs/Guidance%20document%20on%20BAT.e.pdf>.
- UNECE (2010a). *The 1998 Protocol on Persistent Organic Pollutants, including the Amendments Adopted by the Parties on 18 December 2009*, Rep. No. <http://www.unece.org/fileadmin/DAM/env/lrtap/full%20text/ece.eb.air.104.e.pdf>.
- UNECE (2010b). *Hemispheric transport of air pollution 2010. Part C: Persistent organic pollutants* Rep. No. United Nations, Geneva, Switzerland http://www.htap.org/publications/2010_report/2010_Final_Report/HTAP%202010%20Part%20C%20110408.pdf.
- UNECE ad hoc expert group on POPs (2003). *Short chain chlorinated paraffins (SCCPs) Substance Dossier. Final Draft II*, Rep. No. http://www.unece.org/fileadmin/DAM/env/lrtap/TaskForce/popsxg/2000-2003/dossier_sccp_may03.pdf.
- UNEP (2002). *Ridding the world of POPs: A guide to the Stockholm Convention on persistent organic pollutants*, Rep. No. Secretariat of the Stockholm Convention on Persistent Organic Pollutants, United Nations Environment Programme (UNEP) Chemicals http://www.pops.int/documents/guidance/beg_guide.pdf.
- UNEP. *List of signatories and ratifications to the Stockholm Convention on POPs*. <http://www.pops.int/documents/signature/signstatus.htm>. 2003. Accessed April 08
- UNEP. *Status of ratifications*. <http://chm.pops.int/Countries/StatusofRatifications/tabid/252/Default.aspx>. 2014. Accessed April 08
- UNEP (2007). *Guidance on the Global Monitoring Plan for Persistent Organic Pollutants-Preliminary version*, Secretariat of the Stockholm Covention on Persitent Organic Pollutants, Geneva.

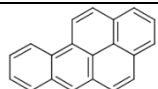
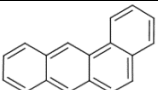
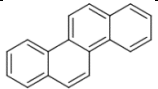
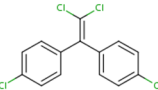
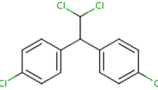
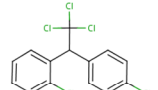
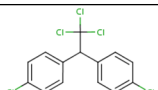
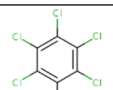
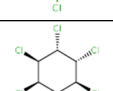
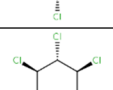
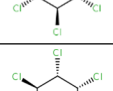
- UNEP (2009a). *Adoption of amendments to annexes A, B and C*, Rep. No. Secretariat of the Stockholm Convention United Nations Environment Programme, Geneva.
<http://chm.pops.int/TheConvention/Overview/TextoftheConvention/tabid/2232/>.
- UNEP (2009b). *Stockholm Convention on Persistent Organic Pollutants (POPs) as amended in 2009. Text and annexes*, Rep. No. United Nation Environment Program
- UNEP (2011). *Adoption of an amendment to Annex A*, Rep. No., Geneva.
<http://chm.pops.int/Home/tabid/2121/mctl/ViewDetails/EventModID/871/EventID/230/xmid/6921/Default.aspx>.
- UNEP (2012). *Report of the Persistent Organic Pollutants Review Committee on the work of its eighth meeting* Rep. No. United Nations Environment Program
- UNEP (2013). *Listing of hexabromocyclododecane* Rep. No.
<https://treaties.un.org/doc/Publication/CN/2013/CN.934.2013-Eng.pdf>.
- Vallack, H. W., Bakker, D. J., Brandt, I., Brostrom-Lunden, E., Brouwer, A., Bull, K. R., Gough, C., Guardans, R., Holoubek, I., Jansson, B., Koch, R., Kuylenstierna, J., Lecloux, A., Mackay, D., McCutcheon, P., Mocarelli, P., and Taalman, R. D. F. (1998). Controlling persistent organic pollutants - what next? *Environmental Toxicology and Pharmacology* **6**, 143-175.
- van Pul, W. A. J., de Leeuw, F., van Jaarsveld, J. A., van der Gaag, M. A., and Sliggers, C. J. (1998). The potential for long-range transboundary atmospheric transport. *Chemosphere* **37**, 113-141.
- Walse, S. S., Scott, G. I., and Ferry, J. L. (2003). Stereoselective degradation of aqueous endosulfan in modular estuarine mesocosms: formation of endosulfan gamma-hydroxycarboxylate. *Journal of Environmental Monitoring* **5**, 373-379.
- Wang, J. X., Tuduri, L., Millet, M., Briand, O., and Montury, M. (2009). Flexibility of solid-phase microextraction for passive sampling of atmospheric pesticides. *Journal of Chromatography A* **1216**, 3031-3037.
- Wang, Y. W., Fu, J. J., Wang, T., Liang, Y., Pan, Y. Y., Cai, Y. Q., and Jiang, G. B. (2010). Distribution of Perfluorooctane Sulfonate and Other Perfluorochemicals in the Ambient Environment around a Manufacturing Facility in China. *Environmental Science & Technology* **44**, 8062-8067.
- Wania, F., and Daly, G. L. (2002). Estimating the contribution of degradation in air and deposition to the deep sea to the global loss of PCBs. *Atmospheric Environment* **36**, 5581-5593.
- Wania, F., and Haugen, J. E. (1999). Long term measurements of wet deposition and precipitation scavenging of hexachlorocyclohexanes in Southern Norway. *Environmental Pollution* **105**, 381-386.
- Wania, F., and Mackay, D. (1993). Global fractionation and cold condensation of low volatility organochlorine compounds in polar-regions. *Ambio* **22**, 10-18.
- Wania, F., and Mackay, D. (1996). Tracking the distribution of persistent organic pollutants. *Environmental Science & Technology* **30**, A390-A396.
- Wania, F., and McLachlan, M. S. (2001). Estimating the influence of forests on the overall fate of semivolatile organic compounds using a multimedia fate model. *Environmental Science & Technology* **35**, 582-590.
- Wania, F., Shen, L., Lei, Y. D., Teixeira, C., and Muir, D. C. G. (2003). Development and calibration of a resin-based passive sampling system for monitoring persistent organic pollutants in the atmosphere. *Environmental Science & Technology* **37**, 1352-1359.
- Weber, J., Halsall, C. J., Muir, D., Teixeira, C., Small, J., Solomon, K., Hermanson, M., Hung, H., and Bidleman, T. (2010). Endosulfan, a global pesticide: A review of its fate in the environment and occurrence in the Arctic. *Science of the Total Environment* **408**, 2966-2984.
- Webster, E., Mackay, D., and Wania, F. (1998). Evaluating environmental persistence. *Environmental Toxicology and Chemistry* **17**, 2148-2158.
- Wennrich, L., Popp, P., and Hafner, C. (2002). Novel integrative passive samplers for the long-term monitoring of semivolatile organic air pollutants. *Journal of Environmental Monitoring* **4**, 371-376.

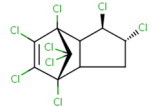
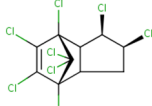
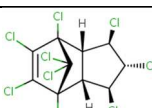
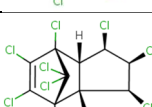
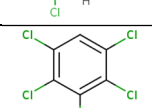
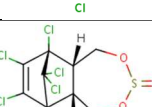
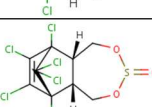
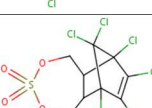
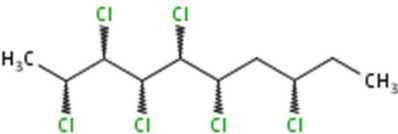
- Wilcockson, J. B., and Gobas, F. A. P. (2001). Thin-film solid-phase extraction to measure fugacities of organic chemicals with low volatility in biological samples. *Environmental Science & Technology* **35**, 1425-1431.
- Wilford, B. H., Harner, T., Zhu, J. P., Shoeib, M., and Jones, K. C. (2004). Passive sampling survey of polybrominated diphenyl ether flame retardants in indoor and outdoor air in Ottawa, Canada: Implications for sources and exposure. *Environmental Science & Technology* **38**, 5312-5318.
- Wong, F., and Wania, F. (2011). Visualising the equilibrium distribution and mobility of organic contaminants in soil using the chemical partitioning space. *Journal of Environmental Monitoring* **13**, 1569-1578.
- Xiao, H., Li, N. Q., and Wania, F. (2004). Compilation, evaluation, and selection of physical-chemical property data for alpha-, beta-, and gamma-hexachlorocyclohexane. *Journal of Chemical and Engineering Data* **49**, 173-185.
- Yao, Y., Harner, T., Ma, J. M., Tuduri, L., and Blanchard, P. (2007). Sources and occurrence of dacthal in the Canadian atmosphere. *Environmental Science & Technology* **41**, 688-694.
- Yum, S., Woo, S., Kagami, Y., Park, H. S., and Ryu, J. C. (2010). Changes in gene expression profile of medaka with acute toxicity of Arochlor 1260, a polychlorinated biphenyl mixture. *Comparative Biochemistry and Physiology C-Toxicology & Pharmacology* **151**, 51-56.
- Zeng, L. X., Wang, T., Han, W. Y., Yuan, B., Liu, Q. A., Wang, Y. W., and Jiang, G. B. (2011). Spatial and Vertical Distribution of Short Chain Chlorinated Paraffins in Soils from Wastewater Irrigated Farmlands. *Environmental Science & Technology* **45**, 2100-2106.
- Zhang, X. M., Wong, C., Lei, Y. D., and Wania, F. (2012). Influence of Sampler Configuration on the Uptake Kinetics of a Passive Air Sampler. *Environmental Science & Technology* **46**, 397-403.
- Økland, T. (2005). *Kostholdsråd i norske havner og fjorder. En gjennomgang av kostholdsråd i norske havner og fjorder fra 1960-tallet til i dag.*, Rep. No. VKM, SFT.
Mattilsynet http://www.mattilsynet.no/mattilsynet/multimedia/archive/00018/Ny_rapport_Kosthold_18114a.pdf.

Appendix

Table A1. Physical chemical data

Trivial name	CAS	IUPAC	log K _{OA} ¹	log K _{AW} ^{2*}	log K _{OW} ³	Reference 1,2,3	Structural formula
PCB-28	7012-37-5	2,4,4'-trichlorobiphenyl	7,85	-2,19	5,66	(Li et al., 2003)	
PCB-52	35693-99-3	2,2',5,5'-tetrachlorobiphenyl	8,22	-2,31	5,91		
PCB-101	37680-73-2	2,2',4,5,5'-pentachlorobiphenyl	8,73	-2,40	6,33		
PCB-118	31508-00-6	2,3',4,4',5-pentachlorobiphenyl	9,36	-2,67	6,69		
PCB-138	35065-28-2	2,2',3,4,4',5'-hexachlorobiphenyl	9,66	-2,45	7,21		
PCB-153	35065-27-1	2,2',4,4',5,5'-hexachlorobiphenyl	9,44	-2,57	6,87		
PCB-180	35065-29-3	2,2',3,4,4',5,5'-heptachlorobiphenyl	10,16	-3,00	7,16		
Fluorene	86-73-7	2,2'-Methylenebiphenyl	6,85	-2,74	4,11	(Ma et al., 2010)	
Phenanthrene	85-01-8	-	7,64	-3,17	4,47		
Anthracene	120-12-7	-	7,7	-3,13	4,57		
Fluoranthene	206-44-0	1,2'-(1,8-Naphthylene)benzene	8,81	-3,84	4,97		
Pyrene	129-00-0	Benzo[def]phenanthrene	8,86	-3,85	5,01		

Benzo[a]pyrene	50-32-8	3,4-Benz[a]pyrene	11,48	-5,43	6,05	(Ma et al., 2010)	
Benz[a]anthracene	56-55-3	1,2-Benz[a]anthracene	10,28	-4,45	5,83		
Chrysene	218-01-9	1,2-Benzophenanthrene	10,3	-4,63	5,67		
p,p'-DDE	72-55-9	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethene	9,7	-2,77	6,93	(Shen and Wania, 2005)	
p,p'-DDD	72-54-8	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	10,03	-3,7	6,33		
o,p'-DDT	789-02-6	1,1,1-Trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane	-	-	-		
p,p'-DDT	50-29-3	1,1,1-Trichloro-2,2-bis(4-chlorophenyl)ethane	9,73	-3,34	6,39		
HCB	118-74-1	1,2,3,4,5,6-hexachlorobenzene	7,21	-1,57	5,64		
α-HCH	319-84-6	α-1,2,3,4,5,6-Hexachlorocyclohexane	7,464	-3,524	3,94	(Xiao et al., 2004)	
β-HCH	319-85-7	β-1,2,3,4,5,6-Hexachlorocyclohexane	8,74	-4,82	3,92		
γ-HCH	58-89-9	γ-1,2,3,4,5,6-Hexachlorocyclohexane	7,74	-3,91	3,83		

<i>trans</i> -Chlordane	39765-80-5	1,2,3,4,5,6,7,8,8-nonachloro-2,3,3a,4,7,7a-hexahydro-, (1 α ,2 β ,3 α ,3a α ,4 β ,7 β ,7a α)-4,7-Methano-1H-indene	8,83	-2,56	6,27	(Shen and Wania, 2005)	
<i>cis</i> -Chlordane	57-74-9	1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-Methano-1H-indene	8,83	-2,63	6,2		
<i>trans</i> -Nonachlor	39765-80-5	1,2,3,4,5,6,7,8,8-nonachloro-2,3,3a,4,7,7a-hexahydro-, (1 α ,2 β ,3 α ,3a α ,4 β ,7 β ,7a α)-4,7-Methano-1H-indene	-	-	-		
<i>cis</i> -Nonachlor	5103-73-1	1,2,3,4,5,6,7,8,8-nonachloro-2,3,3a,4,7,7a-hexahydro-, (1 <i>R</i> ,3 <i>S</i> ,3a <i>R</i> ,4 <i>S</i> ,7 <i>R</i> ,7a <i>S</i>)- <i>rel</i> -4,7-Methano-1H-indene	-	-	-		
PeCB	608-93-5	1,2,3,4,5-pentachlorobenzene	6,73	-1,54	5,19		
α -endosulfan	959-98-8	6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-,3-oxide, (3 α ,5a β ,6 α ,9 α ,9a β)-6,9-Methano-2,4,3-benzodioxathiepin	8,49	-3,55	4,94		
β -endosulfan	33213-65-9	6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-,3 oxide, 3 α ,5a α ,6 β ,9 β ,9a α)-6,9-Methano-2,4,3-benzodioxathiepin	9,53	-4,75	4,78		
endosulfan sulfate	1031-07-8	6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-,3,3-dioxide-6,9-Methano-2,4,3-benzodioxathiepin	8,537	-4,877	3,66	(U.S. EPA, 2011)	
SCCPs	85535-84-8	Alkanes, C ₁₀₋₁₃ , chloro (C ₁₀ Cl ₂)	4,86	0,37	5,23	(Gawor and Wania, 2013)	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₀ Cl ₇)	7,71	-2,88	4,83		
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₀ Cl ₈)	8,72	-3,69	5,03		
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₀ Cl ₉)	9,86	-4,52	5,34		
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₁ Cl ₂)	5,46	0,29	5,75		
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₁ Cl ₃)	5,63	-0,17	5,46		

SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₁ Cl ₄)	5,99	-0,74	5,25	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₁ Cl ₅)	6,51	-1,37	5,14	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₁ Cl ₆)	7,18	-2,07	5,11	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₁ Cl ₇)	7,99	-2,82	5,17	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₁ Cl ₈)	8,93	-3,62	5,31	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₁ Cl ₉)	9,99	-4,44	5,55	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₁ Cl ₁₀)	11,13	-5,27	5,86	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₂ Cl ₂)	6,06	0,21	6,27	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₂ Cl ₃)	6,2	-0,24	5,96	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₂ Cl ₄)	6,51	-0,78	5,73	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₂ Cl ₅)	6,97	-1,38	5,59	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₂ Cl ₆)	7,58	-2,06	5,52	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₂ Cl ₇)	8,33	-2,79	5,54	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₂ Cl ₈)	9,19	-3,56	5,63	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₂ Cl ₉)	10,17	-4,36	5,81	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₂ Cl ₁₀)	11,25	-5,19	6,06	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₂ Cl ₁₁)	12,43	-6,03	6,4	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₃ Cl ₃)	6,77	-0,3	6,47	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₃ Cl ₄)	7,04	-0,82	6,22	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₃ Cl ₅)	7,46	-1,41	6,05	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₃ Cl ₆)	8,01	-2,06	5,95	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₃ Cl ₇)	8,69	-2,76	5,93	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₃ Cl ₈)	9,49	-3,51	5,98	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₃ Cl ₉)	10,41	-4,31	6,1	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₃ Cl ₁₀)	11,42	-5,11	6,31	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₃ Cl ₁₁)	12,53	-5,95	6,58	
SCCPs		Alkanes, C ₁₀₋₁₃ , chloro (C ₁₃ Cl ₁₂)	13,71	-6,78	6,93	
SCCPs	-	Alkanes, C ₁₀₋₁₃ , chloro	9,07	-3,07	6	(European Chemicals Bureau, 2008)

^{*)} $\log K_{AW} = \log K_{OW} - \log K_{OA}$, all figures are obtained from: <http://chem.sis.nlm.nih.gov/chemidplus/>

Table A2: Estimated log K_{OA} , and number of days until 25% (t_{25}) and 95% (t_{95}) of equilibrium stage has been reached (Shoeib and Harner, 2002), at 3 different air temperatures.

Compounds	log K_{OA}			t_{25} (days)			t_{95} (days)		
	8°C	14°C	17°C	8°C	14°C	17°C	8°C	14°C	17°C
HCB	8.01	7.71	7.57	<i>30</i>	<i>20</i>	<i>16</i>	312	204	166
PCB-28	8.68	8.37	8.23	<i>81</i>	<i>52</i>	<i>42</i>	838	536	432
PCB-52	9.08	8.76	8.61	146	92	73	1506	948	757
PCB-101	9.62	9.29	9.13	319	199	158	3302	2054	1631
PCB-118	10.30	9.96	9.79	877	528	413	9069	5466	4277
PCB-138	10.57	10.24	10.07	1296	793	625	13409	8206	6469
PCB-153	10.44	10.07	9.89	1062	623	481	10991	6442	4973
PCB-180	11.15	10.79	10.61	3016	1779	1377	31200	18401	14248
α -HCH	8.12	7.88	7.76	<i>36</i>	<i>25</i>	<i>21</i>	369	259	219
γ -HCH	8.35	8.13	8.02	<i>50</i>	<i>36</i>	<i>31</i>	520	374	319
<i>p,p'</i> -DDT	10.58	10.27	10.12	1308	830	666	13531	8583	6885
<i>p,p'</i> -DDE	10.55	10.24	10.09	1252	794	637	12949	8214	6589
<i>p,p'</i> -DDD	10.88	10.57	10.42	2030	1288	1033	21005	13324	10687
trans-Chlordane	9.85	9.48	9.30	451	261	200	4667	2697	2067
cis-Chlordane	9.87	9.49	9.30	464	265	202	4796	2743	2093
Fluorene	7.59	7.29	7.14	<i>16</i>	<i>11</i>	<i>8</i>	170	109	88
Phenanthrene	8.36	8.07	7.94	<i>51</i>	<i>33</i>	<i>27</i>	526	345	282
Anthracene	8.43	8.16	8.03	<i>56</i>	<i>38</i>	<i>31</i>	578	391	324
Fluoranthene	9.49	9.18	9.02	267	168	134	2760	1735	1385
Pyrene	9.46	9.18	9.04	253	168	138	2615	1741	1429
Benzo(a)pyrene	11.81	11.56	11.45	7920	5556	4680	81928	57480	48411
Benz(a)anthracene	10.80	10.46	10.29	1821	1093	854	18841	11310	8832
Chrysene	11.52	11.04	10.81	5219	2583	1837	53987	26722	19007

Values in cursive are < the longest deployment period in this study, ~ 90 days (**Papers I, II**).

Paper 1

5	3			7				
6			1	9	5			
	9	8					6	
8				6				3
4			8		3			1
7				2				6
	6					2	8	
			4	1	9			5
				8			7	9

Spatial variability of POPs in European background air

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Received: 20 July 2010 – Published in Atmos. Chem. Phys. Discuss.: 1 October 2010

Revised: 7 January 2011 – Accepted: 4 February 2011 – Published: 17 February 2011

Abstract. Passive air samplers (PAS) were deployed at 86 European background sites during summer 2006 in order (i) to gain further insight into spatial patterns of persistent organic pollutants (POPs) in European background air and, (ii) to evaluate PAS as an alternative sampling technique under EMEP (Co-operative programme for monitoring and evaluation of the long-range transmissions of air pollutants in Europe). The samples were analyzed for selected PCBs, HCHs, DDTs, HCB, PAHs and chlordanes, and air concentrations were calculated on the basis of losses of performance reference compounds. Air concentrations of PCBs were generally lowest in more remote areas of northern Europe with elevated levels in more densely populated areas. γ -HCH was found at elevated levels in more central parts of Europe, whereas α -HCH, β -HCH and DDTs showed higher concentrations in the south-eastern part. There was no clear spatial pattern in the concentrations for PAHs, indicative of influence by local sources, rather than long range atmospheric transport (LRAT). HCB was evenly distributed across Europe, while the concentrations of chlordanes were typically low or non-detectable. A comparison of results obtained on the basis of PAS and active air sampling (AAS) illustrated that co-ordinated PAS campaigns have the potential serve as useful inter-comparison exercises within and across existing monitoring networks. The results also highlighted limitations of the current EMEP measurement network with respect to spatial coverage. We finally adopted an existing Lagrangian transport model (FLEXPART) as recently modified to incorporate key processes relevant for POPs to evaluate potential source regions affecting observed concentrations at selected

sites. Using PCB-28 as an example, the model predicted concentrations which agreed within a factor of 3 with PAS measurements for all except 1 out of the 17 sites selected for this analysis.

1 Introduction

Persistent organic pollutants (POPs) constitute a group of organic chemicals that are semi-volatile, bio-accumulative, persistent and toxic (e.g. Vallack et al., 1998). A key feature of these chemicals is their intrinsic potential for long range atmospheric transport (LRAT). Two international agreements have come into effect in order to protect human health and the environment from these substances. These are the global Stockholm Convention on POPs (UNEP, 2003) and the regional 1998 Aarhus Protocol on Persistent Organic Pollutants under the 1979 Geneva Convention on Long-range Transboundary Air Pollution (CLRTAP). The latter Protocol entered into force in 2003, and its ultimate goal is to eliminate any discharges, emissions and losses of POPs to the environment. The Aarhus Protocol initially focuses on 16 substances which include eleven pesticides, two industrial chemicals and three by-products/contaminants (UNECE, 1998).

Within EMEP (Co-operative programme for monitoring and evaluation of the long-range transmissions of air pollutants in Europe) the current measurement programme for POPs in air is based on a limited network of conventional active air samplers (AAS) at background sites, mainly located in the north-western part of Europe (Aas and Breivik, 2009) (Fig. S1 in Supplement). The high costs associated with AAS have in part motivated the development of passive air samplers (PAS). These samplers, which have become



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increasingly popular over the last decade, have the potential to be used as a complimentary technique to conventional AAS (e.g. Shoeib and Harner, 2002b; Jaward et al., 2004a; Pozo et al., 2004; Harner et al., 2006b). Of key relevance to this study are the first European campaign using PAS (Jaward et al., 2004a, b) and the Global Atmospheric Passive Sampling (GAPS) studies (e.g. Pozo et al., 2009) which have measured POPs at both urban and rural sites on a European and global scale, respectively.

An important objective of this study has been to improve the knowledge of spatial patterns of POPs in background air across Europe using PAS. Altogether 92 samplers were deployed for ~3 months at 86 sites in 34 European countries during the late summer of 2006. Unlike the former European-wide survey carried out in 2002 (Jaward et al. 2004a,b), our main focus is on the occurrence of POPs across Europe in the context of LRAT. This study therefore targets background sites only. As PAS were mainly located at established EMEP sites which additionally monitor POPs using AAS on a regular basis, this study offered a unique opportunity to investigate similarities and differences in levels and patterns on the basis of complementary air measurements.

The results of these investigations are also used to discuss limitations of the current EMEP measurement network with respect to spatial coverage. These results may also be used to evaluate LRAT models, both within EMEP (e.g. Malanichev et al., 2004) and beyond. As an illustration, we have also included an assessment of differences in predicted source-receptor relationships at selected sites as exemplified for PCB-28, using an existing model (Eckhardt et al., 2009).

2 Materials and methods

2.1 Theory

Polyurethane foam (PUF) disks have gained increasing use as PAS (Shoeib and Harner, 2002b; Harner et al., 2004, 2006b; Jaward et al., 2004a; Pozo et al., 2004, 2006; Motelay-Massei et al., 2005). These PUF disks have high affinity and capacity to sorb organic chemicals. Accumulation of a chemical during exposure is equivalent to the rate of uptake minus rate of loss. Uptake of POPs is airside controlled and is initially linear and a function of the mass transfer coefficient (k_A), the planar area of the sampling media (A_{PSM}) and concentration of the compound in air (C_A). Ideally, these are the functioning conditions to the sampler out in the field, but as the chemical builds up in the sampling medium, the rate of uptake will be reduced and finally reach equilibrium (Shoeib and Harner, 2002b). The duration of the linear phase is dependent on the octanol-air partition coefficient (K_{OA}), and chemicals with low K_{OA} will reach equilibrium with the atmosphere faster than chemicals with higher K_{OA} (Harner et al., 2004). Uptake is also found to increase at

elevated wind speeds, as this causes an increase in the mass transfer coefficient (k_A) (Tuduri et al., 2006).

The PUF disk sampler typically contains a PUF foam disk placed between two stainless steel metal domes in a so called “flying saucer” design (Wilford et al., 2004). This design aims to protect the foam disk from precipitation, sunlight, wind speed effects and coarse particle deposition. Air flows through a gap between the two domes (Pozo et al., 2004). Different passive sampler housings have been tested, and a relatively recent study (Tuduri et al., 2006), shows that the “flying saucer” design dampens the wind speed effect adequately. The specific housing design used in this study with metal tubes inside the sampler, offers the additional advantage that the width of the gap between the two domes is kept identical from site to site.

The PUF disks were spiked with depuration compounds (Performance Reference Compounds – PRCs) of different volatility prior to exposure (Huckins et al., 2002), which were either isotopically labelled or other non-native compounds. The loss rate of PRCs experienced during deployment are in turn used to back-calculate air concentrations in the PAS (e.g. Tuduri et al., 2006).

2.2 Deployment and sample preparation

Samplers were exposed in the field for about 3 months in various European countries in a coordinated campaign during late summer 2006. The study region included 34 countries and 86 sites, located from Spitsbergen (78° N) in the north to Cyprus (33° N) in the south, and from Greenland (38° W) in the west to Kazakhstan (75° E) in the east (see Table S1). Most of the sites included in this study ($N=71$) are part of the EMEP measurement network (see e.g. Aas and Breivik, 2008) although additional remote sites ($N=15$) were included to improve spatial coverage in certain regions. PAS were additionally co-deployed with AAS at EMEP sites (Fig. S1) where POPs are monitored under EMEP on a routine basis to evaluate possible differences in results, along with duplicated PAS samplers and field blanks.

2.3 Analysis

In the following section, only a brief overview of the sample treatment and analysis will be given. More detailed information of the sample preparation, including pre-cleaning and clean-up of the PUF disks and analysis is presented in the Supplement.

The PUF disks were pre-cleaned by soxhlet extraction, dried and spiked with PRCs prior deployment, and returned to the laboratory for clean-up and analysis after end of deployment (~3 months) (Supplement S1.1). A mixture of internal standards was added to the PUFs before Soxhlet extraction and further clean-up. The clean-up procedure involves separation into two extracts, with acid treatment and silica fractionation for analysis of the

persistent compounds, and silica fractionation for the PAH extract (Supplement S1.2). The extracts were further concentrated by a gentle stream of nitrogen to $\sim 50\ \mu\text{L}$ and added recovery standards (Supplement S1.3). Identification and quantification of individual substances was carried out using a gas chromatograph coupled to a high resolution (PCBs, HCHs, HCB, DDTs) and low resolution (PAHs, chlordanes) mass spectrometer, with gas chromatograph conditions as explained in Supplement (Table S3, Supplement S1.3).

2.4 Deriving concentrations in air/effective air sample volume

In order to back-calculate the actual air concentrations for individual compounds in air, information on the PUF characteristics, air temperature, measured loss of individual PRCs and their temperature dependent K_{OA} -values were used in an initial step to calculate site-specific sampling rates (e.g. Shoeib and Harner, 2002b; Pozo et al., 2004, 2009). The average air temperatures at each site for the exposure period are based on meteorological data from European Centre for Medium-Range Weather Forecasts (ECMWF) to ensure a consistent approach. Here, at 2 meter above ground level, the temperature was averaged every 3 hour over the period for which the respective sample was taken. The altitude for each site (Table S1) was next compared against the model altitude. For five high altitude sites where large differences were noted (Jungfraujoch, Moussala, Zavizan, Chopok and Longobucco), the ECMWF data were adjusted by assuming a temperature decrease by altitude of $-0.65\ ^\circ\text{C}$ per 100 m. Loss of PRCs from individual samples was estimated on the basis of the ratio between the amount of PRCs in individual samples and the average amount of PRCs in the field blanks. For PCBs (23, 30, 32, 107, 198), temperature dependent K_{OA} -values were derived on the basis of data reported by Harner and Bidleman (1996) and relative retention times from Harju et al. (1998). For PCB-12 and -14, we used data from Li et al. (2003), and for D6 γ -HCH, information presented by Shoeib and Harner (2002a). Only PRCs which experienced a loss of 40% or more were used to calculate an average site-specific sampling rate (Pozo et al., 2009). The resulting sampling rates and number of PRCs used in these calculations are presented in Table S1. These sampling rates were then used to convert measured values into air concentration by dividing the amounts in the sampler by the effective air volumes as detailed by Shoeib and Harner (2002b). For a few sites experiencing insufficient loss of the PRCs (Nuuk, Summit, Spitsbergen, Sniezka), the default sampling rate proposed by Harner et al. (2006c) was used to estimate effective air volumes for individual substances. The resulting air concentrations for these sites should therefore be interpreted with caution.

2.5 Model

Simulations of atmospheric POP transport were made using the Lagrangian particle dispersion model FLEXPART (Stohl et al., 1998, 2005; Stohl and Thomson, 1999). FLEXPART was driven with analyses from the European Centre for Medium-Range Weather Forecasts (ECMWF, 1995) with $1^\circ \times 1^\circ$ resolution (derived from T319 spectral truncation). Analyses at 00:00, 06:00, 12:00 and 18:00 UTC, and 3-h forecasts at 03:00, 09:00, 15:00 and 21:00 UTC were used. There are 23 ECMWF model levels below 3000 m, and 91 in total. FLEXPART calculates the trajectories of so-called tracer particles and accounts for turbulence, convection, deposition (wet and dry) and atmospheric reaction by hydroxyl (OH) radicals (Eckhardt et al., 2009). It was run in backward mode, in order to identify the source regions of air pollutants at a particular site (Stohl et al., 2003; Seibert and Frank, 2004). These were found by following all 4 million particles equally released over the sample duration, 20 days backward in time. These source regions are expressed as emission sensitivities (ES) in the footprint layer (0–100 m above ground) during each deployment period at different sites. The ES unit is nanoseconds per cubic meter, which is the residence time of air masses normalized by the volume. The ES maps for the footprint layer thus illustrates where the air mass had the ability to collect pollutants from sources near the ground. Multiplying this ES with emission fluxes from the PCB-28 emission inventory (Breivik et al., 2007) yields the geographical distribution of sources contributing to the simulated concentration at the given measurement site. Emission contributions (EC), which gives the simulated air concentration at the receptor, may then be obtained by areal integration. For further details we refer to the original publications listed above.

3 Quality Assurance/Quality Control (QA/QC)

The analytical procedures were monitored using NS/EN ISO/IEC 17025 accredited routines for quality assurance and quality control. A calibration solution was injected after every fourth sample, and was used to quantify the samples. Regarding PCBs, HCHs, DDTs, HCB and the chlordanes, a standard reference material (SRM 1588) from the National Institute of Standards and Technology (NIST) containing organic compounds in cod liver oil was analyzed routinely. In addition, for the quantification control, the retention for ^{12}C -labeled compound should not be more than 3 seconds later than its corresponding ^{13}C -labeled isomer. Furthermore the isotope ratio based on a 3:1 relationship between ^{12}C and ^{13}C , for the two monitored masses, must be within $\pm 20\%$ of the theoretical value. For the PAHs, the SRM solution, SRM 1491 (NIST) was analyzed during each run.

Table 1. Concentrations of selected PCBs, HCHs, DDTs, chlordanes and HCB (pg m^{-3}) and selected PAHs (ng m^{-3}) at European background sites.

Compounds	Average \pm S.D	Median	Measured range		MDL	% above MDL	Max/min ratio (MMR)
			Deployed samples	Blanks			
PCB-28	5 ± 4	4	0.6–20	0.06–0.3	0.4	100	34
PCB-52	5 ± 4	4	0.8–20	0.05–0.3	0.3	100	25
PCB-101	4 ± 5	3	0.4–34	0.03–0.3	0.3	100	84
PCB-118	1.5 ± 1.5	1.0	0.2 ^a –8.3	0.001 ^b –0.2	0.2	95	> 55
PCB-138	2.0 ± 2.4	1.2	0.2 ^a –18.3	0.001 ^b –0.2	0.2	95	> 102
PCB-153	3 ± 4	2	0.3 ^a –28	0.004 ^b –0.3	0.3	94	> 87
PCB-180	0.8 ± 0.9	0.6	0.05 ^a –6	0.001–0.04	0.05	98	> 122
Σ_7 PCBs	21 ± 19	17	2–121				> 55
α -HCH	26 ± 24	21	5–156	0.1–0.8	1	100	33
β -HCH	2 ± 7	1	0.13 ^a –49	0.01–0.2	0.13	85	> 380
γ -HCH	35 ± 38	19	1.8–170	0.1–1.3	1.3	100	94
Σ_3 HCHs	64 ± 59	46	9–311				> 36
<i>p, p'</i> -DDE	21 ± 47	6	1.6 ^a –281	0.06–2	1.6	74	> 177
<i>p, p'</i> -DDD	0.5 ± 1.1	0.2	0.06 ^a –10	0.004 ^b –0.07	0.06	79	> 169
<i>o, p'</i> -DDT	4 ± 7	2	0.3 ^a –39	0.001 ^b –0.3 ^d	0.3	87	> 143
<i>p, p'</i> -DDT	6 ± 9	2	0.2 ^a –46	0.001 ^b –0.2	0.2	86	> 240
Σ_4 DDTs	32 ± 62	10	1.1–356				> 312
Fluorene	1.7 ± 1.8	1.0	0.1 ^a –9.7	0.01 ^b –0.1	0.1	98	> 83
Phenanthrene	3 ± 3	2	0.1 ^a –20	0.01 ^b –0.1	0.1	95	> 147
Anthracene	0.07 ± 0.1	0.03	0.007 ^a –0.9	0.007 ^c	0.007	88	> 130
Fluoranthene	0.7 ± 0.8	0.4	0.03 ^a –3.5	0.01 ^b –0.03	0.03	95	> 117
Pyrene	0.4 ± 0.4	0.2	0.02 ^a –2.4	0.01 ^b –0.02	0.02	99	> 153
Benz[a]anthracene	0.02 ± 0.03	0.01	0.004 ^a –0.2	0.005 ^c	0.004	68	> 49
Chrysene	0.07 ± 0.07	0.03	0.004 ^a –0.3	0.004 ^c	0.004	95	> 58
Benzo[a]pyrene	0.008 ± 0.01	0.002	0.004 ^a –0.06	0.004 ^c	0.004	43	> 15
Σ_8 PAHs	6 ± 6	4	0.2–35				> 205
HCB	49 ± 18	45	23–115	0.2–3	3	100	5
trans-chlordane	0.8 ± 1.1	0.4	0.07 ^a –7.3	0.003 ^e –0.1	0.07	95	> 104
cis-chlordane	1.2 ± 0.7	1.2	0.1 ^a –4.6	0.006 ^e –0.1	0.1	98	> 46
trans-nonachlor	1.3 ± 1.0	1.2	0.1 ^a –7.0	0.002 ^e –0.08	0.1	98	> 77
cis-nonachlor	0.16 ± 0.1	0.15	0.05 ^a –0.5	0.001 ^e –0.04	0.05	87	> 11
Σ_4 chlordanes	3.5 ± 2.7	3.2	0.2–19.4				> 114

^a MDL (method detection limit) ^b The lower limit is 1/2 of the IDL (instrument detection limit) ^c The component were not detected in the blanks ^d Interference in one of the blanks
^e Lower and upper concentrations in the blanks were below IDL

3.1 Method and field blanks values

Method and field blanks consisted of pre-cleaned PUF disks which were extracted and analyzed in the same way as the exposed samples. Method blanks were only stored at NILU, whereas field blanks were brought in field with the deployed samples but not exposed. The field and method blank values were converted into an air concentration by using the average sampling rate ($4.9 \text{ m}^3 \text{ day}^{-1}$), temperature (14°C) and exposure time (94 days). The method and field blank values had similar values.

3.2 Method detection limit (MDL)

The method detection limit (MDL) was calculated as the average of the field and method blank concentrations ($N=18$) plus 3 times the standard deviations (SD) (Table 1). When the target compound was not detected in the blanks (method blank and field blank), an instrumental detection limit (IDL) value derived from signal/noise values 3:1 divided by two, was used to derive a MDL (Pozo et al., 2009). This was not the case for the PAHs, where the lowest measured ranges for air samples for the instrument were $0.01\text{--}0.02 \text{ ng m}^{-3}$.

For the components studied here (fluorene – benzo(a)pyrene) only 0.01 ng m^{-3} was used. For values that fell below this limit, half of this measured value was used. Furthermore, when the target compound in the exposed samples fell below the calculated method detection limit (MDL), half of the MDL from the field and method blanks was used for statistical treatment (Pozo et al., 2009). Table 1 provides more information regarding the blanks.

3.3 Recoveries

Two types of recoveries were compiled, namely recovery of the internal standards and of the PRCs. Quantification of the analytes is based on the added ^{13}C or ^{2}D -labeled internal standards and therefore the results must not be corrected for low recoveries. Recovery rates are listed and discussed in the Supplement (S1.4, S1.5 and Table S2).

The concentrations were not blank corrected due to both low and not stable concentrations in the blanks, whereas they were automatically corrected for the recoveries.

3.4 Uncertainties in the chemical analysis

Different factors influence the uncertainty in the chemical analysis: loss during sample extraction and clean-up, accuracy of the standard concentrations, instrumental parameters, in addition to interferences from other compounds and possible sample contamination. To compensate for possible loss of analytes due to sample clean-up, internal standards were used in combination with a recovery standard. Field blanks were used to evaluate possible contamination during transport, and the method blanks to evaluate the laboratory conditions (e.g. solvents, adsorbents) respectively. Different approaches were applied to quantify these uncertainties, i.e. performance of intra laboratory/inter laboratory experiments and a critical step-by-step evaluation of all analytical steps. Both approaches result in a similar estimate for the uncertainty of the chemical analysis in the range of 20–35%, but will vary for different compounds/groups.

3.5 Uncertainties in back-calculated PAS air concentrations

The PAS results are converted into air concentrations, rather than presented as sequestered amount per sampler, as this is essential to facilitate a direct comparison with both AAS results (4.2.1) and model outputs (4.4). The use of back-calculated air concentrations introduces additional uncertainties which are likely to exceed those that are associated with the chemical analysis alone (3.4). Past evaluations have suggested that the PAS method enables estimates of “true” air concentrations within a factor of 2–3 (Gouin et al., 2005a; Harner et al., 2006a; Klanova et al., 2008). Errors in estimated air concentrations reflect in part uncertainties in input parameters used to calculate uptake rates (e.g. Shoeib and Harner, 2002a), such as octanol-air partition coefficients and

their temperature dependencies (e.g. Li et al., 2003), the use of modeled rather than measured chamber air temperatures (Kennedy et al., 2010), and in the selection/loss of PRCs (e.g. Bartkow et al., 2006a; Moeckel et al., 2009). Furthermore, there are uncertainties associated with sampling performance under variable environmental conditions, such as elevated wind speeds (Tuduri et al., 2006; Chaemfa et al., 2009b), sun-light intensity (Bartkow et al., 2006b), humidity (Santiago and Cayetano, 2007), temperatures (Klanova et al., 2008) and potential artifacts caused by inadvertent particle-phase sampling of POPs (e.g. Klanova et al., 2008; Chaemfa et al., 2009b). To further characterize uncertainties associated with uptake rates, a range of different field studies have previously been carried out whereby results obtained on the basis of AAS and PAS have been compared and contrasted (e.g. Gouin et al., 2005a, 2008; Klanova et al., 2008; Chaemfa et al., 2008, 2009a; Moeckel et al., 2009; Hayward et al., 2010). We refer to these studies for a more detailed account of uncertainties in uptake rates.

4 Results and discussion

4.1 Overall results

Table 1 shows the calculated air concentrations (average, median, range) of selected POPs at European background sites ($N=86$), while data for individual sites are included in the Supplement. PCBs 28, 52, 101, α - and γ -HCH and HCB were detected in all samples, while some samples were below the method detection limit (MDL) for all other compounds. The spatial variability in the overall results is initially evaluated by the ratio between maximum and minimum air concentrations (MMR). For samples with concentrations below the MDL, the minimum concentration was replaced by the MDL when calculating the MMR and set to 1/2 MDL for the calculation of average, and median air concentrations in Table 1.

PCBs

The average concentration of $\Sigma_7\text{PCBs}$ was 21 pg m^{-3} ($\text{SD} \pm 19 \text{ pg m}^{-3}$). The most abundant PCBs were PCB-52, –28, –101 and –153 which contributed 23%, 22%, 20% and 15% to the average concentration of $\Sigma_7\text{PCBs}$, respectively. $\Sigma_7\text{PCBs}$ has a MMR of more than 55 which shows that there is still a marked spatial variability, even across European background sites. This may be interpreted as a continuing influence of primary emissions on atmospheric levels. Alternatively, it cannot be excluded that some of the sites have been influenced by the presence of one or more local emission sources. The range is anyhow smaller than previously reported for $\Sigma_{29}\text{PCBs}$ in a similar study across Europe in 2002 (Jaward et al., 2004a). The former study reported a variability of more than 2 orders of magnitude between the

highest and lowest samples, but included a combination of both urban areas as well as remote background sites. MMR furthermore tended to increase with increasing chlorination (Table 1), suggesting lighter PCBs to be more evenly distributed in European background air in comparison to their heavier counterparts. This may in part be seen as a reflection of a more limited long-range atmospheric transport potential of heavier PCBs, causing larger variability in air concentrations (and thus MMR) for these substances (Wania and Daly, 2002).

HCHs

The average concentration of Σ_3 HCHs (α , β , γ) was 64 pg m^{-3} ($\text{SD} \pm 59 \text{ pg m}^{-3}$). The concentration of Σ_3 HCHs varied from $9\text{--}311 \text{ pg m}^{-3}$, with γ -HCH and α -HCH contributing on average 55% and 41%, respectively. β -HCH, which was close to MDL in some samples (Table 1), was less abundant and contributed only 4% on average. The median concentrations of γ -HCH and α -HCH were similar, although the average concentration for γ -HCH (35 pg m^{-3}) was higher than for α -HCH (26 pg m^{-3}). This illustrates a more homogenous distribution of α -HCH in European background air in comparison to γ -HCH, as also illustrated by the MMR for these two HCH isomers (Table 1). γ -HCH is less volatile than α -HCH (Xiao et al., 2004), which in turn may help to explain observed differences in air concentrations and environmental fates between the two isomers (Breivik and Wania, 2002). The results for β -HCH should be interpreted with caution as several samples ($N=13$) were below MDL (Table 1). However, the large spatial variability for this isomer ($\text{MMR} > 380$) suggests a highly skewed distribution. This is noteworthy and may in part be attributed to the fact that β -HCH is much more water-soluble than the other two isomers and hence more easily subject to wash-out by rain in spite of a similar emission history to α -HCH (Li et al., 2002).

DDTs

The average concentration of Σ_4 DDTs was 32 pg m^{-3} ($\text{SD} \pm 62 \text{ pg m}^{-3}$), and ranged from 1.1 pg m^{-3} to 356 pg m^{-3} with p,p' -DDE as the major contributing isomer (67% on average). The second most prominent isomer was p,p' -DDT with an average contribution of 18%. MMRs were all high within the group of DDTs and ranged from >143 (o,p' -DDT) to >240 (p,p' -DDT).

PAHs

The average concentration of Σ_8 PAHs was 6 ng m^{-3} ($\text{SD} \pm 6 \text{ ng m}^{-3}$) and ranged from $0.2\text{--}35 \text{ ng m}^{-3}$. The more abundant PAHs include phenanthrene and fluorene

which each contributed on average 49% and 29%, respectively. As expected, the contribution from heavier PAHs, such as benz(a)anthracene, chrysene and benzo(a)pyrene, was typically low with average contributions of 0.35%, 1.2% and 0.14% to Σ_8 PAHs, respectively. This is also consistent with earlier studies (e.g. Halsall et al., 1994; Lohmann et al., 2000). MMR furthermore ranged from >15 (benzo(a)pyrene) to >153 (pyrene). The results for Σ_8 PAHs compares favourably with similar results from the previous European campaign by Jaward et al. (2004b), which reported a measured range between 0.004 and 26 ng m^{-3} for the same PAHs and also noted that lighter PAHs tended to dominate in the samples since they occur in the gas-phase and hence have higher ability for transport, while heavier PAHs (benzo(a)pyrene) are more related to the particle phase (Lohmann et al., 2000).

HCB

HCB was detected in all samples with an average concentration of 49 pg m^{-3} ($\text{SD} \pm 18 \text{ pg m}^{-3}$; range: $23\text{--}115 \text{ pg m}^{-3}$). The variability was limited with a MMR of 5, very similar to what has been previously reported for Europe (Jaward et al., 2004a). This has been interpreted as evidence of the long atmospheric lifetime of this volatile compound, combined with the absence of significant point sources of HCB in Europe (Jaward et al., 2004a). However, similar studies in Asia have reported larger variability, indicative of continuing emissions (Jaward et al., 2005). We also note that the range in air concentrations reported here ($23\text{--}115 \text{ pg m}^{-3}$) are higher than previously reported for Europe ($11\text{--}50 \text{ pg m}^{-3}$) by Jaward et al. (2004a). Interestingly, a recent study on levels and trends of POPs in Arctic air suggest an increase in HCB in recent years, and attribute this to a potential increase in worldwide usage of certain pesticides contaminated with HCB (Hung et al., 2010).

Chlordanes

The average concentration for the Σ_4 chlordanes was 3.5 pg m^{-3} ($\text{SD} \pm 2.7 \text{ pg m}^{-3}$). The concentrations varied from 0.2 pg m^{-3} to 19.4 pg m^{-3} , with trans-nonachlor and cis-chlordane contributing 38% and 35%, respectively. The least abundant compound was cis-nonachlor with 5%. Concentrations of individual chlordanes were typically low in comparison to the other substances studied and MMR ranged from >11 (cis-nonachlor) to >104 (trans-chlordane).

4.2 Duplicate passive air sampling and comparison with active air sampling

Two passive air samplers were co-deployed close to each other at each EMEP-site where POPs are monitored on a regular basis using conventional AAS techniques

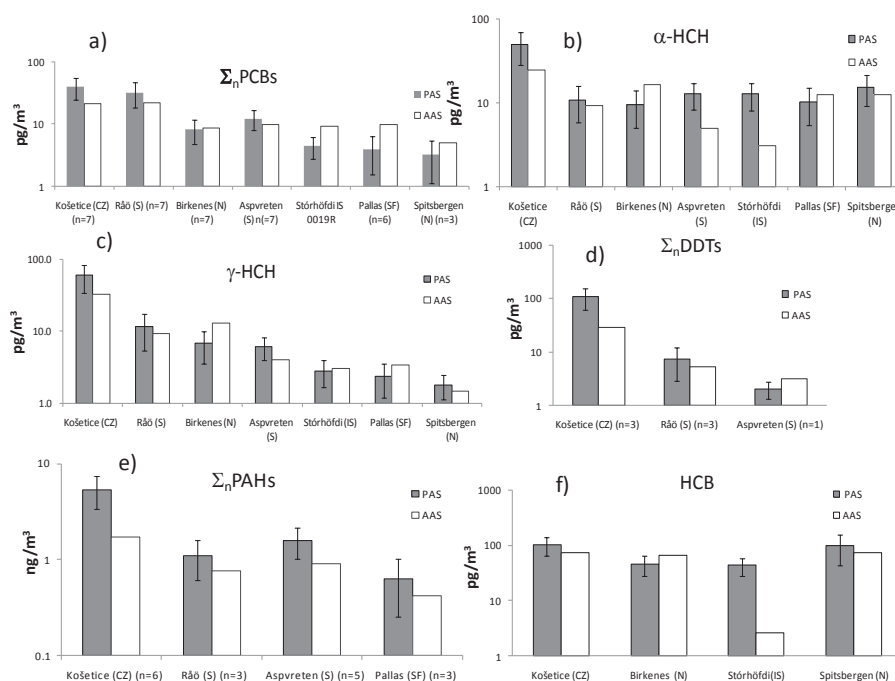


Fig. 1. (a)–(f): Comparison of results obtained on the basis of PAS (average of two parallels) and AAS (see text for details).

(Košetice, Pallas, Stórhöfði, Birkenes, Spitsbergen, Råö, Aspvreten) (Aas and Breivik, 2008), see also Fig. S1. This was done to gain further insights into the reproducibility of the PAS method (e.g. Harner et al., 2006b) as further discussed in the Supplement (Supplement S1.6), and to evaluate possible differences between PAS and AAS results (e.g. Gouin et al., 2005a, b; Mari et al., 2008). Regrettably, one of the samplers from the Aspvreten site was lost. The comparison for this EMEP AAS site is thus restricted to one PAS sample only.

4.2.1 Passive air sampling in comparison with active air samplers

One of the objectives of this study has been to further assess the potential of PAS as a complementary technique to conventional AAS within the EMEP monitoring program. For this purpose direct comparisons of results obtained on the basis of AAS and PAS have been carried out. Although such comparisons have been reported previously (Gouin et al., 2005a; Mari et al., 2008), past evaluations of this kind have typically been carried out on the basis of results obtained at the same chemical laboratory. In this work, AAS results are mainly obtained on the basis of results originating from different chemical laboratories, hence both intra and inter laboratory uncertainties must be taken into account. Exceptions to this are the samples from the two Norwegian sites (Birkenes and Spitsbergen) which were both analyzed at the NILU laboratories. We should further note that the AAS monitoring strategies within EMEP vary in terms of both sampling durations and frequencies and hence temporal cov-

erage (Table S5). Only Stórhöfði and Råö collect samples on a continuous basis, while Košetice, Birkenes, Aspvreten, Pallas and Spitsbergen have sampling coverage of less than 30% (Table S5). A direct comparison between AAS and PAS for the latter five EMEP sites is therefore difficult as the different samplers have been exposed to different air masses. AAS and PAS sampling strategies are also fundamentally different as data obtained on the basis of AAS typically represent the sum of the particulate and gaseous air concentrations. Finally, we note again that all results for Spitsbergen obtained on the basis of PAS in this study may be questioned as they rely on the default uptake rate (2.4).

Concentrations from the AAS were averaged over the same sampling period (or as close as possible) as for the passive air samplers (i.e. 3 months). The average air concentrations for the two PAS parallels from each EMEP site were used. Figure 1a–f illustrates the absolute differences between PAS and AAS results. The error bars included in Fig. 1 represent an estimate of the cumulative uncertainty associated with both the chemical analysis ($\pm 35\%$) plus the relative deviations between the two parallels (Table S4). However, the latter source of uncertainty is not captured for Spitsbergen as this site relies on the default sampling rate (Table S1) as well as Aspvreten which is based on one PAS sample only. Thus, whenever significant difference are observed in Fig. 1 (with the exception of the two sites noted), the more plausible explanations may be that these differences are caused by (i) sampling of different air masses, or (ii) analysis of the samples by different laboratories.

Relative deviations for individual substances, expressed as $(C_{\text{PAS}} - C_{\text{AAS}})/C_{\text{AAS}}$, are additionally included in Table S5 whereby a positive deviation illustrates higher concentration in the PAS, relative to the AAS.

PCBs

The percentage deviation relative to AAS results varied from -59% (Pallas) up to $+86\%$ (Košetice) for Σ_n PCBs, where n denotes the number of congeners (see Table S5). Larger relative deviations were observed for some congeners and sites, such as PCBs 101 ($+178\%$), 138 (257%) and 153 (193%) at Košetice. One possible explanation for the large deviations seen at the Košetice site is that the AAS is only operating one day per week (Table S5) and hence the air masses sampled deviate significantly between the AAS and the PAS. This effect may be particularly significant at Košetice as this site is located close to major source regions in Europe (Breivik et al., 2007). Air concentrations at this site may thus be expected to fluctuate significantly over time as the air masses would be expected to be less well-mixed. This issue is further explored for PCB-28 in Sect. 4.4. However, if difference in sampling coverage was the only factor to consider, significant deviations would also be expected at those other sites which do not operate the AAS on a continuous basis (Birkenes, Aspvreten, Pallas and Spitsbergen). The best agreement between AAS and PAS for Σ_n PCBs was obtained for Birkenes (-5%) (Table S5), which may be due to a combination of air concentrations being well above MDL and the fact that the samples being analyzed at the same chemical laboratory. The latter may indeed represent an important factor to consider as it has recently been indicated that differences up to a factor of 2 can be expected for atmospheric samples of semi-volatile organic compounds when comparing results from different laboratories (Su and Hung, 2010). It must be cautioned that this comparison is of limited significance for Spitsbergen and Pallas as some PAS results were close to or below MDL (Table S5). For the latter site, a relatively large difference in the estimated uptake rate between the two PAS parallels was also noted (Supplement S1.6).

HCHs

α - and γ -HCH were reported for all sites (Fig. 1b,c). The percentage deviation relative to AAS for the α - and γ -HCH isomers ranged from -43% (Birkenes) to $+318\%$ (Stórhöfði) and from -48% (Birkenes) to $+85\%$ (Košetice) for these two isomers, respectively (Table S5). With the exception of Birkenes, Pallas and Stórhöfði (latter only for γ -HCH), positive deviations ($C_{\text{PAS}} > C_{\text{AAS}}$) were typically observed for these two isomers. For the α -HCH isomer, minor deviations were seen for Råö ($+19\%$), Spitsbergen ($+23\%$) and Pallas (-17%). Likewise, good agreement for γ -HCH was found for Stórhöfði (-8%), Spitsbergen ($+22\%$) and Råö (24%).

Given that the AAS at Stórhöfði operates on a continuous basis (Table S5) it is difficult to offer an explanation for the large differences seen for α -HCH at but not for γ -HCH at this site. It is interesting to note that there are significant differences for both HCHs at Birkenes in spite of both AAS and PAS being analyzed at the same laboratory. Again, a plausible explanation is that differences between AAS and PAS are caused by differences in sampling coverage as the sampling frequency at Birkenes is only one day per week (Table S5).

DDTs

As several DDTs were either not reported by AAS, or because several results from PAS were found to be below MDL (Table S5, Fig. 1d), a comparison was only possible for Košetice, Råö and Aspvreten. The percentage deviation for Σ_n DDTs varies from -34% (Aspvreten) to $+282\%$ (Košetice).

PAHs

For the same reasons as for the DDTs, the comparison for PAHs had to be carried out for a variable number of compounds (phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)pyrene, benz(a)anthracene) and limited to four stations (Košetice, Råö, Aspvreten and Pallas), see Fig. 1e. The percentage deviations relative to AAS for Σ_n PAHs (Table S5) ranged from $+45\%$ (Råö) to $+216\%$ (Košetice). The relative deviations for the individual PAHs were mostly positive, except pyrene and benz(a)anthracene at Aspvreten, and benzo(a)pyrene at Košetice. The best agreement between the two air sampling techniques was found for Råö and Pallas ($+45\%$ and $+52\%$ for Σ_n PAHs, respectively).

HCB

Results for HCB obtained on the basis of AAS are only available for Košetice, Birkenes, Spitsbergen and Stórhöfði (Fig. 1f). For all these sites, except for the latter, the relative deviation was between $+36\%$ and -31% (Table S5). This is in striking contrast to Stórhöfði for which C_{PAS} exceeded C_{AAS} by as much as $+1540\%$. Hung et al. (2010) recently pointed out that all Arctic monitoring stations showed similar air concentrations after year 2000 with annual average air HCB concentrations between 29 and 76 pg m^{-3} , while Stórhöfði had much lower concentrations (2 to 6.8 pg m^{-3}). As the PAS results for the other sites compare favourably with AAS results, the large discrepancy for HCB at Stórhöfði merits further investigation. This example also illustrates how coordinated PAS campaigns has the potential to serve as an inter-comparison exercise within and across existing monitoring programs, which could complement other relevant efforts, e.g. inter laboratory comparisons.

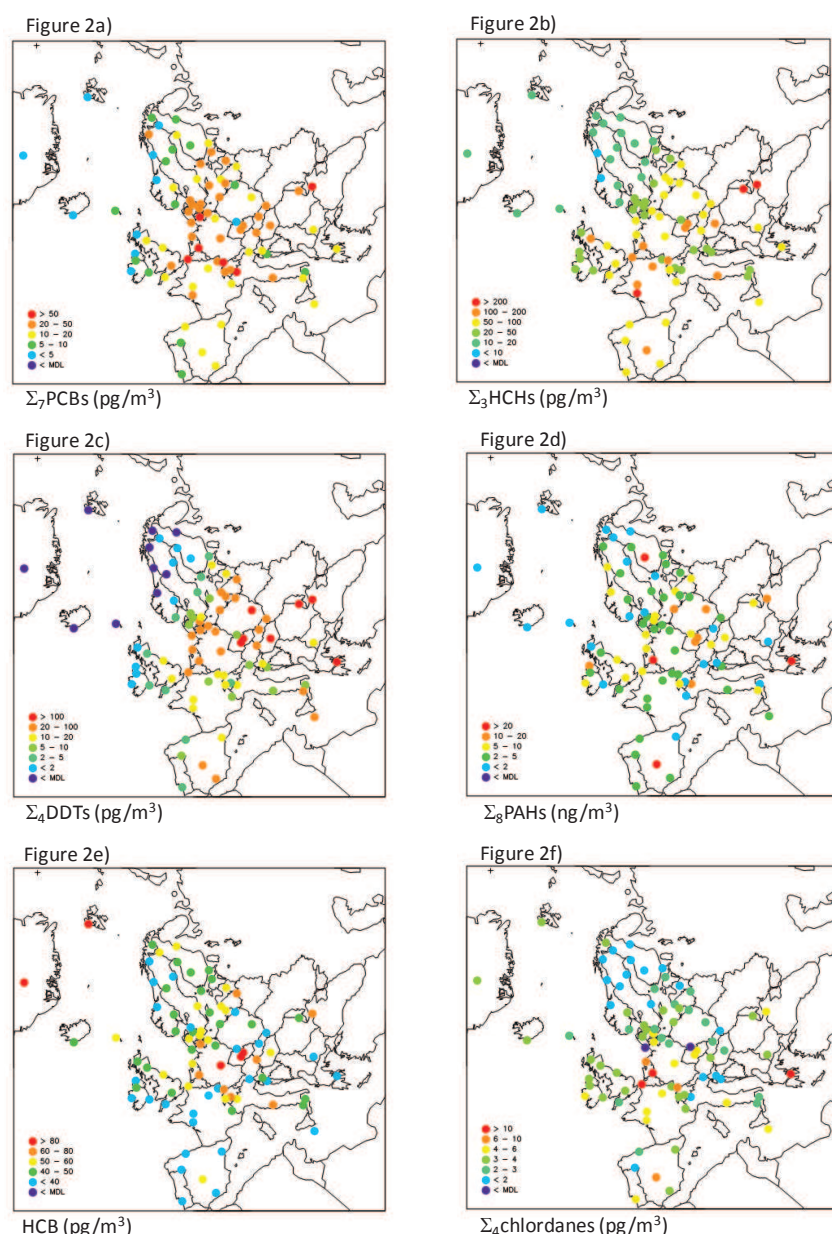


Fig. 2. (a)–(f): Spatial patterns of $\Sigma_7\text{PCBs}$, $\Sigma_3\text{HCHs}$, $\Sigma_4\text{DDTs}$, $\Sigma_8\text{PAHs}$, HCB and $\Sigma_4\text{chlordanes}$ in European background air.

4.3 Spatial patterns

As most EMEP monitoring stations reporting POPs in air are mainly located in the northwestern part of Europe (Aas and Breivik, 2008), an additional objective of this study was to evaluate potential limitations in the current EMEP measurement network with respect to spatial coverage. Improved spatial coverage is not only considered important to support relevant modelling activities within EMEP (e.g. Malanichev et al., 2004) and beyond, but it may also provide useful information for future monitoring strategies within EMEP.

PCBs

Figure 2a shows the results for $\Sigma_7\text{PCBs}$ while Fig. S3a–g presents the spatial patterns of individual PCB congeners across Europe. Similar to past studies, elevated levels of PCBs were typically found in more densely populated areas in central parts of Europe (Jaward et al., 2004a). Lower levels of PCBs tended to occur along the western coast of Scandinavia, the British Isles and to some extent Spain/Portugal, which may be explained by the prevailing wind regimes with transport from west to east. Elevated levels of $\Sigma_7\text{PCBs}$

(>50 pg m⁻³) were detected at sites in Belgium, Germany, Italy, the Netherlands and Ukraine, while the highest concentrations were observed at a site in Denmark (121 pg m⁻³). Whenever significantly elevated levels are measured at a specific site, this may indicate an influence from one or more nearby sources as may be the case with the elevated levels seen at the Danish site.

HCHs

The spatial patterns for Σ_3 HCHs and individual HCHs across Europe are shown in Fig. 2b) and Fig. S4(a–c), respectively. HCHs are insecticides which have been extensively used in Europe (Breivik et al., 1999) and the rest of the world (e.g. Li et al., 1996, 1999). The results for Σ_3 HCHs shows a fairly consistent pattern with low levels (<20 pg m⁻³) at most Scandinavian and Arctic sites. Elevated levels (>200 pg m⁻³) were recorded at certain sites in France, Moldova and Ukraine. HCHs ultimately originate from the production and use of technical HCH (55–80% α -HCH, 2–16% β -HCH, 8–15% γ -HCH) or lindane (>99% γ -HCH) (Breivik et al., 1999). Hence, while the occurrence of γ -HCH may be attributed to either technical HCH or lindane, α - and β -HCH were only major constituents in the technical mixture. In general terms, lindane usage tended to dominate in the western part of Europe, while technical HCH tended to dominate in the eastern part (Breivik et al., 1999). This pattern is also reflected in the results, whereby elevated levels of α - and β -HCH are mainly seen at some sites in the southeastern areas of Europe (Fig. S4a,b). As β -HCH is more easily washed out by rain than α -HCH, elevated atmospheric concentrations of β -HCH may hence be a more useful indicator to identify proximity to regions or areas that are affected by ongoing or past historical usage of technical HCH. Elevated levels of γ -HCH tend to occur across central parts of Europe (Fig. S4c). Given the remoteness from key source areas, relatively high levels of α -HCH are also observed at the sites in Iceland, Greenland and Spitsbergen, which may be seen as a reflection of the elevated long-range atmospheric transport potential of this isomer (Li et al., 2002; Wania and Mackay, 1996; Beyer et al., 2000).

DDTs

The spatial patterns of Σ_4 DDTs and individual DDTs are presented in Fig. 2c and Fig. S5(a–d), respectively. The technical mixture of DDT contains up to 80–85% of the p,p' -DDT isomer and only small amounts of the o,p' -DDT isomer (15–20%) (Motelay-Massei et al., 2005) and was banned in European countries during the 1970s and 1980s (Pacyna et al., 2003). Levels of Σ_4 DDTs were generally low and frequently below the MDL in Northern Europe but with increasing air concentrations towards Central and Eastern Europe (Fig. 2c). Concentrations of

Σ_4 DDTs above 100 pg m⁻³ occurred at sites in the Czech Republic, Greece, Hungary, Moldova, Poland and Ukraine (Fig. 2c). The spatial pattern for individual isomers (Fig. S5) generally reflected that of Σ_4 DDTs, although absolute air concentrations varied. A p,p' -DDE/ p,p' -DDT ratio lower than 1 has been proposed as an indication of fresh use of technical DDT (Pozo et al., 2006). This ratio is shown in Fig. S5e). Jaward (2004a) previously noted low p,p' -DDE/ p,p' -DDT ratios in European air, which suggest a fresh p,p' -DDT signal. This is in contrast to our results four years later, which indicates a more weathered signal with an average ratio of 3.8 (range 0.9–8.5) (Fig. S5e). A ratio higher than 1 is also in better accordance with observations based on AAS from various EMEP sites (Košetice, Pallas, Stórhöfði, Spitsbergen and Råö) which show a mean value for this ratio in the range between 1.3 and 10.9 during 2006 (Aas and Breivik, 2008). The ratio o,p' -DDT/ p,p' -DDT (Fig. S5f) has previously been used to evaluate possible influence from dicofol, a miticide which contains 10% of the o,p' -DDT isomer (Becker, 2008; Gillespie et al., 1994; Qiu et al., 2005). Several countries in Europe (e.g. Italy, United Kingdom, Spain and Turkey) utilize dicofol in agriculture (Gillespie et al., 1994; Turgut et al., 2009). This study confirms several sites which had higher values for the o,p' -DDT isomer in comparison to the p,p' -DDT isomer. The average ratio (\pm SD) was 0.86 ± 0.26 and spanned from 0.3–1.6 which may suggest some influence from dicofol at certain sites. A ratio higher than 1 was found at sites in Austria, Denmark, Finland, France, Ireland, Italy, Kazakhstan, Lithuania, Moldova, the Netherlands, Norway, Poland, Sweden and United Kingdom (Fig. S5f).

PAHs

Figure 2d shows the spatial pattern for Σ_8 PAHs across Europe (see also Fig. S6). PAHs are by-products from incomplete combustion processes with many different sources (Lohmann et al., 2000). No clear trend in spatial patterns could be found, and it seems likely that the sites which are experiencing elevated concentrations are mainly affected by local sources. Hence, many of the sites included may not be considered true background sites with respect to PAHs. Elevated concentrations of Σ_8 PAHs (>20 ng m⁻³) were observed at sites in Finland, Greece, the Netherlands and Spain (Fig. 2d).

HCB

The spatial pattern for HCB is presented in Fig. 2e. HCB is highly volatile, persistent in air and expected to be extensively re-emitted from secondary sources like soil and vegetation (Bailey, 2001; Barber et al., 2005). As previously recognized in this study (Table 1) and elsewhere (Jaward et

al., 2004a) concentrations are relatively uniform across Europe. Elevated air concentrations ($>100 \text{ pg m}^{-3}$) occurred at four sites, two of which are found at high elevation (Summit, Spitsbergen). Yet, as the uptake rate for these two sites rely on the default value, we suspect air concentrations may have been overestimated as the true uptake rates at these exposed sites may have been underestimated due to wind speed effects (Tuduri et al., 2006).

Chlordanes

The spatial pattern for Σ_4 chlordanes is presented in Fig. 2f), and for individual compounds in Fig. S7. The technical mixture of chlordane consists mainly of trans-chlordane, cis-chlordane and trans-nonachlor (Sovocool et al., 1977; Dearth and Hites, 1990). Chlordane were formerly used in agriculture as an insecticide and termiticide up to the mid 1980s (Bidleman et al., 2002). The levels of the individual chlordanes were typically low and several sites were below MDL. The predominating compounds were trans-chlordane and trans-nonachlor, while cis-nonachlor were found at lowest levels. Elevated levels of Σ_4 chlordanes ($>10 \text{ pg m}^{-3}$) were found at sites in Belgium, Greece and the Netherlands. The trans-chlordane/cis-chlordane (TC/CC) ratio is 1.56 in the technical chlordane mixture (Bidleman et al., 2002). trans-chlordane is more easily degraded than cis-chlordane in the environment and ratio values for TC/CC close to 1 implies a weathered signal. Consequently elevated ratios may indicate fresh usage of technical chlordane (Pozo et al., 2004). The average ratio ($\pm\text{SD}$) was 0.5 ± 0.4 and spanned from 0.03–2.6. Sites with a ratio >1.56 were found in Moldova (1.57), the Netherlands (1.61, 1.63) and Malta (2.58).

4.4 Model evaluations

The atmospheric transport model FLEXPART was used in a time-reverse mode to identify the source regions responsible for the PCB-28 loading at the respective sampling site in addition the meteorological parameters driving the transport. In contrast to classical trajectory calculations (Gouin et al., 2005a) turbulence, convection and removal processes (dry and wet deposition, reaction with OH) are taken into account. In this manner the source regions for each sample can be identified and an emission sensitivity (ES) map can be derived. Combining this information with the PCB-28 emission inventory (Breivik et al., 2007) a concentration for each receptor can be predicted, resulting in a emission contribution (EC) map. We selected PCB-28 to illustrate the model approach as (a) unlike several compounds included in this study, PCB-28 exists solely in the gaseous state in the atmosphere, and (b) a spatially resolved emission inventory is available which is essential as model input. The model was run for 17 of the sites included in this study, including all

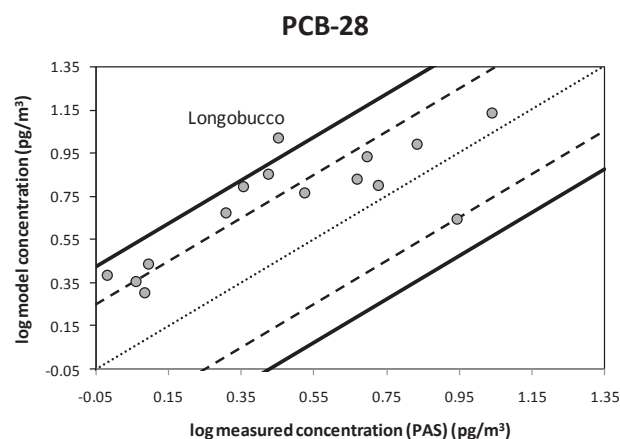


Fig. 3. Modelled versus observed (PAS) air concentrations for PCB-28 at selected sites. The dashed and solid lines represent agreement within a factor of 2 and 3, respectively.

EMEP AAS to also facilitate a comparison between model and measurements derived using on the basis of both AAS and PAS. Table S6 presents the sites along with predicted and observed concentrations, including percentage deviation between model and PAS measurement results, while Fig. 3 shows the modelled versus observed air concentrations, both expressed on a logarithmic basis. The agreement between PAS and model results were found to be within a factor of 3 for 16 out of 17 sites (solid black lines), with most results within a factor of 2 (dashed lines). It is possible that the overestimation of the model is caused by too high emissions in the inventory. The overall results also show that the model predicted values in comparison to AAS results which were ~ 2 –3 times higher at four out of seven sites (Košetice, Birkenes, Råö, Aspvreten) and ~ 2 –12 times lower for the other sites (Pallas, Stórhöfði, Spitsbergen) (Table S6).

The results for PCB-28 also allow us to explore whether it is likely that the air masses sampled by PAS and AAS differed during the campaign and hence could have led to some of the discrepancies observed (Fig. 1 and Table S5). This was explored for the two sites where sampling coverage were most different (Košetice and Birkenes) by averaging the model predicted air concentration corresponding to the AAS sampling times at each of the sites. While the average PAS concentration at Košetice was 69% higher than the air concentration derived on the basis of AAS, the average PAS concentration at Birkenes was 4% lower than results obtained on the basis of AAS (Table S5). Contrary to what would be expected if differences in air masses sampled would be the main reason for difference noted (Table S5), the model results for Košetice corresponding to the AAS sampling period alone was 93% (12.6 pg m^{-3}) compared with the air concentration derived over the entire PAS sampling period (Table S6). Similarly, air concentrations at Birkenes for the AAS sampling period alone represented only 64%

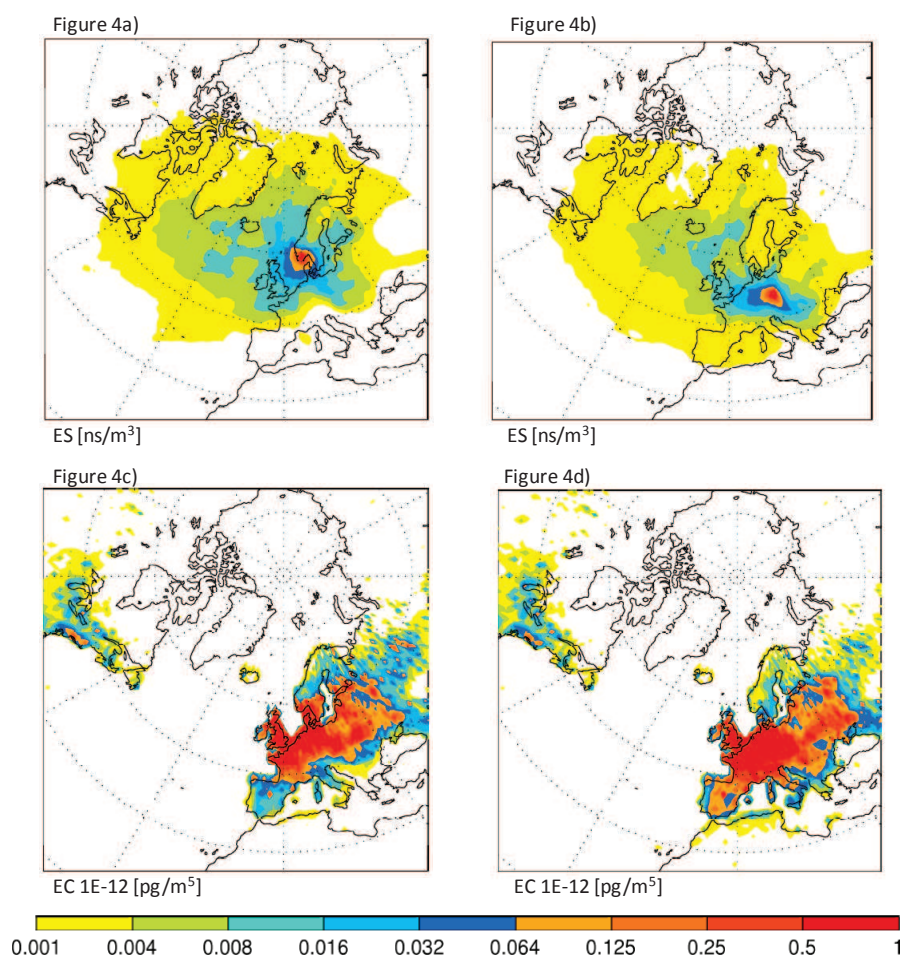


Fig. 4. (a–d): Maps of Footprint ES (emission sensitivity) (a), (b) and EC (emission contribution) (c), (d) for PCB-28 for the PAS sampling period at Birkenes (a), (c) and Košetice (b), (d) (see text for details).

(2.98 pg m^{-3}) of the average air concentration derived for the PAS deployment period. For Košetice it thus seems likely that some of the discrepancy may be better explained by other factors, such as a tendency for the model to overestimate air concentrations as noted above and/or due to inter-laboratory differences. The latter explanation cannot be the reason for Birkenes as both AAS and PAS were analyzed at the same laboratory.

In a recent study by Eckhardt et al. (2009) the same method was used in order to identify source regions contributing to the loadings of PCB-28 at the Birkenes site (for sampling times of 24 h). Again, Košetice and Birkenes (Fig. 4), where chosen for further discussion of the model results, while additional model results can be found in the Supplement (Figs. S8 to S22). As the air masses controlling observed air concentrations are expected to differ between PAS and AAS results, we have additionally included results representing AAS sampling times alone for the Košetice and Birkenes sites in Figs. S23–S24. Yet, these results were

rather similar to the results obtained for the entire PAS campaign (Fig. 4) and are thus not discussed any further. The ES maps in Fig. 4a,b) shows the residence time of the air masses in the so called the footprint layer (0–100 m a.g.l.) where potential uptake of emissions can take place. Looking at the source regions of the air masses influencing the two sites (upper row) it can be seen for both that the local influence gives the greatest contribution and the prevailing westerly winds extend the source region towards North America. Air masses flow in both cases over the British Isles. For Košetice, also Southern and Eastern Europe is an important influence. This can be seen when looking at the EC-maps (Fig. 4c,d), where emission fluxes (Breivik et al., 2007) are incorporated. Integrating over the maps shown in the lower row of Fig. 4 yields an estimated concentration of 4.7 pg m^{-3} and 13.6 pg m^{-3} for Birkenes and Košetice respectively (Table S6). The influence of Southern and Eastern Europe is larger for Košetice than for Birkenes. We caution, however, that these model results rest on the critical assumption that air concentrations

of PCB-28 are controlled by primary emissions alone. This assumption may be criticized as it is well established that PCBs have the potential to undergo reversible atmospheric deposition. For example, soils have a large capacity to retain PCBs (Meijer et al., 2003) and several recent studies have indicated that lower molecular weight PCBs may be subject to significant re-volatilization from urban and industrial soils, following reductions in primary emissions (Li et al., 2010; Ruzickova et al., 2008). At the same time, Li et al. (2010) also conclude that air concentrations at remote and background sites were mostly influenced by primary sources, which is both in agreement with long-term time trends of PCBs in European background air (Schuster et al., 2010) and in line with the model assumptions made herein.

5 Conclusions

This study presents new data on the spatial pattern of selected POPs in European background air. As illustrated for PCB-28, these data are expected to be of significant value for future attempts to evaluate relevant atmospheric fate and transport models for Europe, both within EMEP and beyond. The results combined further illustrates that PAS may complement future monitoring strategies within the EMEP program. The observed spatial variability of POPs in air also highlighted limitations of the current EMEP measurement network with respect to spatial coverage. Finally, we conclude that co-ordinated PAS campaigns may have the potential to serve as useful inter-comparison exercises within and across existing monitoring networks which could complement inter-laboratory comparison studies.

Supplementary material related to this article is available online at:

<http://www.atmos-chem-phys.net/11/1549/2011/acp-11-1549-2011-supplement.zip>.

Acknowledgements. The authors thank Tom Harner, Eva Brorström-Lundén, and Ivan Holoubek for advice and colleagues at NILU (S. Manø, A. Borgen, H. Gundersen, M. Ghebremeskel, A. G. Hjellbrekke and S. E. Walker) for support. We would also like to thank the volunteers within and outside the European Monitoring and Evaluation Programme (EMEP) for their valuable assistance in the field. Isabel Bey has provided the OH fields and the Norwegian MetOffice have given us access to the ECMWF data. This study received financial support from the Research Council of Norway (183437/S30), EMEP and the Nordic Council of Ministers. Lancaster University acknowledge financial support from the UK Department of Food and Rural Affairs for research and monitoring work on persistent organic pollutants.

Edited by: H. C. Hansson

References

- Aas, W. and Breivik, K.: Heavy metals and POPs measurements, 2006 Co-operative programme for monitoring and evaluation of long range transmission of air pollutants in Europe (EMEP), NILU, Kjeller, 2008.
- Aas, W. and Breivik, K.: Heavy metals and POP measurements 2007, Co-operative programme for monitoring and evaluation of long-range transmissions of air pollutants in Europe, NILU, Kjeller O-95038/O-99050, 3-117, 2009.
- Bailey, R. E.: Global hexachlorobenzene emissions, *Chemosphere*, 43, 167–182, 2001.
- Barber, J. L., Sweetman, A. J., van Wijk, D., and Jones, K. C.: Hexachlorobenzene in the global environment: Emissions, levels, distribution, trends and processes, *Sci. Total Environ.*, 349, 1–44, doi:10.1016/j.scitotenv.2005.03.014, 2005.
- Bartkow, M. E., Jones, K. C., Kennedy, K. E., Holling, N., Hawker, D. W., and Müller, J. F.: Evaluation of performance reference compounds in polyethylene-based passive air samplers, *Environ. Pollut.*, 144, 365–370, doi:10.1016/j.envpol.2005.12.043, 2006a.
- Bartkow, M. E., Kennedy, K. E., Huckins, J. N., Holling, N., Komarova, T., and Müller, J. F.: Photodegradation of polyaromatic hydrocarbons in passive air samplers: Field testing different deployment chambers, *Environ. Pollut.*, 144, 371–376, doi:10.1016/j.envpol.2005.12.050, 2006b.
- Becker, S.: Trends and behaviour of semi-volatile organic compounds in the Arctic Atmosphere, Ph.D., Environmental Science Department, Lancaster University, Lancaster, UK, 2008.
- Beyer, A., Mackay, D., Matthies, M., Wania, F., and Webster, E.: Assessing long-range transport potential of persistent organic pollutants, *Environ. Sci. Technol.*, 34, 699–703, 2000.
- Bidleman, T. F., Jantunen, L. M. M., Helm, P. A., Brorstrom-Lunden, E., and Junto, S.: Chlordane enantiomers and temporal trends of chlordane isomers in arctic air, *Environ. Sci. Technol.*, 36, 539–544, doi:10.1021/es011142b, 2002.
- Breivik, K. and Wania, F.: Mass budgets, pathways, and equilibrium states of two hexachlorocyclohexanes in the Baltic Sea environment, *Environ. Sci. Technol.*, 36, 1024–1032, doi:10.1021/es001972+, 2002.
- Breivik, K., Pacyna, J. M., and Munch, J.: Use of alpha-, beta- and gamma-hexachlorocyclohexane in Europe, 1970–1996, *Sci. Total Environ.*, 239, 151–163, 1999.
- Breivik, K., Sweetman, A., Pacyna, J. M., and Jones, K. C.: Towards a global historical emission inventory for selected PCB congeners – A mass balance approach-3. An update, *Sci. Total Environ.*, 377, 296–307, doi:10.1016/j.scitotenv.2007.02.026, 2007.
- Chaemfa, C., Barber, J. L., Gocht, T., Harner, T., Holoubek, I., Klanova, J., and Jones, K. C.: Field calibration of polyurethane foam (PUF) disk passive air samplers for PCBs and OC pesticides, *Environ. Pollut.*, 156, 1290–1297, doi:10.1016/j.envpol.2008.03.016, 2008.
- Chaemfa, C., Barber, J. L., Kim, K. S., Harner, T., and Jones, K. C.: Further studies on the uptake of persistent organic pollutants (POPs) by polyurethane foam disk passive air samplers, *Atmos. Environ.*, 43, 3843–3849, doi:10.1016/j.atmosenv.2009.05.020, 2009a.
- Chaemfa, C., Wild, E., Davison, B., Barber, J. L., and Jones, K. C.: A study of aerosol entrainment and the influence of wind speed, chamber design and foam density on polyurethane foam passive

- air samplers used for persistent organic pollutants, *J. Environ. Monit.*, 11, 1135–1139, doi:10.1039/b823016a, 2009b.
- Dearth, M. A. and Hites, R. A.: Highly chlorinated dimethanofluorenes in technical chlordane and in human adipose-tissue, *J. Am. Soc. Mass. Spectr.*, 1, 99–103, 1990.
- Eckhardt, S., Breivik, K., Li, Y. F., Manø, S., and Stohl, A.: Source regions of some persistent organic pollutants measured in the atmosphere at Birkenes, Norway, *Atmos. Chem. Phys.*, 9, 6597–6610, doi:10.5194/acp-9-6597-2009, 2009.
- Gillespie, M. J., Lythgo, C. M., Plumb, A. D., and Wilkins, J. P. G.: A survey comparing the chemical composition of dicofol formulations sold in the UK before and after the introduction of the EC prohibition directive 79/117/EEC, *Pestic. Sci.*, 42, 305–314, 1994.
- Gouin, T., Harner, T., Blanchard, P., and Mackay, D.: Passive and active air samplers as complementary methods for investigating persistent organic pollutants in the Great Lakes basin, *Environ. Sci. Technol.*, 39, 9115–9122, doi:10.1021/ES051387f, 2005a.
- Gouin, T., Harner, T., Daly, G. L., Wania, F., Mackay, D., and Jones, K. C.: Variability of concentrations of polybrominated diphenyl ethers and polychlorinated biphenyls in air: implications for monitoring, modeling and control, *Atmos. Environ.*, 39, 151–166, doi:10.1016/j.atmosenv.2004.09.022, 2005b.
- Gouin, T., Wania, F., Ruepert, C., and Castillo, L. E.: Field testing passive air samplers for current use pesticides in a tropical environment, *Environ. Sci. Technol.*, 42, 6625–6630, doi:10.1021/es8008425, 2008.
- Halsall, C. J., Coleman, P. J., Davis, B. J., Burnett, V., Waterhouse, K. S., Hardingjones, P., and Jones, K. C.: Polycyclic aromatic-hydrocarbons in UK urban air, *Environ. Sci. Technol.*, 28, 2380–2386, 1994.
- Harju, M., Haglund, P., and Naikwadi, K., P.: Gas-chromatographic properties of the 209 PCB congeners on non-polar, chiral and liquid-crystal columns, *Organohalogen compounds*, 35, 111–114, 1998.
- Harner, T. and Bidleman, T. F.: Measurement of octanol-air partition coefficients for polychlorinated biphenyls, *J. Chem. Eng. Data*, 41, 895–899, 1996.
- Harner, T., Shoeib, M., Diamond, M., Stern, G., and Rosenberg, B.: Using passive air samplers to assess urban – Rural trends for persistent organic pollutants. 1. Polychlorinated biphenyls and organochlorine pesticides, *Environ. Sci. Technol.*, 38, 4474–4483, doi:10.1021/es040302r, 2004.
- Harner, T., Bartkow, M., Holoubek, I., Klanova, J., Wania, F., Gioia, R., Moeckel, C., Sweetman, A. J., and Jones, K. C.: Passive air sampling for persistent organic pollutants: Introductory remarks to the special issue, *Environ. Pollut.*, 144, 361–364, doi:10.1016/j.envpol.2005.12.044, 2006a.
- Harner, T., Pozo, K., Gouin, T., Macdonald, A. M., Hung, H., Caine, J., and Peters, A.: Global pilot study for persistent organic pollutants (POPs) using PUF disk passive air samplers, *Environ. Pollut.*, 144, 445–452, doi:10.1016/j.envpol.2005.12.053, 2006b.
- Harner, T., Shoeib, M., Diamond, M., Ikonou, M., and Stern, G.: Passive sampler derived air concentrations of PBDEs along an urban-rural transect: Spatial and temporal trends, *Chemosphere*, 64, 262–267, doi:10.1016/j.chemosphere.2005.12.018, 2006c.
- Hayward, S. J., Gouin, T., and Wania, F.: Comparison of Four Active and Passive Sampling Techniques for Pesticides in Air, *Environ. Sci. Technol.*, 44, 3410–3416, doi:10.1021/es902512h, 2010.
- Huckins, J. N., Petty, J. D., Lebo, J. A., Almeida, F. V., Booij, K., Alvarez, D. A., Clark, R. C., and Mogensen, B. B.: Development of the permeability/performance reference compound approach for in situ calibration of semipermeable membrane devices, *Environ. Sci. Technol.*, 36, 85–91, doi:10.1021/es010991w, 2002.
- Hung, H., Kallenborn, R., Breivik, K., Su, Y., Brorström-Lundén, E., Olafsdottir, K., Thorlacius, J. M., Leppänen, S., Bossi, R., Skov, H., Manø, S., Patton, G. W., Stern, G., Sverko, E., and Fellin, P.: Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993–2006, *Sci. Total Environ.*, in press, Corrected Proof, doi:10.1016, 2010.
- Jaward, F. M., Farrar, N. J., Harner, T., Sweetman, A. J., and Jones, K. C.: Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe, *Environ. Sci. Technol.*, 38, 34–41, doi:10.1021/es034705n, 2004a.
- Jaward, F. M., Farrar, N. J., Harner, T., Sweetman, A. J., and Jones, K. C.: Passive air sampling of polycyclic aromatic hydrocarbons and polychlorinated naphthalenes across Europe, *Environ. Toxicol. Chem.*, 23, 1355–1364, 2004b.
- Jaward, T. M., Zhang, G., Nam, J. J., Sweetman, A. J., Obbard, J. P., Kobara, Y., and Jones, K. C.: Passive air sampling of polychlorinated biphenyls, organochlorine compounds, and polybrominated diphenyl ethers across Asia, *Environ. Sci. Technol.*, 39, 8638–8645, doi:10.1021/es051382h, 2005.
- Kennedy, K., Hawker, D. W., Bartkow, M. E., Carter, S., Ishikawa, Y., and Mueller, J. F.: The potential effect of differential ambient and deployment chamber temperatures on PRC derived sampling rates with polyurethane foam (PUF) passive air samplers, *Environ. Pollut.*, 158, 142–147, doi:10.1016/j.envpol.2009.07.031, 2010.
- Klanova, J., Eupr, P., Kohoutek, J., and Harner, T.: Assessing the influence of meteorological parameters on the performance of polyurethane foam-based passive air samplers, *Environ. Sci. Technol.*, 42, 550–555, doi:10.1021/es072098o, 2008.
- Li, N. Q., Wania, F., Lei, Y. D., and Daly, G. L.: A comprehensive and critical compilation, evaluation, and selection of physical-chemical property data for selected polychlorinated biphenyls, *J. Phys. Chem. Ref. Data.*, 32, 1545–1590, doi:10.1063/1.1562632, 2003.
- Li, Y. F.: Global technical hexachlorocyclohexane usage and its contamination consequences in the environment: from 1948 to 1997, *Sci. Total Environ.*, 232, 121–158, 1999.
- Li, Y. F., McMillan, A., and Scholtz, M. T.: Global HCH usage with 1 degrees x 1 degrees longitude/latitude resolution, *Environ. Sci. Technol.*, 30, 3525–3533, 1996.
- Li, Y. F., Macdonald, R. W., Jantunen, L. M. M., Harner, T., Bidleman, T. F., and Strachan, W. M. J.: The transport of beta-hexachlorocyclohexane to the western Arctic Ocean: a contrast to alpha-HCH, *Sci. Total Environ.*, 291, 229–246, 2002.
- Li, Y. F., Harner, T., Liu, L. Y., Zhang, Z., Ren, N. Q., Jia, H. L., Ma, J. M., and Sverko, E.: Polychlorinated Biphenyls in Global Air and Surface Soil: Distributions, Air-Soil Exchange, and Fractionation Effect, *Environ. Sci. Technol.*, 44, 2784–2790, doi:10.1021/es901871e, 2010.
- List of signatories and ratifications to the Stockholm Convention on POPs: <http://www.pops.int/documents/signature/signstatus.htm>,

- 2003.
- Lohmann, R., Northcott, G. L., and Jones, K. C.: Assessing the contribution of diffuse domestic burning as a source of PCDD/Fs, PCBs, and PAHs to the UK atmosphere, *Environ. Sci. Technol.*, 34, 2892–2899, doi:10.1021/es991183w, 2000.
- Malanichev, A., Mantseva, E., Shatalov, V., Strukov, B., and Vulykh, N.: Numerical evaluation of the PCBs transport over the Northern Hemisphere, *Environ. Pollut.*, 128, 279–289, doi:10.1016/j.envpol.2003.08.040, 2004.
- Mari, M., Schuhmacher, M., Feliubadalo, J., and Domingo, J. L.: Air concentrations of PCDD/Fs, PCBs and PCNs using active and passive air samplers, *Chemosphere*, 70, 1637–1643, doi:10.1016/j.chemosphere.2007.07.076, 2008.
- Meijer, S. N., Ockenden, W. A., Sweetman, A., Breivik, K., Grimmlt, J. O., and Jones, K. C.: Global distribution and budget of PCBs and HCB in background surface soils: Implications or sources and environmental processes, *Environ. Sci. Technol.*, 37, 667–672, doi:10.1021/es025809l, 2003.
- Moeckel, C., Harner, T., Nizzetto, L., Strandberg, B., Lindroth, A., and Jones, K. C.: Use of Depuration Compounds in Passive Air Samplers: Results from Active Sampling-Supported Field Deployment, Potential Uses, and Recommendations, *Environ. Sci. Technol.*, 43, 3227–3232, doi:10.1021/es802897x, 2009.
- Motelay-Massei, A., Harner, T., Shoeib, M., Diamond, M., Stern, G., and Rosenberg, B.: Using passive air samplers to assess urban-rural trends for persistent organic pollutants and polycyclic aromatic hydrocarbons. 2. Seasonal trends for PAHs, PCBs, and organochlorine pesticides, *Environ. Sci. Technol.*, 39, 5763–5773, doi:10.1021/es0504183, 2005.
- Pacyna, J. M., Breivik, K., Munch, J., and Fudala, J.: European atmospheric emissions of selected persistent organic pollutants, 1970–1995, S119–S131, 2003.
- Pozo, K., Harner, T., Shoeib, M., Urrutia, R., Barra, R., Parra, O., and Focardi, S.: Passive-sampler derived air concentrations of persistent organic pollutants on a north-south transect in Chile, *Environ. Sci. Technol.*, 38, 6529–6537, doi:10.1021/es049065i, 2004.
- Pozo, K., Harner, T., Wania, F., Muir, D. C. G., Jones, K. C., and Barrie, L. A.: Toward a global network for persistent organic pollutants in air: Results from the GAPS study, *Environ. Sci. Technol.*, 40, 4867–4873, doi:10.1021/es060447t, 2006.
- Pozo, K., Harner, T., Lee, S. C., Wania, F., Muir, D. C. G., and Jones, K. C.: Seasonally Resolved Concentrations of Persistent Organic Pollutants in the Global Atmosphere from the First Year of the GAPS Study, *Environ. Sci. Technol.*, 43, 796–803, doi:10.1021/es802106a, 2009.
- Qiu, X. H., Zhu, T., Yao, B., Hu, J. X., and Hu, S. W.: Contribution of dicofol to the current DDT pollution in China, *Environ. Sci. Technol.*, 39, 4385–4390, doi:10.1021/es050342a, 2005.
- Ruzickova, P., Klanova, J., Cupr, P., Lammel, G., and Holoubek, I.: An assessment of air-soil exchange of polychlorinated biphenyls and organochlorine pesticides across Central and Southern Europe, *Environ. Sci. Technol.*, 42, 179–185, doi:10.1021/es071406f, 2008.
- Santiago, E. C. and Cayetano, M. G.: Polycyclic aromatic hydrocarbons in ambient air in the Philippines derived from passive sampler with polyurethane foam disk, *Atmos. Environ.*, 41, 4138–4147, doi:10.1016/j.atmosenv.2007.01.021, 2007.
- Schuster, J. K., Gioia, R., Breivik, K., Steinnes, E., Scheringer, M., and Jones, K. C.: Trends in European Background Air Reflect Reductions in Primary Emissions of PCBs and PBDEs, *Environ. Sci. Technol.*, 44, 6760–6766, doi:10.1021/es101009x, 2010.
- Seibert, P. and Frank, A.: Source-receptor matrix calculation with a Lagrangian particle dispersion model in backward mode, *Atmos. Chem. Phys.*, 4, 51–63, doi:10.5194/acp-4-51-2004, 2004.
- Shoeib, M. and Harner, T.: Using measured octanol-air partition coefficients to explain environmental partitioning of organochlorine pesticides, 21, 984–990, 2002a.
- Shoeib, M. and Harner, T.: Characterization and comparison of three passive air samplers for persistent organic pollutants, *Environ. Sci. Technol.*, 36, 4142–4151, doi:10.1021/es020635t, 2002b.
- Sovocool, G. W., Lewis, R. G., Harless, R. L., Wilson, N. K., and Zehr, R. D.: Analysis of technical chlordane by gas chromatography mass spectrometry, *Anal. Chem.*, 49, 734–740, 1977.
- Stohl, A., Hittenberger, M., and Wotawa, G.: Validation of the Lagrangian particle dispersion model FLEXPART against large-scale tracer experiment data, *Atmos. Environ.*, 32, 4245–4264, 1998.
- Stohl, A. and Thomson, D. J.: A density correction for Lagrangian particle dispersion models, *Bound.-Lay. Meteorol.*, 90, 155–167, 1999.
- Stohl, A., Forster, C., Eckhardt, S., Spichtinger, N., Huntrieser, H., Heland, J., Schlager, H., Wilhelm, S., Arnold, F., and Cooper, O.: A backward modeling study of intercontinental pollution transport using aircraft measurements, *J. Geophys. Res.-Atmos.*, 108(18), 4370, doi:10.1029/2002jd002862, 2003.
- Stohl, A., Forster, C., Frank, A., Seibert, P., and Wotawa, G.: Technical note: The Lagrangian particle dispersion model FLEXPART version 6.2, *Atmos. Chem. Phys.*, 5, 2461–2474, doi:10.5194/acp-5-2461-2005, 2005.
- Su, Y. S. and Hung, H. L.: Inter-laboratory comparison study on measuring semi-volatile organic chemicals in standards and air samples, *Environ. Pollut.*, 158, 3365–3371, doi:10.1016/j.envpol.2010.07.041, 2010.
- Tuduri, L., Harner, T., and Hung, H.: Polyurethane foam (PUF) disks passive air samplers: Wind effect on sampling rates, *Environ. Pollut.*, 144, 377–383, doi:10.1016/j.envpol.2005.12.047, 2006.
- Turgut, C., Gokbulut, C., and Cutright, T. J.: Contents and sources of DDT impurities in dicofol formulations in Turkey, *Environ. Sci. Pollut. R.*, 16, 214–217, doi:10.1007/s11356-008-0083-3, 2009.
- The 1998 Aarhus Protocol on persistent organic pollutants (POPs): United Nations Economics Commission for Europe: <http://www.unece.org/env/lrtap/welcome.html>, 1998.
- Vallack, H. W., Bakker, D. J., Brandt, I., Brostrom-Lunden, E., Brouwer, A., Bull, K. R., Gough, C., Guardans, R., Holoubek, I., Jansson, B., Koch, R., Kuyslenstierna, J., Lecloux, A., Mackay, D., McCutcheon, P., Mocarelli, P., and Taalman, R. D. F.: Controlling persistent organic pollutants – what next?, *Environ. Toxicol. Pharmacol.*, 6, 143–175, 1998.
- Wania, F. and Mackay, D.: Tracking the distribution of persistent organic pollutants, *Environ. Sci. Technol.*, 30, A390–A396, 1996.
- Wania, F. and Daly, G. L.: Estimating the contribution of degradation in air and deposition to the deep sea to the global loss of PCBs, *Atmos. Environ.*, 36, 5581–5593, 2002.
- Wilford, B. H., Harner, T., Zhu, J. P., Shoeib, M., and Jones, K.

C.: Passive sampling survey of polybrominated diphenyl ether flame retardants in indoor and outdoor air in Ottawa, Canada: Implications for sources and exposure, *Environ. Sci. Technol.*, 38, 5312–5318, doi:10.1021/es049260x, 2004.

Xiao, H., Li, N. Q., and Wania, F.: Compilation, evaluation, and selection of physical-chemical property data for alpha-, beta-, and gamma-hexachlorocyclohexane, *J. Chem. Eng. Data*, 49, 173–185, doi:10.1021/je034214i, 2004.

SUPPORTING INFORMATION

for

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Spatial variability of POPs in European background air

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Tables

Table S1 Site description and details.

Country	EMEP sites	Station name	Latitude	Longitude	M.a.s.l. ⁽⁵⁾	Sample start	Sample end	Sampling rate (m ³ day ⁻¹)	PRCs ⁽¹⁾
Austria	X	Illmitz	N 47°46	E 16°46	117	27.07.06	02.11.06	4.93	5
Austria	X	Vorhegg	N 46°40	E 12°58	1020	18.07.06	23.10.06	4.69	5
Belgium	-	Koksijde	N 51°07	E 02°29	7	04.07.06	03.10.06	3.48	6
Bulgaria	-	Moussala	N 42°11	E 23°35	2925	06.07.06	05.10.06	11.07 ⁽³⁾	5
Croatia	X	Zavizan	N 44°49	E 14°59	1594	10.07.06	10.10.06	17.88 ⁽³⁾	6
Cyprus	-	Ayia Marina	N 33°02	E 33°03	532	29.06.06	02.10.06	5.30	6
Czech Rep	X	Košetice	N 49°35	E 15°05	534	12.07.06	12.10.06	3.59/3.97 ⁽⁴⁾	5/5 ⁽⁴⁾
Czech Rep	X	Svratouch	N 49°44	E 16°02	737	13.07.06	13.10.06	3.72	5
Denmark	X	Tange	N 56°21	E 09°36	13	07.07.06	06.10.06	3.03	5
Denmark	X	Keldsnor	N 54°44	E 10°44	10	11.07.06	19.10.06	3.12	6
Denmark	X	Anholt	N 56°43	E 11°31	40	06.07.06	06.10.06	4.52	6
Denmark	X	Lille Valby	N 55°41	E 12°08	10	13.07.06	13.10.06	4.32	6
Estonia	X	Laheema	N 59°30	E 25°54	32	06.07.06	10.10.06	3.83	6
Färöe Islands	-	Norðuri á Fossum	N 62°11	W 07°12	~300	01.07.06	02.10.06	4.61	3
Finland	X	Pallas	N 67°58	E 24°07	566	19.07.06	19.10.06	2.80/4.45 ⁽⁴⁾	2/4 ⁽⁴⁾
Finland	X	Ähtari	N 62°33	E 24°13	162	01.07.06	02.10.06	3.78	6
Finland	X	Utö	N 59°47	E 21°23	7	30.06.06	02.10.06	8.10	6
Finland	X	Violahti	N 60°31	E 27°41	4	01.07.06	01.10.06	4.51	6
Finland	X	Oulanka	N 66°19	E 29°24	310	30.06.06	30.09.06	4.18	5
Finland	X	Hailuoto	N 65°00	E 24°41	4	04.07.06	03.10.06	4.19	6
France	X	Donon	N 48°30	E 07°08	775	05.07.06	05.10.06	3.95	6
France	X	Peyrusse Vieille	N 47°37	E 00°11	236	11.07.06	10.10.06	4.23	6
France	X	La Tardiere	N 46°39	W 00°45	133	04.07.06	03.10.06	4.03	6
France	X	Le Casset	N 45°00	E 06°28	1750	04.07.06	03.10.06	3.96	5
France	X	Porspoder	N 48°31	E 04°45	50	10.07.06	16.10.06	7.31	6
Germany	X	Westerland	N 54°56	E 08°19	12	07.07.06	09.10.06	5.01	6
Germany	X	Schmücke	N 50°39	E 10°46	937	10.07.06	10.10.06	2.99	4

Germany	X	Zingst	N 54°26	E 12°44	1	10.07.06	09.10.06	4.01	6
Germany	X	Schauinsland	N 47°54	E 07°54	1205	10.07.06	10.10.06	3.75	5
Germany	X	Neuglobsow	N 53°09	E 13°02	62	24.07.06	24.10.06	3.29	6
Greece	X	Aliartos	N 38°22	E 23°05	110	11.07.06	12.10.06	3.42	6
Greenland	-	Nuuk	N 64°11	W 51°44	~5	04.07.06	08.10.06	3.50 ²⁾	-
Greenland	-	Summit	N 72°52	W 38°46	3250	28.07.06	20.10.06	3.50 ²⁾	-
Hungary	X	K-pusztá	N 46°58	E 19°35	125	18.07.06	19.10.06	3.45	5
Iceland	X	Stórhöfði	N 63°27	W 20°15	118	11.07.06	08.10.06	11.53/10.90	6/6
Ireland	X	Mace Head	N 53°20	W 09°54	25	10.07.06	18.10.06	7.90	6
Ireland	-	Malin Head	N 55°22	W 07°20	22	06.07.06	08.10.06	5.86	6
Ireland	-	Carnsore Point	N 52°11	W 06°22	9	19.07.06	11.10.06	9.51	6
Italy	X	Ispra	N 45°48	E 08°38	209	07.09.06	04.12.06	4.13	2
Italy	X	Montelibretti	N 42°06	E 12°38	48	03.07.06	20.09.06	3.63	6
Italy	-	Longobucco	N 39°39	E 16°61	1379	28.07.06	07.11.06	3.02 ³⁾	4
Italy	-	San Lucido	N 39°19	E 16°02	49	27.07.06	13.11.06	2.88	6
Kazakhstan	-	Borovoye	N 44°08	E 75°51	~300	15.08.06	17.11.06	2.07	2
Latvia	X	Rucava	N 56°13	E 21°13	18	17.07.06	17.10.06	3.55	5
Latvia	X	Zoseni	N 57°08	E 25°55	183	17.07.06	17.10.06	3.49	5
Lithuania	X	Preila	N 55°21	E 21°04	5	22.07.06	01.10.06	4.91	6
Lithuania	-	Rugstelis	N 55°26	E 26°04	120	15.07.06	30.09.06	2.56	2
Malta	X	Giordan lighthouse	N 36°06	E 14°12	160	02.08.06	07.11.06	6.90	6
Moldova	X	Leovo	N 46°30	E 28°16	156	10.07.06	10.10.06	4.60	4
Netherlands	X	Kollumerwaard	N 53°20	E 06°17	0	26.07.06	22.11.06	5.77	6
Netherlands	X	Vredepeel	N 51°32	E 05°51	28	25.07.06	21.11.06	5.69	5
Norway	X	Birkenes	N 58°23	E 08°15	190	02.07.06	01.10.06	3.03/3.58 ⁴⁾	5/6 ⁴⁾
Norway	X	Tustervatn	N 65°50	E 13°55	439	28.06.06	09.10.06	4.03	4
Norway	X	Kårvatn	N 62°47	E 08°53	210	29.06.06	10.10.06	3.88	6
Norway	X	Spitsbergen	N 78°54	E 11°53	474	14.07.06	26.09.06	3.50/3.50 ²⁾	-/ ⁴⁾
Norway	X	Hurdal	N 60°22	E 11°04	300	01.07.06	02.10.06	3.59	5
Norway	X	Karasjok	N 69°28	E 25°13	333	26.06.06	29.09.06	4.34	6
Poland	X	Diabla Góra	N 54°09	E 22°04	157	06.07.06	06.10.06	4.92	5
Poland	X	Jarczew	N 51°19	E 21°59	180	01.07.06	02.10.06	4.05	6

Poland	X	Sniezka	N 50°44	E 15°44	1604	10.07.06	10.10.06	3.50 ²⁾	-
Poland	X	Leba	N 54°45	E 17°32	2	13.07.06	13.10.06	4.40	6
Portugal	X	Bragança	N 41°49	W 06°46	691	19.07.06	19.10.06	4.44	6
Portugal	X	Monte Velho	N 38°05	W 08°48	43	19.07.06	19.10.06	3.29	6
Slovakia	X	Chopok	N 48°56	E 19°35	2008	02.07.06	03.10.06	19.18 ³⁾	5
Slovakia	X	Starina	N 49°03	E 22°16	345	04.07.06	04.10.06	4.23	5
Slovenia	X	Iskrba	N 45°34	E 14°52	520	07.07.06	06.10.06	3.53	5
Spain	X	Víznar	N 37°14	W 03°32	1265	14.07.06	14.10.06	4.34	6
Spain	X	Niembro	N 43°27	W 04°51	134	12.07.06	12.10.06	5.63	6
Spain	X	Els Torms	N 41°24	E 00°43	470	15.07.06	15.10.06	3.55	6
Spain	X	Risco Llamo	N 39°31	W 04°21	1241	13.07.06	13.10.06	3.63	6
Sweden	X	Råö	N 57°24	E 11°55	5	04.07.06	02.10.06	8.33/6.24 ⁴⁾	6/6 ⁴⁾
Sweden	X	Aspvreten	N 58°48	E 17°23	20	06.07.06	06.10.06	1.66	2
Sweden	X	Vavihill	N 56°01	E 13°09	172	11.07.06	08.10.06	3.47	5
Sweden	X	Bredkälen	N 63°51	E 15°20	404	06.06.06	06.09.06	2.56	3
Sweden	X	Hoburg	N 56°55	E 18°09	58	30.06.06	03.10.06	6.71	6
Sweden	-	Abisko	N 68°21	E 18°49	~385	06.07.06	11.10.06	6.11	6
Sweden	X	Vindeln	N 64°15	E 19°46	225	28.06.06	28.09.06	3.41	6
Switzerland	X	Jungfrauoch	N 46°33	E 07°59	3573	06.07.06	13.10.06	8.0 ³⁾	5
Switzerland	X	Payerne	N 46°48	E 06°57	510	05.07.06	11.10.06	3.42	5
Ukraine	-	Zmeiny Island	N 45°15	E 30°12	n.a.	17.07.06	08.11.06	7.58	5
United Kingdom	X	Harwell	N 51°34	W 01°19	137	05.07.06	09.10.06	3.92	6
United Kingdom	-	Auchencorth Moss	N 55°80	W 03°20	255	03.07.06	13.10.06	3.75	4
United Kingdom	X	Lough Navar	N 54°26	W 07°54	126	03.07.06	11.10.06	3.97	6
United Kingdom	X	Yarner Wood	N 50°36	W 03°43	119	30.06.06	02.10.06	3.90	6
United Kingdom	X	High Muffles	N 54°20	W 00°48	267	05.07.06	04.10.06	2.89	4
United Kingdom	X	Strath Vaich Dam	N 57°44	W 04°46	270	30.06.06	02.10.06	4.25	6

1) Number of PRCs with more than 40 % loss during deployment. 2) No significant loss of PRCs, default value used. 3) Adjusted temperature as detailed in section 2. 4) Results for two PAS parallels: Sample A / Sample B. 5) Meters above sea level.

Table S2 Range in recoveries for the internal standard for exposed samples, field blanks, method blanks as well as PRCs for field and method blanks, respectively (in %).

Internal standards and PRCs	Range		
	Exposed samples	Field blank	Method blank
Metylnaphtalene-d ₁₀	24-45	29-40	31-40
Acenaphtene- d ₁₀	34-77	33-44	33-61
Antracene- d ₁₀	40-78	52-64	34-69
Pyrene- d ₁₀	49-91	61-71	51-83
Benz(a)antracene- d ₁₂	53-137	75-93	27-111
Benz(e)pyrene- d ₁₂	54-126	76-85	66-96
Benzo(ghi)perylene- d ₁₂	50-114	64-81	41-96
¹³ C-PeCB	21-49	22-31	23-37
¹³ C-PCB (28)	48-89	55-72	62-79
¹³ C -PCB (52)	48-89	58-78	65-82
¹³ C -PCB (101)	59-104	74-90	80-97
¹³ C -PCB (105)	69-127	90-112	98-115
¹³ C -PCB (114)	66-124	85-105	90-110
¹³ C -PCB (118)	68-119	86-108	92-114
¹³ C -PCB (123)	64-127	88-108	92-112
¹³ C -PCB (153)	70-119	86-107	87-114
¹³ C -PCB (138)	74-125	93-115	100-116
¹³ C -PCB (167)	72-136	96-122	104-127
¹³ C -PCB (156)	73-137	103-124	107-129
¹³ C -PCB (157)	74-140	103-123	108-130
¹³ C -PCB (180)	76-129	99-120	100-125
¹³ C -PCB (189)	81-132	108-124	108-128
¹³ C -PCB (209)	76-129	102-119	107-127
¹³ C -HCB	30-63	27-37	34-47
¹³ C - <i>p,p'</i> -DDE	55-139	78-119	68-115
¹³ C - <i>p,p'</i> -DDT	32-218 ¹⁾	85-198 ¹⁾	77-119

¹³ C -α-HCH	32-118	31-48	35-67
¹³ C -β-HCH	19-117	45-76	61-88
¹³ C -γ-HCH	44-136	51-75	57-88
¹³ C -trans-Chlordane	42-122	70-94	71-122 ²⁾
¹³ C -trans-Nonachlor	29-121	33-44	43-121 ²⁾
¹³ C Mirex	11-132	74-116	73-160 ²⁾
PRCs			
d6-γ-HCH	-	86-103	72-106
PCB-12	-	73-94	76-107
PCB-14	-	61-80	69-100
PCB-23	-	72-85	74-103
PCB-30	-	57-74	66-90
PCB-32	-	78-91	81-105
PCB-107	-	87-100	75-110
PCB-198	-	80-93	75-116

1) Two sites showed higher recovery. Highest % recovery for the deployed samples was for one of the parallels at the Spitsbergen site, while the highest % recovery for the field blanks occurred for the Košetice site.

2) The higher recovery originates from one method blank

Table S3 Instrumental parameters for analysis of the compound groups.

Compound groups	Type of instrument	Type of column	Column size	Carrier gas	Operational parameters	
					Temp.interv.	Target ion
PCBs & HCB	GC/HRMS in EI mode (Agilent6890 GC coupled to Waters AutoSpec)	Fused silica capillary column from SGE	HT-8, 50 m length, 0.22 mm I.D, 0.15 mm film thickness	Helium	Start (°C): 90 (2 min.) Intervall 1: 25°C/min to 170°C Intervall 2: 308°C by 3°C/min Injector temp. (°C): 280	[M] ⁺
HCHs & DDTs	GC/HRMS in EI mode (Agilent6890 GC coupled to Micromass AutoSpec).	Fused silica capillary column from J&W Scientific	HP-1, 25 m length, 0.2 mm I.D, 0.33 mm film thickness	Helium	Start (°C): 95 (1.5 min.) Intervall: 280°C by 20°C/min (5 min.) Injector temp. (°C): 220	[M] ⁺
PAHs	GC/LRMS in EI mode (Agilent6890 GC coupled to Agilent5973 MSD)	Fused silica capillary column from Zebron	ZB-5, 30 m length, 0.25 mm I.D, 0.10 mm film thickness	Helium	Start (°C):50 Intervall 1: 100°C/min by 20°C/min. Intervall 2: 320°C by 5°C/min Injector temp. (°C): 300	[M] ⁺
Chlordanes	GC/LRMS in ENCI mode, (Agilent6890 GC coupled to a Agilent5973 MSD)	Fused silica capillary column from J&W Scientific	Ultra 2, 25 m length, 0.2 mm I.D, 0.11 mm film thickness	Helium	Start (°C): 90 (2 min.) Intervall 1: 170°C by 20°C/min (3 min) Intervall 2: 235°C by 5°C/min (2 min.) Injector temp. (°C): 260	[M-Cl]- and [M-2Cl]-

Table S4 Relative deviations from the average value of two parallel PAS.

Compounds/compound- groups	Košetice CZ 0003R	Pallas FI 0096G	Stórhöfði IS 0019R	Birkenes NO 0001R	Spitsbergen NO 0042G	Råö SE 0014R
PCB-28	±1	±23	±8	±8	±46	±27
PCB-52	±1	±26	±7	±9	±19	±20
PCB-101	±6	±27	±5	±8	±10	±6
PCB-118	±7	±24	±1	±9	n.d.	±3
PCB-138	±7	±32	±1	±8	n.d.	±0,3
PCB-153	±8	n.d.	±3	±9	n.d.	±1
PCB-180	±12	±38	±12	±8	n.d.	±4
Σ_nPCBs	±4	±26 (n=6) ¹⁾	±4	±8	±30 (n=3) ¹⁾	±8
α-HCH	±7	±13	±1	±13	±6	±12
γ-HCH	±7	±15	±6	±13	±2	±18
<i>p,p'</i>-DDE	±9	n.d.	n.d.	n.d.	n.d.	±35
<i>p,p'</i>-DDD	±9	n.d.	n.d.	n.d.	n.d.	±23
<i>o,p'</i>-DDT	±6	n.d.	n.d.	±18	n.d.	±8
<i>p,p'</i>-DDT	±5	n.d.	n.d.	±13	n.d.	±24
Σ_nDDTs	±8	n.d.	n.d.	±15 (n= 2) ¹⁾	n.d.	±26
Fluorene	±9	±20	n.d.	±10	n.d.	±11
Phenanthrene	±2	±26	n.d.	±13	n.d.	±9
Anthracene	±0.02	n.d.	n.d.	n.d.	n.d.	n.d.
Fluoranthene	±8	±31	n.d.	±14	n.d.	±8
Pyrene	±8	±31	±15	±20	n.d.	±6
Benzo[a]pyrene	±12	n.d.	n.d.	n.d.	n.d.	n.d.
Benz[a]anthracene	±14	n.d.	n.d.	n.d.	n.d.	n.d.
Chrysene	±11	±36	n.d.	±8	n.d.	±10
Σ_nPAH	±2	±25 (n=5) ¹⁾	±15 (n=1) ¹⁾	±12 (n=5) ¹⁾	n.d.	±9 (n=5) ¹⁾
HCB	±2	±19	±1	±4	±22	±8

n.d.: one or both samples below MDL

¹⁾ Sum PCBs, DDTs and PAHs only include the sum of substances where both samples are above MDL (number in parantheses).

Table S5 Percentage deviation between PAS and AAS at EMEP sites $[(C_{PAS}-C_{AAS})/C_{AAS}]$. A positive deviation indicates higher concentrations in the PAS.

Compound/compound group	Košetice CZ CZ0003R	Råö SE 0014R	Birkenes NO 0001R	Aspvreten SE 0012 ¹⁾ R	Stórhöfði IS 0019R	Pallas FI 0096G	Spitsbergen NO 0042G
PCB-28	69	49	-4	102	-77	-70	-54
PCB-52	48	39	5	64	-48	-62	22
PCB-101	178	40	24	-22	-37	-34	111
PCB-118	56	47	-12	-30	50	-5	n.d.
PCB-138	257	33	-13	4	11	-26	n.d.
PCB-153	193	65	-24	34	35	n.d.	n.d.
PCB-180	-27	66	-53	64	9	41	n.d.
Σ_n PCB	86	47	-5	25	-51	-59 (n=6)	-35 (n=3)
α -HCH	98	19	-43	154	318	-17	23
γ -HCH	85	24	-48	54	-8	-30	22
<i>p,p'</i> -DDE	264	63	n.a.	-34	n.d.	n.d.	n.d.
<i>p,p'</i> -DDD	-39	-24	n.a.	n.a.	n.d.	n.d.	n.d.
<i>p,p'</i> -DDT	577	10	n.a.	n.a.	n.d.	n.d.	n.d.
Σ nDDTs	282 (n=3)	40 (n=3)	n.a.	-34 (n=1)	n.d.	n.d.	n.d.
Phenanthrene	211	52	n.a.	109	n.a.	51	n.d.
Anthracene	137	n.d.	n.a.	512	n.a.	n.d.	n.d.
Fluoranthene	270	46	n.a.	13	n.a.	71	n.d.
Pyrene	240	5	n.a.	-16	n.a.	32	n.d.
Benzo[a]pyrene	-49	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.
Benz[a]anthracene	73	n.d.	n.a.	-47	n.a.	n.d.	n.d.
Σ_n PAH	216 (n=6)	45 (n=3)	n.a.	76 (n=5)	n.a.	52 (n=3)	n.d.
HCB	36	n.a.	-31	n.a.	1540	n.a.	34
Sampling duration	1 day	2 weeks	1 day	1 week	2 weeks	1 week	2 days
Sampling frequency	1x week	2x month	1x week	1x month	2x month	1x month	1x week
Sampling coverage (%)	~14	~100	~14	~25	~100	~25	~29

1) Only one PAS sample available for this site.

n.d. : Values below MDL in PAS. n.a. : no available data for the AAS

Table S6 Concentrations (pg/m³) of PCB-28 derived from AAS, PAS and the FLEXPART model for selected sites.

Country	Sites	AAS	PAS	Model	% deviation (Model/PAS)
Czech Republic	Košetice	6.51	10.98 ¹⁾	13.57	24
Finland	Pallas	4.12	1.25 ¹⁾	2.74	119
Iceland	Stórhöfði	4.22	0.96 ¹⁾	0.79	-18
Norway	Birkenes	2.13	2.04 ¹⁾	4.69	130
Norway	Spitsbergen	3.19	1.48 ¹⁾	0.26	-82
Sweden	Råö	3.15	4.68 ¹⁾	6.69	43
Sweden	Aspvreten	1.66	3.34	5.81	74
Ireland	Mace Head	n.d.	1.15	2.28	98
Ireland	Malin Head	n.d.	1.22	2.02	66
Italy	Longobucco	n.d.	1.58	10.36	556
Kazakhstan	Borovoye	n.d.	8.79	4.43	-50
Malta	Giordan lighthouse	n.d.	5.35	6.33	18
Poland	Jarczew	n.d.	6.85	9.81	43
Poland	Leba	n.d.	4.96	8.59	73
Spain	Víznar	n.d.	2.28	6.24	174
Spain	Els Torms	n.d.	2.67	7.11	166
United Kingdom	Strath Vaich Dam	n.d.	0.96	2.42	152

¹⁾ Average of two PAS

Text

S 1.1 Deployment and sample preparation

In the following, the solvents and sulfuric acid used for sample preparation and clean-up were of pesticide grade from Merck (Darmstadt, Germany), except diethyl ether which was purchased from Rathburn (Walkerburn, Scotland). Anhydrous sodium sulfate and silica gel were purchased from Merck (Darmstadt, Germany).

Prior to deployment, the PUF disks (14 cm in diameter, 1.35 cm thick, surface area 0.0364 m², density 2.47 10⁻² g/m³; Sunde Søm & Skumplast A/S, Gan, Norway) were pre-cleaned using Soxhlet extraction with toluene for 24 hours, with acetone for 8 hours and finally with toluene for new 8 hours. The PUF disks were then dried in desiccators at 40°C under vacuum until they were completely dry. The PUF disks were spiked with the following PRC mixture (PCBs 12, 14, 23, 30, 32, 107, 198 and d6 γ -HCH) by adding 25 μ L PRC mixture, with the respective concentrations; 189.4, 188.4, 188.4, 188.3, 193.6, 189.0, 187.9, 186.7 pg/ μ L, in 10 mL of pentane in a small vial. This solution was applied evenly on both sides of the PUF disk using a Pasteur pipette in a clean laboratory environment (class 100000 part/m³/ft). The PUF disks were placed on 3 short metal tubes to minimize the contact area during spiking. The spiked PUFs were next wrapped in double layers of alumina foil, double zip-lock bags and stored in a freezer until shipment. Pre-cleaning of the sampling chambers prior to shipment was carried out by soaking all the parts in soap solution over night, followed by rinsing in tap water and acetone. Each sampling kit was then packed in sealed plastic bags to avoid contamination during shipment.

S 1.2 Clean-up

In order to reduce sample contamination all laboratory equipment was rinsed with *n*-hexane immediately before use. The exposed PUF disks and field blanks were stored in a freezer until extraction and clean-up. Prior to extraction, the PUF disk were unwrapped in a clean-room laboratory environment, spiked with internal standards (see S 1.3), and placed in a Soxhlet

extractor. The disks were Soxhlet extracted for 8-10 hours in approximately 250 mL of *n*-hexane. Extracts were concentrated to about 0.5 mL on a TurboVap 500 System (Zymark, Hopkinton, MA, USA), and transferred to a graduated cylinder. Further sample treatment was done separately and the extracts were therefore divided into two identical aliquots.

The acid resistant part (PCBs, HCHs, DDTs, HCB, pesticides (trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor) of the extract was transferred to a centrifuge tube, adjusted to 2 mL, and treated with 2 mL concentrated sulfuric acid for mixing by vigorous whirling on a whirl mixer. During this treatment the extract turns color to dark yellow. The treatment was repeated until no more color change was visible (2-3 times). The extract was then transferred to an evaporation unit and reduced to 0.5 mL for further clean-up by fractionation with a silica column (15 mm in diameter and 200 mm in length). The column consists of 4 g of activated silica (Silica gel 60 Merck nr. 7734 0.063 – 0.200 mm pretreated 8 h at 550°C) topped with 1 cm anhydrous sodium sulfate (pretreated 12 h at 600°C). The column was prewashed with 30 mL *n*-hexane. The samples were eluted with 30 mL *n*-hexane/10 % diethyl ether. Extracts were reduced to 0.5 mL by evaporation and solvent exchanged into *iso*-octane and transferred to a small vial with a screw-cap.

The PAH part of the extract was solvent exchanged to cyclohexane and cleaned on a silica column (15 mm in diameter and 200 mm in length). This column consists of a slurry of 5 g deactivated silica (deactivated with 8% MilliQ water) and 15 mL cyclohexane overlaid with 1 cm anhydrous sodium sulfate. The column was prewashed with 40 mL cyclohexane. The sample was eluted with 100 mL cyclohexane, and the extract was reduced to 0.5 mL by evaporation and transferred to a small vial with a screw-cap.

Prior to analyses all extracts were further reduced to approximately 50 µL by a gentle stream of nitrogen.

S 1.3 Analyses

In order to monitor recovery rates for the extraction and clean-up procedures, the PUF disk were added a mixture containing 20 µL of each internal standard prior to extraction and clean-up. This

standards consist of a range of ^{13}C – labeled polychlorinated biphenyls (PCB) congeners (^{13}C PCB-28,-52,-101,-105,-114,-118,-123,-138,-153,-156,-157,-167,-180,-189, -209) and organochlorine pesticides (OCPs) (^{13}C α , β , γ - hexachlorocyclohexane (HCH), ^{13}C - hexachlorobenzene (HCB), ^{13}C *p,p'*- dichlorodiphenyldichloroethylene (DDE) and ^{13}C *p,p'*- dichlorobiphenyldichloroethane (DDT), ^{13}C trans-nonachlor, ^{13}C trans-chlordane, ^{13}C dieldrine and ^{13}C Mirex). For the PAHs, a mixture of deuterium labeled polyaromatic hydrocarbons (PAH) congeners (2-methylnaphtalene- d_{10} , acenaphtene- d_{10} , anthracene- d_{10} , pyrene- d_{10} , benz(a)anthracene- d_{12} , benz(e)pyrene- d_{12} , benz(ghi)perylene- d_{12}), were added. All standards were purchased from LGC, formerly Promochem AB (Borås, Sweden). In order to quantify the recovery of the internal standards, the extracts were added recovery standards. 10 μL of recovery standard consisting of deuterated PAHs (biphenyl- d_{10} , fluorantene- d_{10} and perylene- d_{12}) were added to the PAH extracts, while 20 μL of a recovery standard (1.2.3.4-tetrachloronaphtalene) were added to the acid resistant extracts.

Analysis of the PCB congeners, α -HCH, β -HCH, γ -HCH, *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT, HCB, together with the PRC compounds were performed with GC/HRMS on an Agilent 6890N gas chromatograph coupled to a Waters AutoSpec mass spectrometer in electron impact (EI) mode (Table S3). The different PCB congeners and some of the PRCs (PCB-23,-30,-32,-107,-198) were separated using a HT-8 (50 m \times 0.22 mm inner diameter (SGE)) fused silica capillary column (Table S3). The GC was operating in splitless mode with helium as a carrier gas. 1 μL was injected at an injector temperature on 280°C. See Table S3 for more detailed information concerning the temperature program. Separation of α -HCH, β -HCH, γ -HCH, *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT, together with the PRCs (PCB-12,-14, D6 γ -HCH) compounds were done by use of a HP-1 (25 m \times 0.2 mm inner diameter (J&W Scientific)) fused silica column. 1 μL was injected by an autosampler on the split/splitless injection port in splitless mode with helium as a carrier gas (flow rate 1 mL/min). See Table S3 for detailed specification for the temperature program. During the GC run, *p,p'*-DDT could be thermally converted to *p,p'*-DDD and *p,p'*-DDE. This is eluded due to use of ^{13}C labeled *p,p'*-DDT as an internal standard. ^{13}C *p,p'*-DDT may format to ^{13}C -DDD/DDE, which are compounds that are not included in the internal standard. If the peak area of ^{13}C -DDD/DDE >5% of the peak area of ^{13}C *p,p'*-DDT, that result will be rejected.

Analysis of PAHs was carried out by a GC/LRMS on an Agilent 6890N gas chromatograph coupled to an Agilent 5973 mass spectrometer in an electron impact (EI) mode (Table S3). 1 µL was injected by an auto sampler on the split/splitless injection port in splitless mode with helium as a carrier gas (flow rate ~1 mL/min), with a temperature program as detailed in Table S3.

Analysis of the pesticides (trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor) was carried out by a GC/LRMS on a Agilent 6890N gas chromatograph coupled to a Agilent 5973 mass spectrometer in a electron capture negative ion (ENCI) mode. 1 µL was injected by an auto sampler on the split/splitless injection port in splitless mode with helium as a carrier gas (flow rate 1 mL/min). See Table S3 for the temperature program.

S 1.4 Internal standard recoveries

The internal standard recoveries for the deployed samples, field and method blanks, were to a large extent at the same level (Table S2), which address minimal matrix interferences from the deployed samples governed due to exposure. Nonetheless, some sites are experiencing higher recoveries for some of the internal standards. One of the parallels at the Spitsbergen site had a high percentage recovery for ¹³C *p,p'*-DDE. High recovery was also found for the field blank from Košetice for this internal standard.

S 1.5 PRC recoveries

The second recovery values were for the added mixture of PRCs. These values lie in the range of 57-116 % The range in percentage recovery is governed from each PRC (8) in the field and method blank individually (Table S2). The lower values in the range originates from PCB-30, which had to be corrected towards two internal standards (¹³C HCB and ¹³C PCB-28). The higher recovery values for one of the method blanks may be caused by adding too much of the PRC solution to the PUF-disk. i.e. when comparing the recoveries from the different compounds in the same sample, it seems to be over all a high compound recovery for this sample.

S 1.6 Duplicate passive air samplers at selected sites

Figure S2 (a-f) compares selected results for the six EMEP POPs sites where two samplers were co-located (Fig S1), while Table S4 additionally lists relative deviations, expressed as the percentage deviation from the average of these two parallels. The error bars in Fig. S2 are included to illustrate the uncertainty associated with the chemical analysis alone, which was estimated to be ~35 % (Section 3.4).

The relative deviation for PCBs between the two replicates was less than 10 % at four out of six sites and ranged from 4 % (Košetice, Stórhöfði) to 30 % for Σ_n PCBs (Spitsbergen) (Table S4). Among individual PCBs, larger differences tended to occur for substances and sites experiencing lower concentrations (Spitsbergen, Pallas). However, differences of 20% or more were also seen for PCB-28 and 52 at the Råö site (Table S4) in spite of the relatively high air concentrations at this site (Fig S2a). Differences in wind speed experienced between the two replicates may have contributed to some of the deviations observed (Tuduri et al., 2006). If the two parallels were subject to different effective windspeeds, then this would lead to differences in loss of PRCs and hence estimated sampling rates. The resulting site-specific sampling rates and ranges which could be determined for 5 out of 6 sites were: Košetice ($3.78 \text{ m}^3 \text{ day}^{-1} \pm 5.0\%$); Pallas ($3.63 \text{ m}^3 \text{ day}^{-1} \pm 22.8\%$); Stórhöfði ($11.22 \text{ m}^3 \text{ day}^{-1} \pm 2.8\%$); Birkenes ($3.31 \text{ m}^3 \text{ day}^{-1} \pm 8.3\%$) and Råö ($7.29 \text{ m}^3 \text{ day}^{-1} \pm 14.3\%$) (Table S1). Furthermore, sample A had a higher sampling rate than sample B for Stórhöfði and Råö, while sample B was higher than sample A for Košetice, Pallas and Råö. Among the sites for which site-specific sampling rates could be determined, larger differences in loss of PRCs were found at Pallas and Råö. Yet, while loss of 6 PRCs were used to estimate the sampling rate for both samples from Råö, only 2 and 4 PRCs were used for Pallas. Hence, we are less confident about the estimated sampling rate for Sample A from Pallas (Table S1) which, in turn, makes it difficult to conclude that the two parallels at Pallas were subject to significantly different windspeeds. The results for Råö rather suggest that the differences observed between the two parallels are more of an analytical character as sample A had a higher sampling rate in comparison to sample B while estimated air concentrations were consistently higher for sample A (Fig S2). Figure S2 (b,c) show results for α -HCH and γ -HCH. The relative deviations for α - and γ -HCH were always less than 20 % and ranged from 1 to 13 % and 2 to 18 %, respectively (Table S4). Figure S2d) shows the results for Σ_n DDTs where n varies between the sites. Both

replicates at Stórhöfði and Spitsbergen had concentrations below the MDL for all DDTs and are therefore not included in Fig. S2d). Concentrations under the MDL were also experienced at Birkenes and Pallas and hence a comparison for all four DDT isomers was only possible for Košetice and Råö. The larger deviations among the latter two sites were found for Råö where both the relative difference in sampling rates were larger and air concentrations much lower in comparison to Košetice (Fig. S2d). Figure S2e) shows the results for Σ_n PAHs, where n varies from 1 (Stórhöfði) to 8 (Košetice), while no comparison could be made for Spitsbergen. The relative deviation between the replicates ranged from 2 % (Košetice) to 25 % (Pallas) for Σ_n PAHs. The better agreement found for the Košetice (2 %) site (Table S4) may be attributed to the higher concentration of PAHs experienced at this site (Fig. S2e) in combination with a limited difference in sampling rates compared to Pallas. Figure S2f) shows the results for HCB. The difference between the two parallels ranged from 1 to 22 %. A very good agreement was found at Stórhöfði, Košetice, Birkenes and Råö with 1, 2, 4 and 8 % respectively, while larger discrepancies (~20 %) were observed at the northern sites at Pallas and Spitsbergen. In general, we conclude that there is a reasonable agreement between the two replicates for most substances, with a tendency for better agreement for those substances (e.g. HCHs, HCB) and sites (e.g. Košetice) which tend to experience higher concentrations in air.

160 **References**

161 Tuduri, L., Harner, T., and Hung, H.: Polyurethane foam (PUF) disks passive air samplers: Wind effect on
162 sampling rates, *Environmental Pollution*, 144, 377-383, 10.1016/j.envpol.2005.12.047, 2006.

163
164

Figures

Figure S1 EMEP POP measurement network, showing sites for which both air and precipitation measurements are carried out. Sites presented with names are localities for which POPs were monitored in air using AAS in 2006.

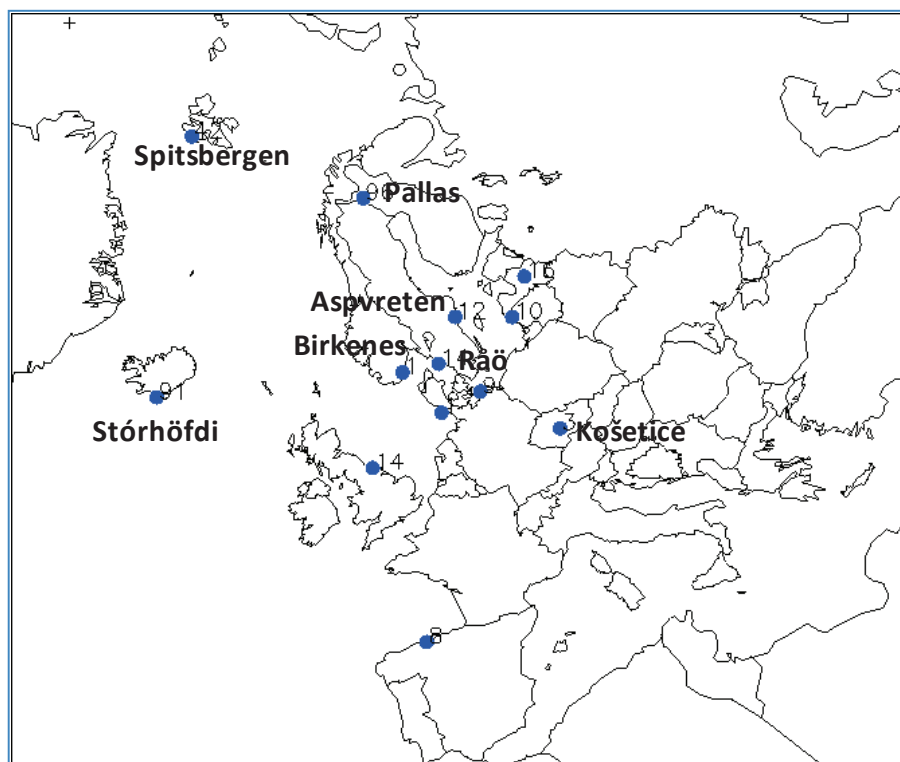


Figure S2 Comparison of selected PAS results for two parallels at six EMEP sites. Note that all results are expressed on a logarithmic scale due to large variability across sites. Secondly, the sum of PCBs, DDTs and PAHs only includes those substances (n) for which both samples at a given site were found to be above MDL. The error bars indicates an estimated uncertainty of +/-35% associated with the chemical analysis alone.

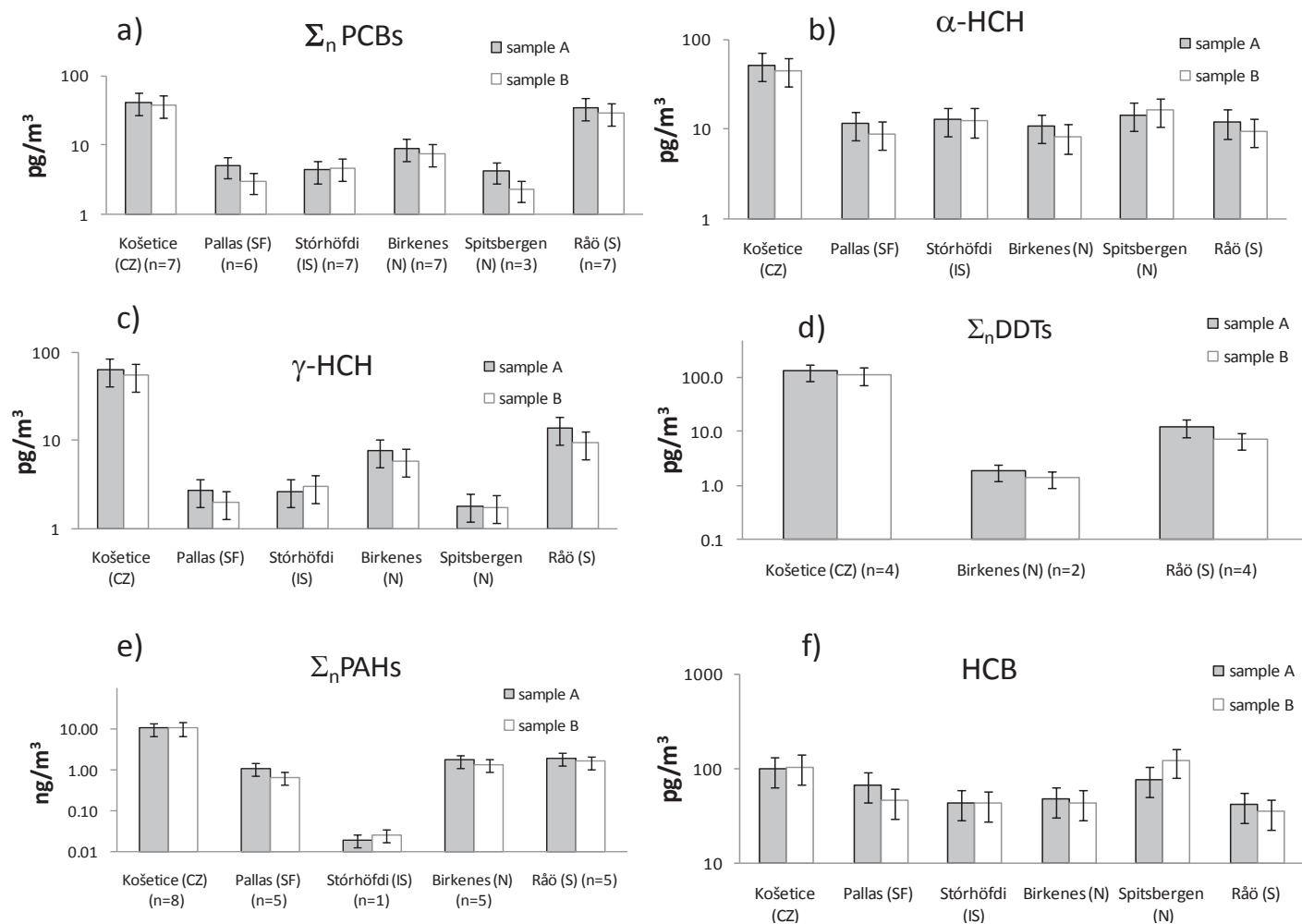
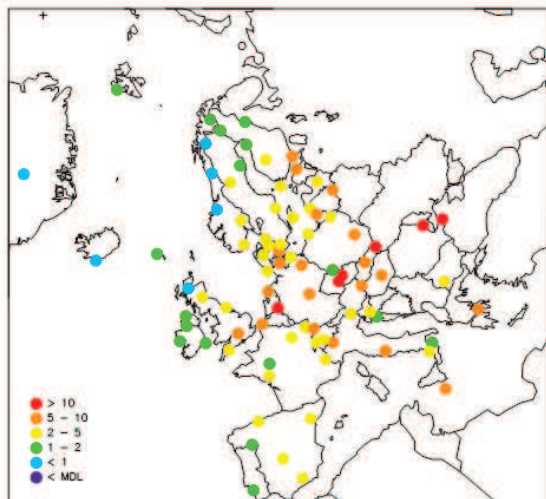


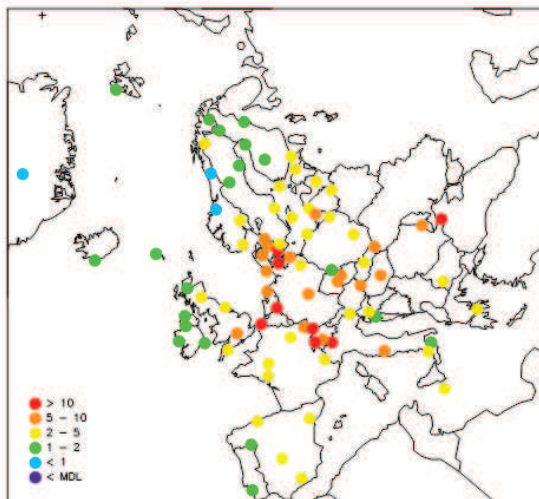
Figure S3 Spatial pattern of individual PCBs in European background air.

Figure S3a)



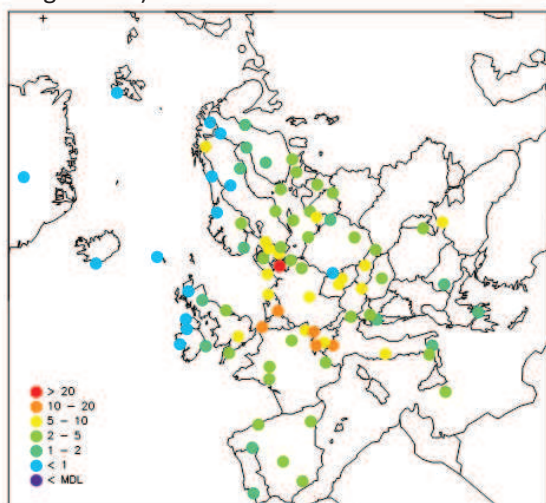
PCB-28 (pg/m³)

Figure S3b)



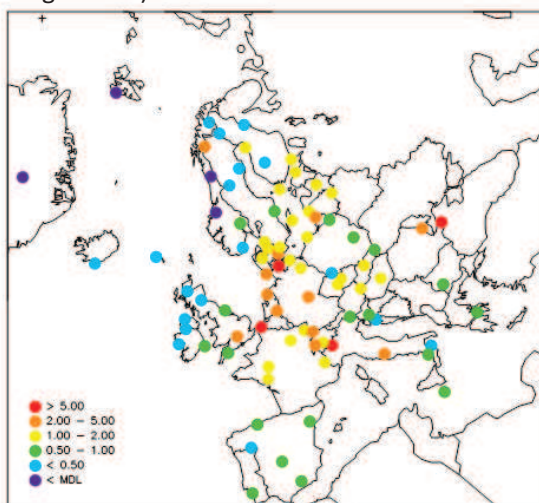
PCB-52 (pg/m³)

Figure S3c)



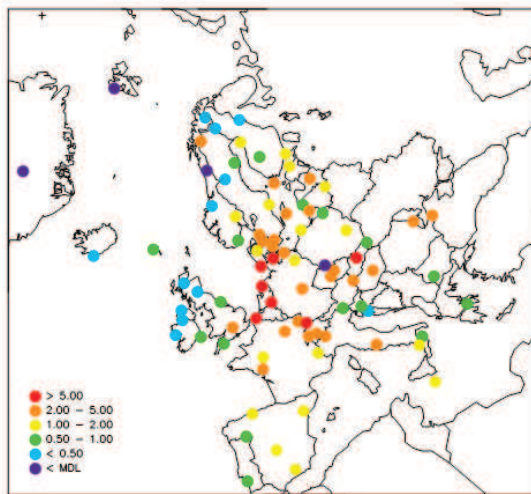
PCB-101 (pg/m³)

Figure S3d)



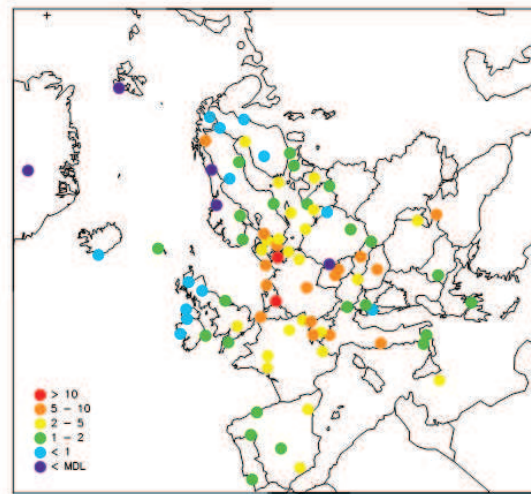
PCB-118 (pg/m³)

Figure S3e)



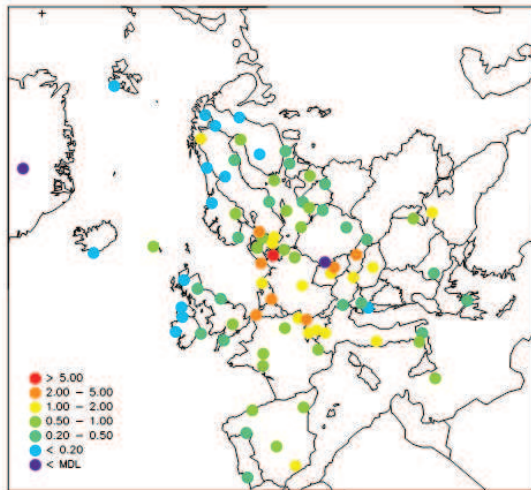
PCB-138 (pg/m³)

Figure S3f)



PCB-153 (pg/m³)

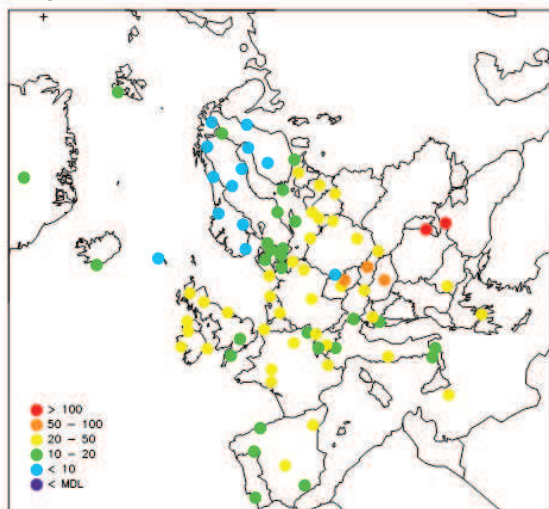
Figure S3g)



PCB-180 (pg/m³)

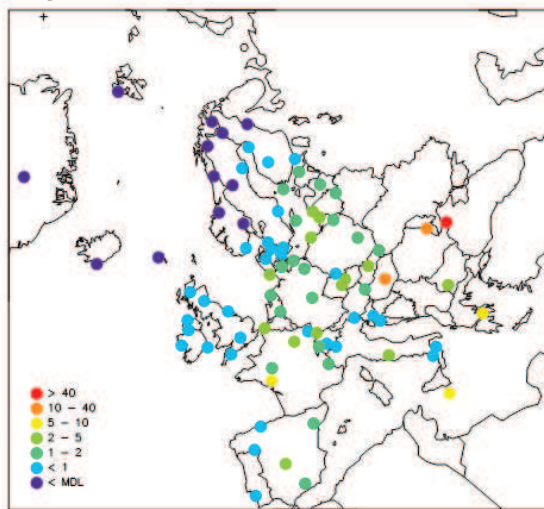
Figure S4 Spatial pattern of individual HCHs in European background air.

Figure S4a)



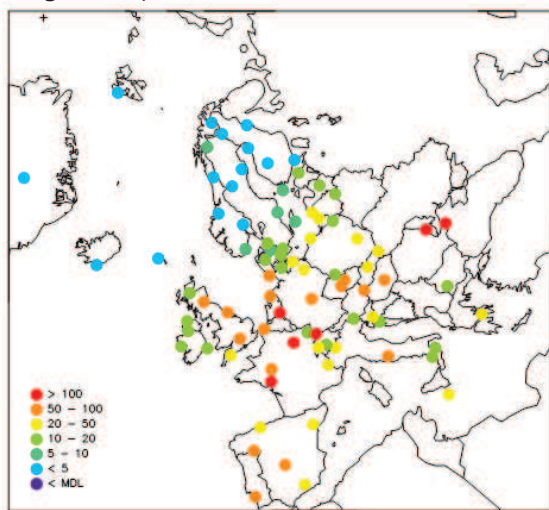
α -HCH (pg/m^3)

Figure S4b)



β -HCH (pg/m^3)

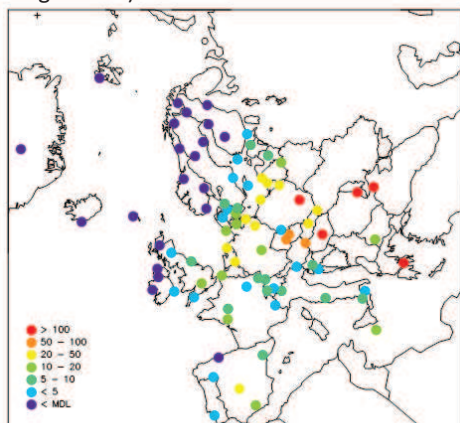
Figure S4c)



γ -HCH (pg/m^3)

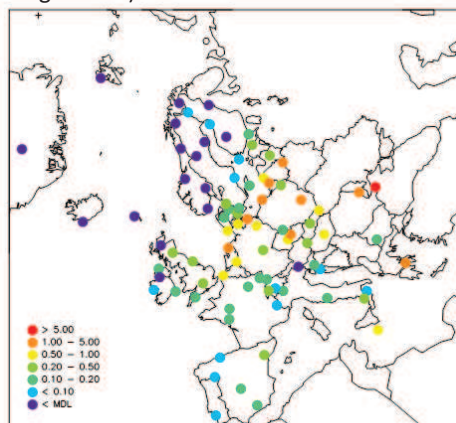
Figure S5 Spatial pattern of individual DDTs in addition to p,p' -DDT/ p,p' -DDE and o,p' -DDT/ p,p' -DDT ratios in European background air.

Figure S5a)



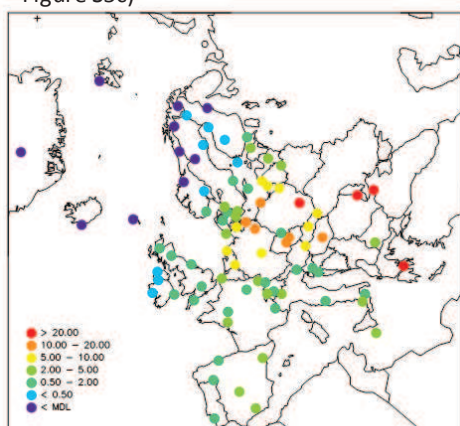
p,p' -DDE (pg/m³)

Figure S5b)



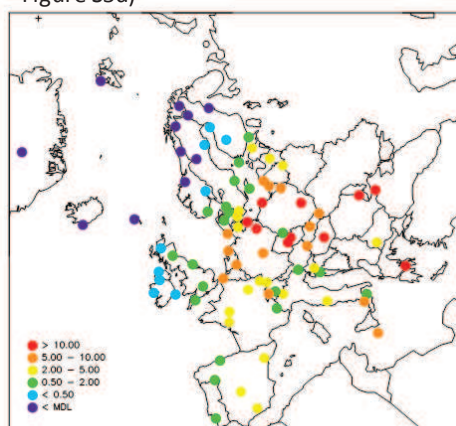
p,p' -DDD (pg/m³)

Figure S5c)



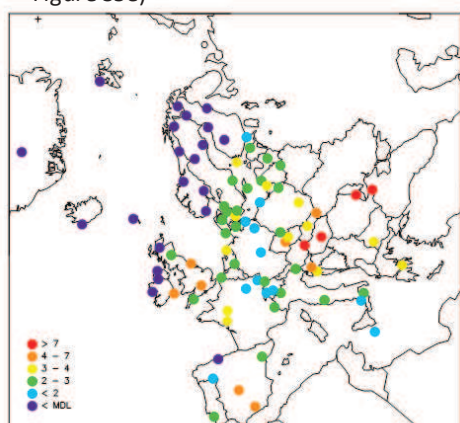
o,p' -DDT (pg/m³)

Figure S5d)



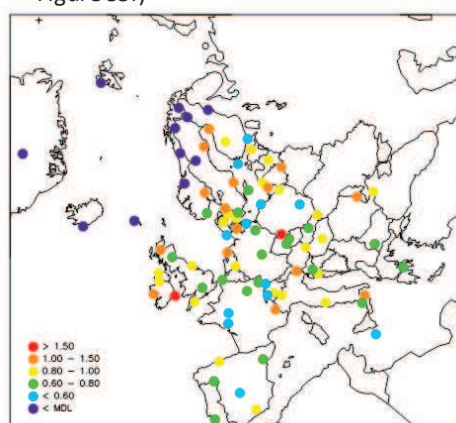
p,p' -DDT (pg/m³)

Figure S5e)



p,p' -DDE/ p,p' -DDT ratio

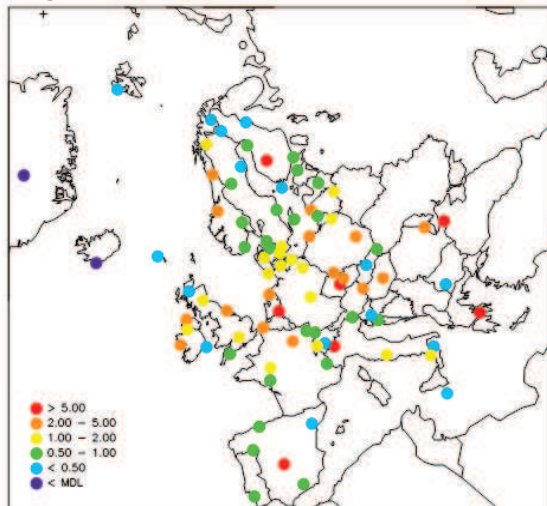
Figure S5f)



o,p' -DDT/ p,p' -DDT ratio

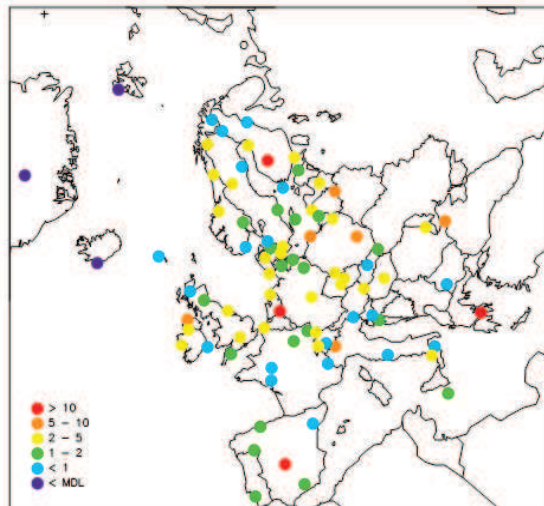
Figure S6 Spatial pattern of individual PAHs in European background air.

Figure S6a)



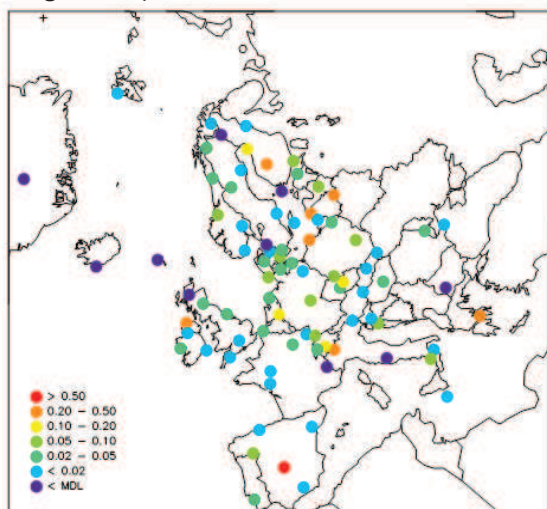
Fluorene (ng/m³)

Figure S6b)



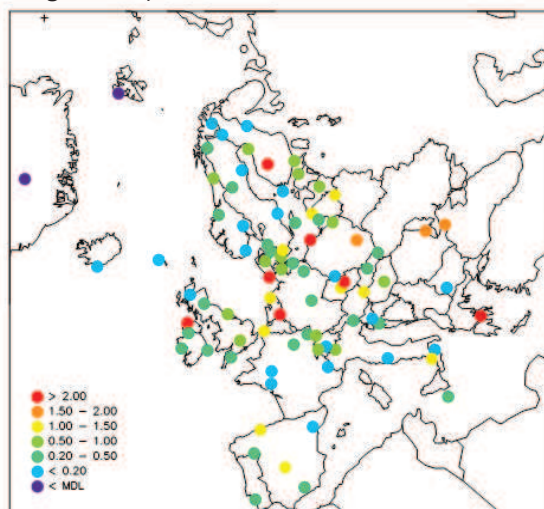
Phenanthrene (ng/m³)

Figure S6c)



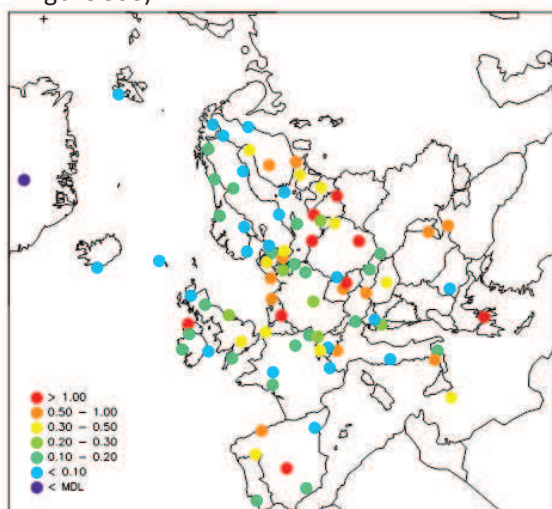
Anthracene (ng/m³)

Figure S6d)



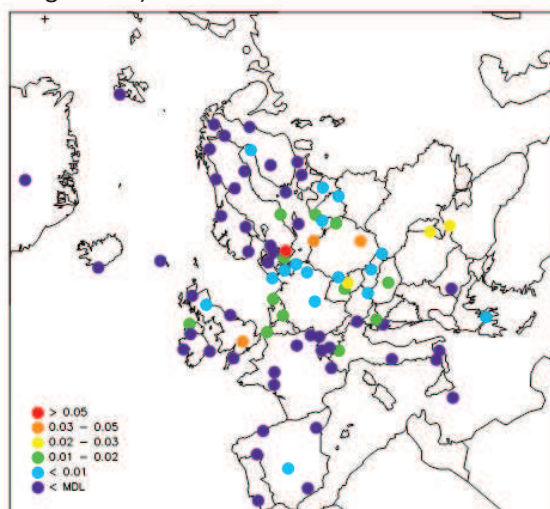
Fluoranthene (ng/m³)

Figure S6e)



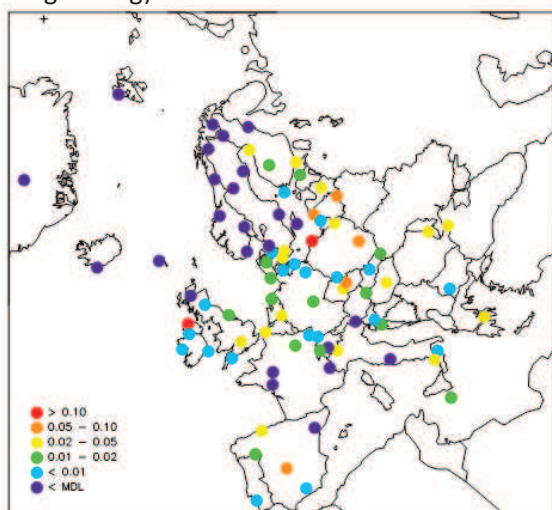
Pyrene (ng/m³)

Figure S6f)



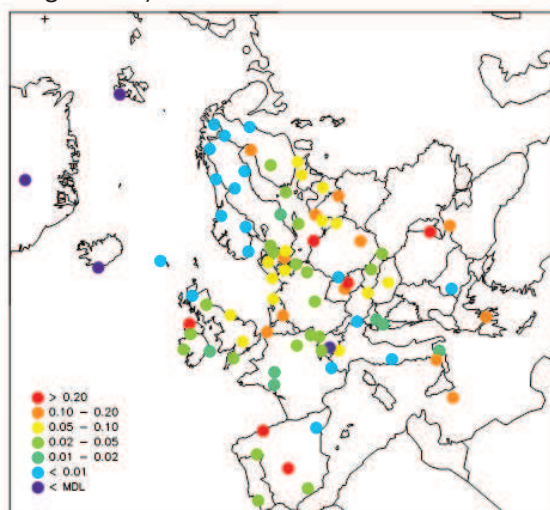
Benzo(a)pyrene (ng/m³)

Figure S6g)



Benzo(a)anthracene (ng/m³)

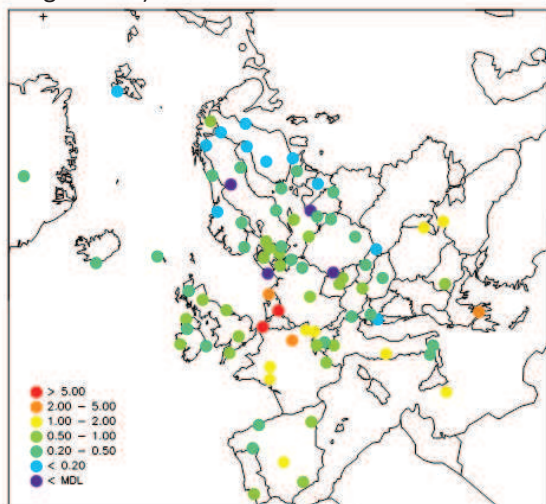
Figure S6h)



Chrysene (ng/m³)

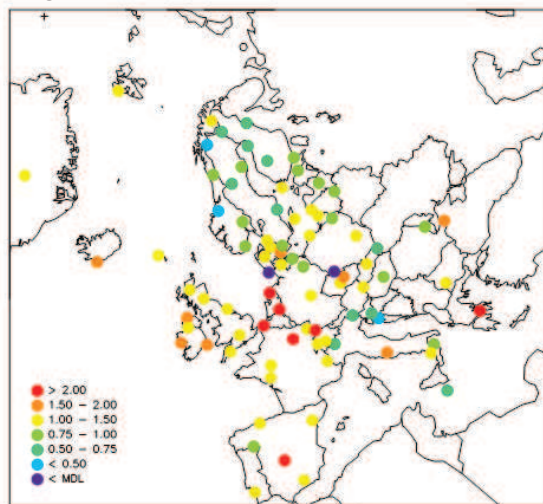
Figure S7 Spatial pattern of individual chlordanes in European background air.

Figure S7a)



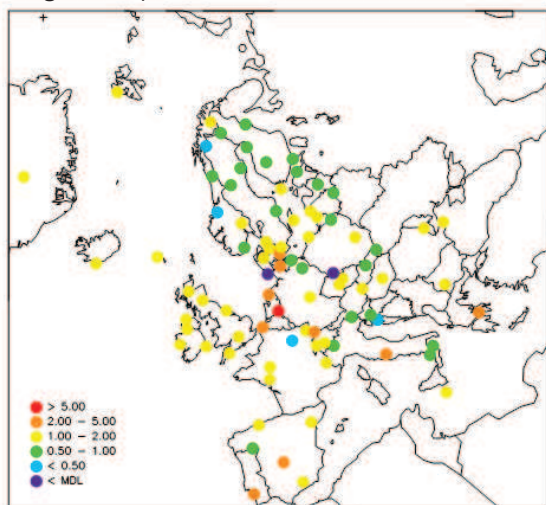
trans-chlordane (pg/m^3)

Figure S7b)



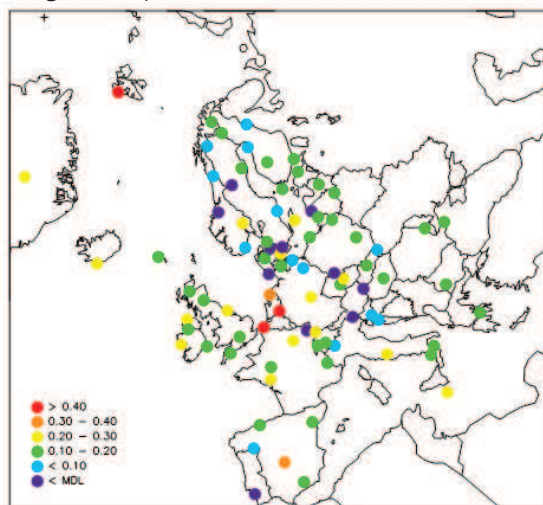
cis-chlordane (pg/m^3)

Figure S7c)



trans-nonachlor (pg/m^3)

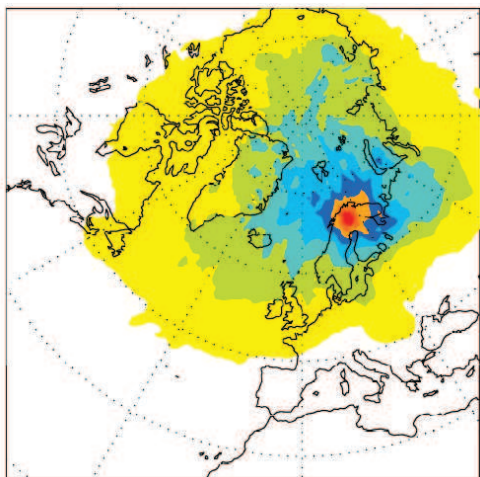
Figure S7d)



cis-nonachlor (pg/m^3)

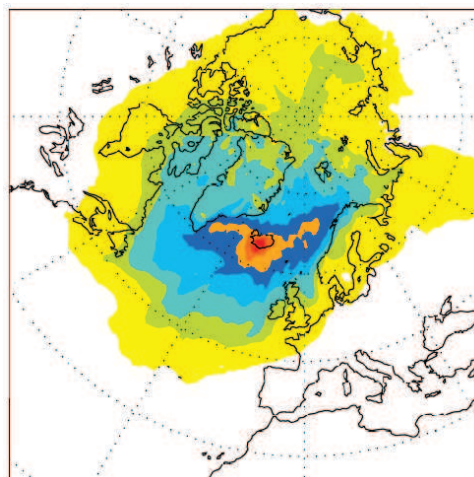
Figures S8-S22: Maps of Footprint ES (emission sensitivity) (a) and EC (emission contribution) (b) for PCB-28 for the PAS sampling period (see text) at selected sites.

Figure S8a)



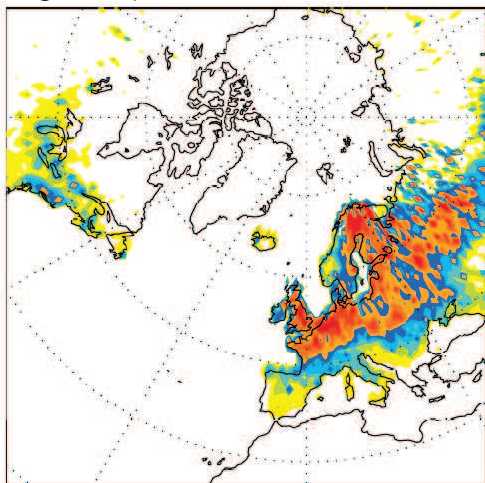
ES map [ns/m³] Pallas

Figure S9a)



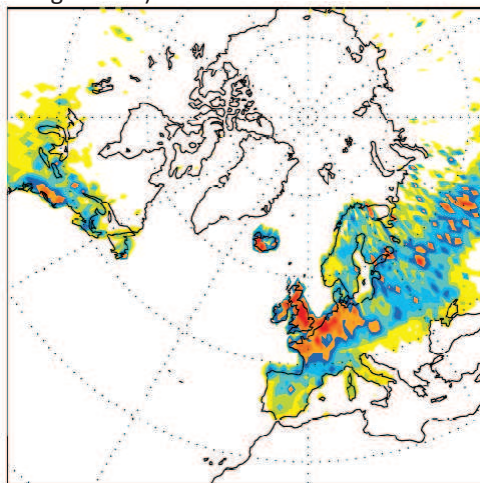
ES map [ns/m³] Stórhöfði

Figure S8b)



EC map 1E-12 [pg/m⁵] Pallas

Figure S9b)



EC map 1E-12 [pg/m⁵] Stórhöfði

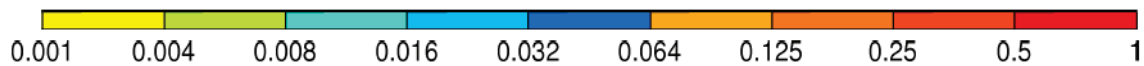
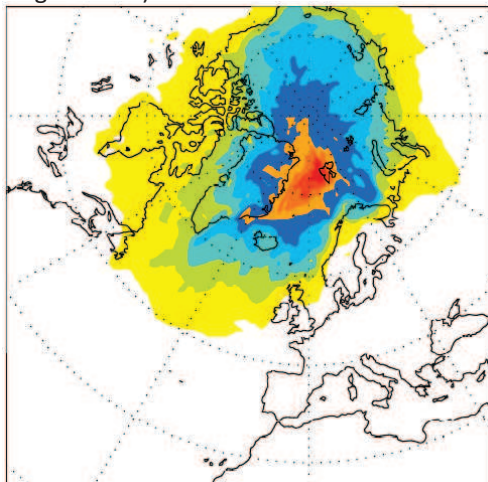
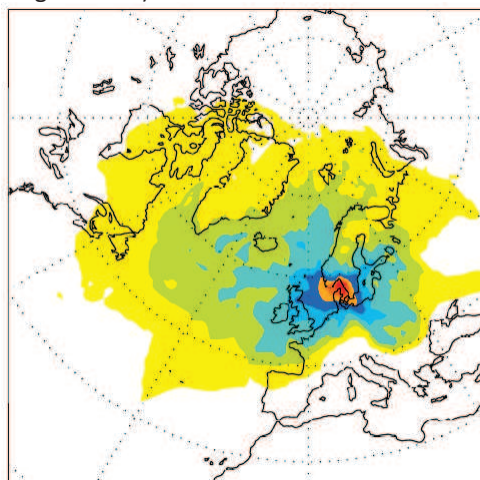


Figure S10a)



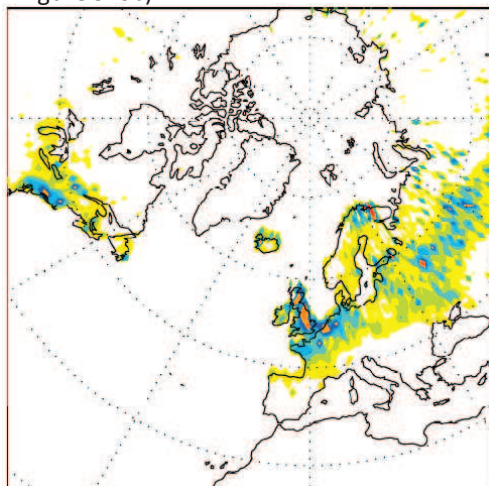
ES map [ns/m^3] Spitsbergen

Figure S11a)



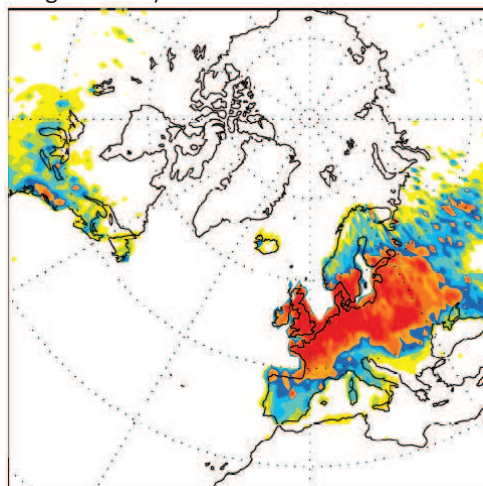
ES map [ns/m^3] Råö

Figure S10b)



EC map $1\text{E-}12 \text{ [pg/m}^5\text{]}$ Spitsbergen

Figure S11b)



EC map $1\text{E-}12 \text{ [pg/m}^5\text{]}$ Råö

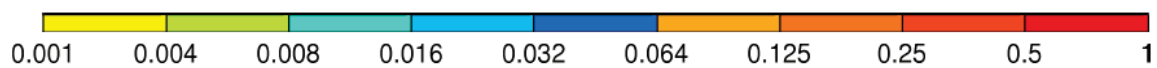
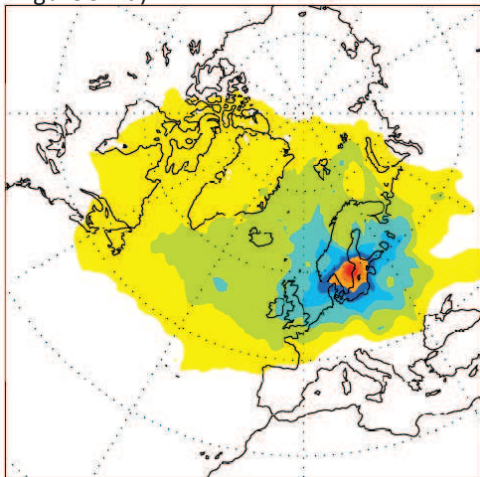
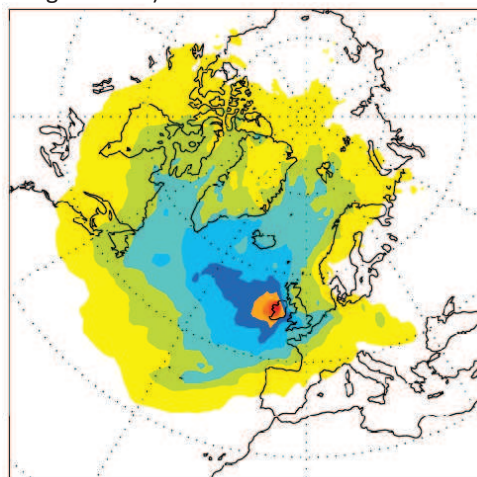


Figure S12a)



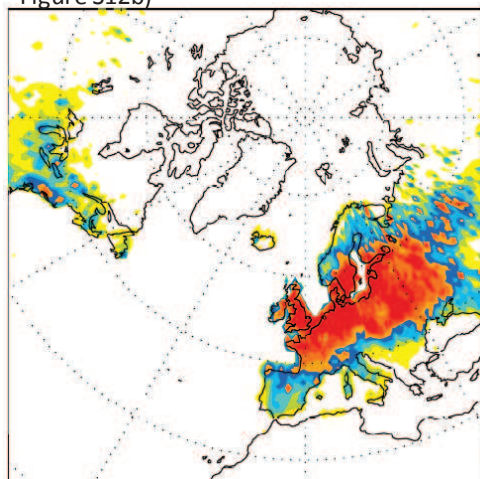
ES map [ns/m³] Aspvreten

Figure S13a)



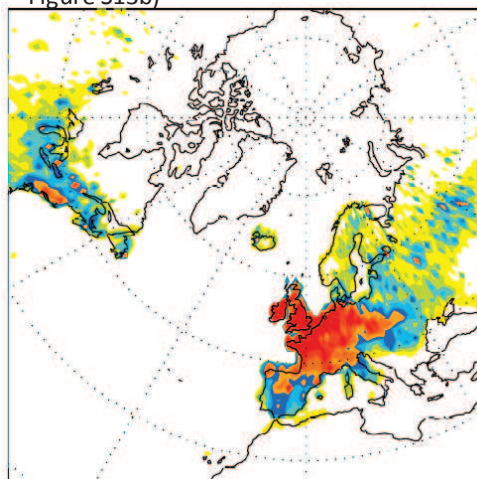
ES map [ns/m³] Mace Head

Figure S12b)



EC map 1E-12 [pg/m³] Aspvreten

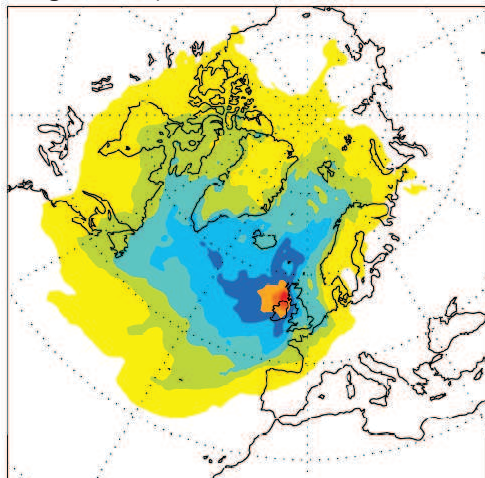
Figure S13b)



EC map 1E-12 [pg/m³] Mace Head

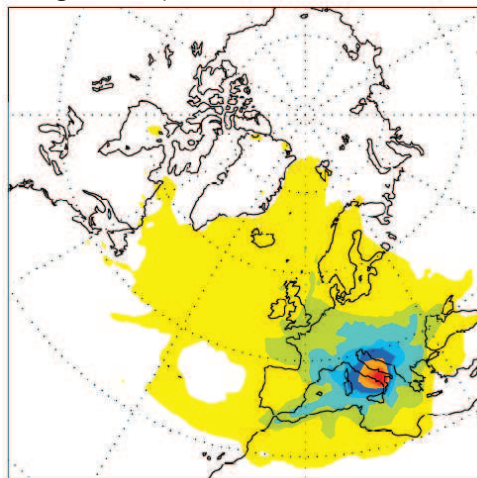


Figure S14a)



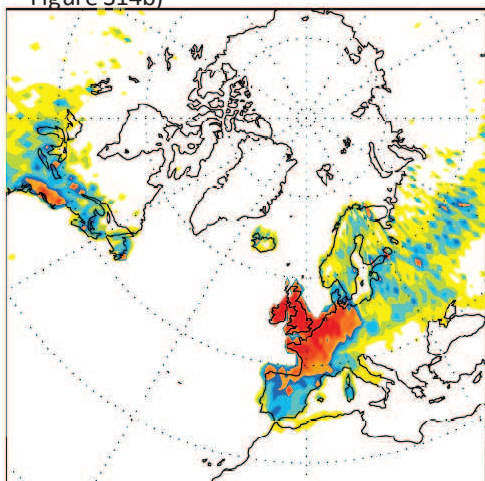
ES map [ns/m³] Malin Head

Figure S15a)



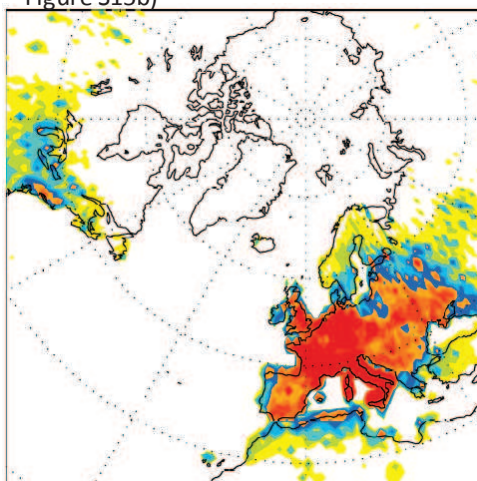
ES map [ns/m³] Longobucco

Figure S14b)



EC map 1E-12 [pg/m⁵] Malin Head

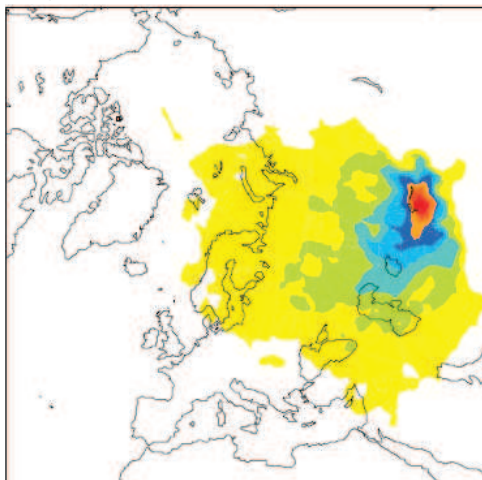
Figure S15b)



EC map 1E-12 [pg/m⁵] Longobucco

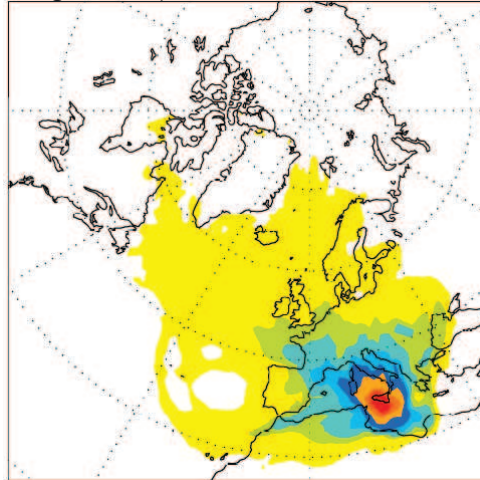


Figure S16a)



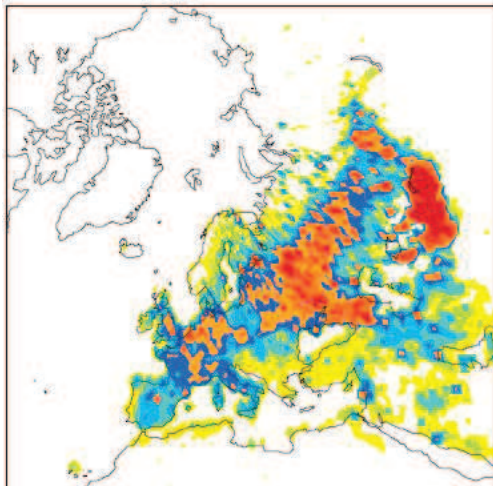
ES map [ns/m³] Borovoje

Figure S17a)



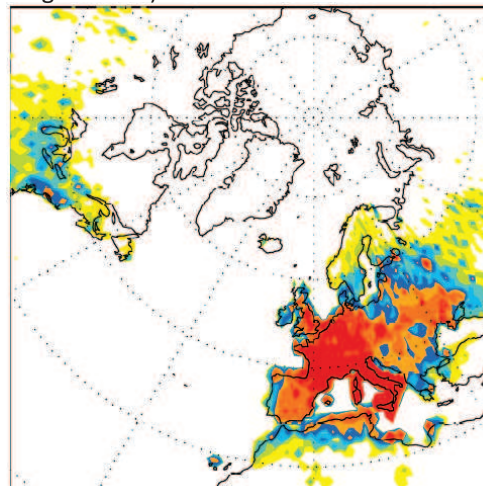
ES map [ns/m³] Giordan Lighthouse

Figure S16b)



EC map 1E-12 [pg/m⁵] Borovoje

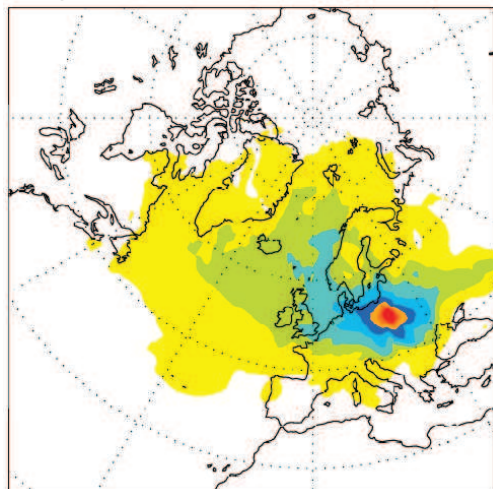
Figure S17b)



EC map 1E-12 [pg/m⁵] Giordan Lighthouse

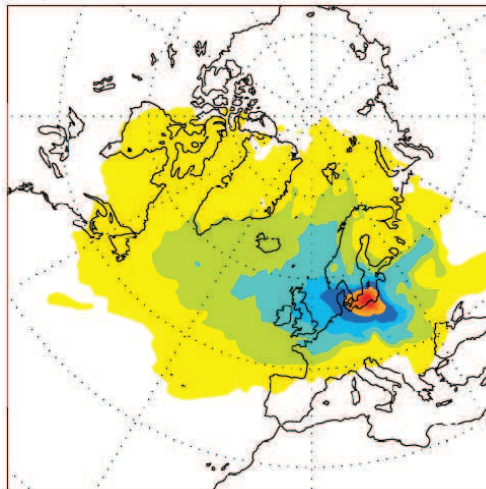


Figure S18a)



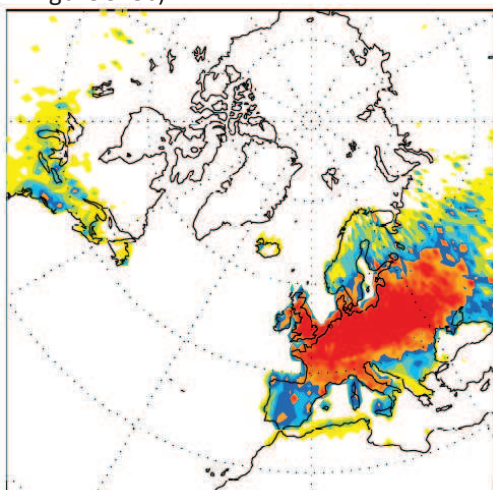
ES map [ns/m³] Jarczew

Figure S19a)



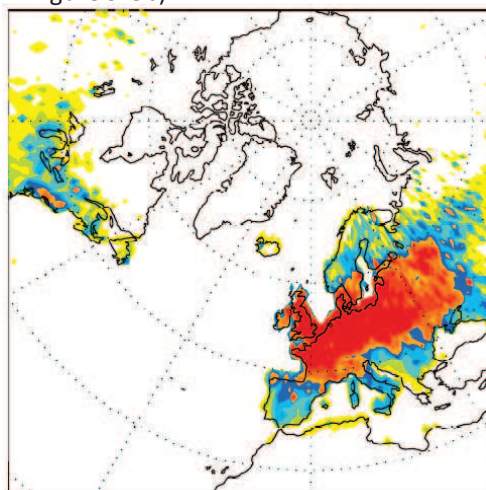
ES map [ns/m³] Leba

Figure S18b)



EC map 1E-12 [pg/m³] Jarczew

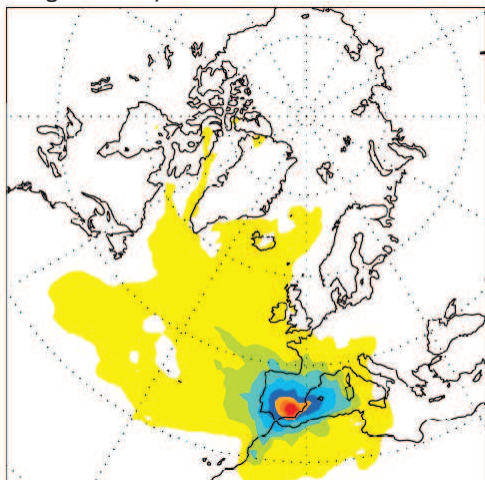
Figure S19b)



EC map 1E-12 [pg/m³] Leba

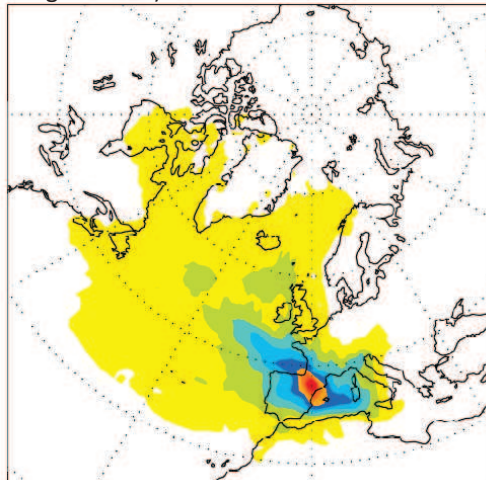


Figure S20a)



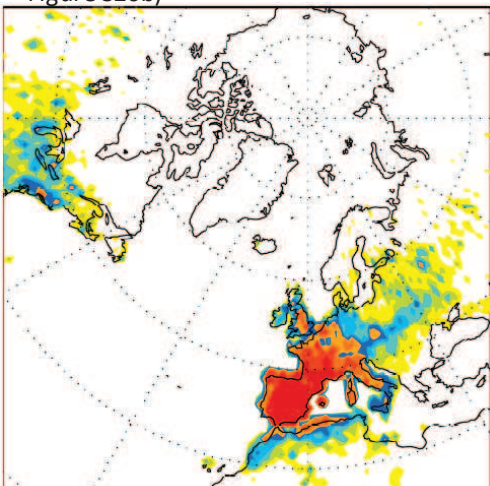
ES map [ns/m³] Viznar

Figure S21a)



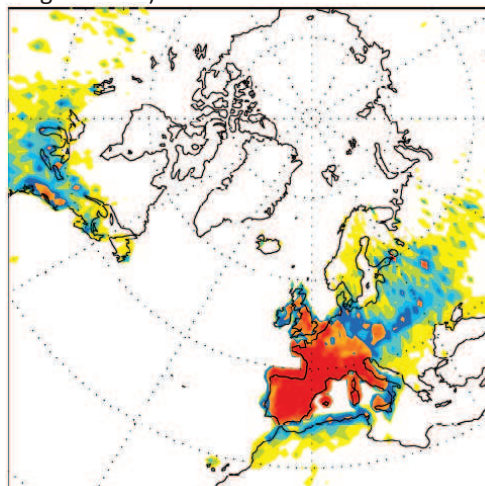
ES map [ns/m³] Els Torms

Figure S20b)



EC map 1E-12 [pg/m⁵] Viznar

Figure S21b)



EC map 1E-12 [pg/m⁵] Els Torms

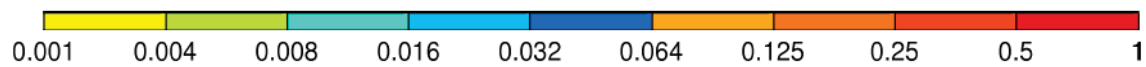
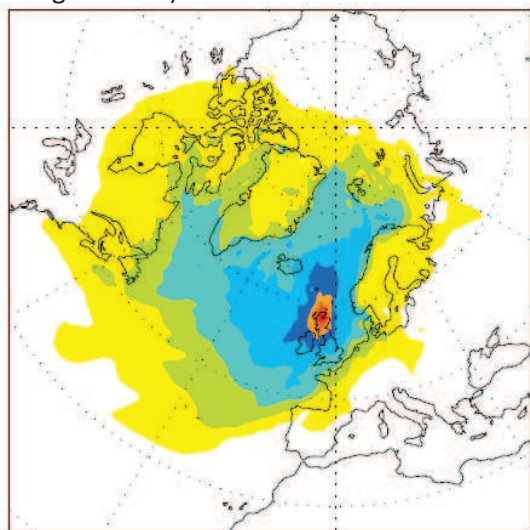
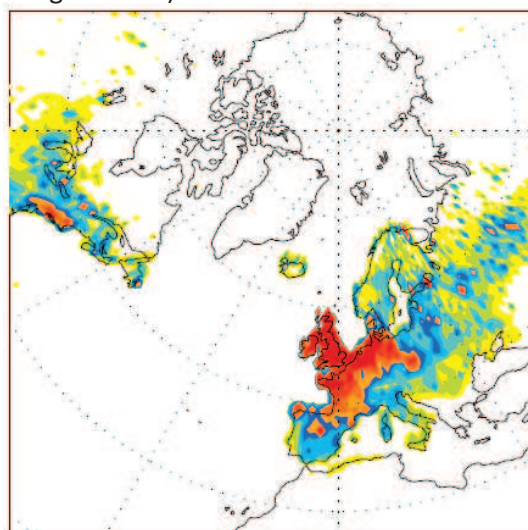


Figure S22a)



ES map [ns/m³] Strath Vaich Dam

Figure S22b)



EC map 1E-12 [pg/m³] Strath Vaich Dam

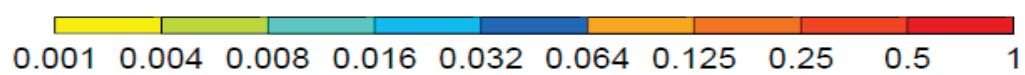
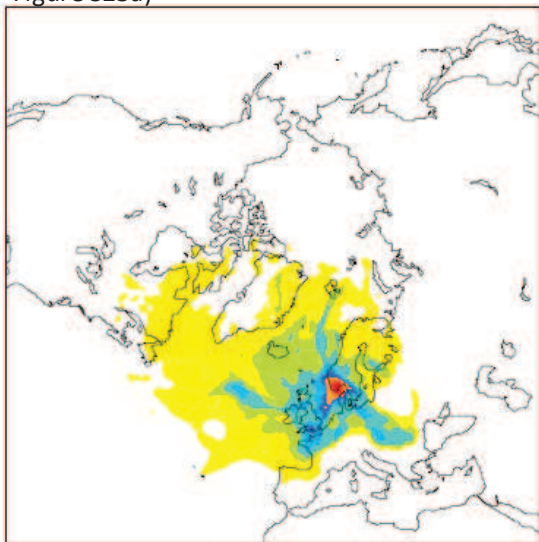


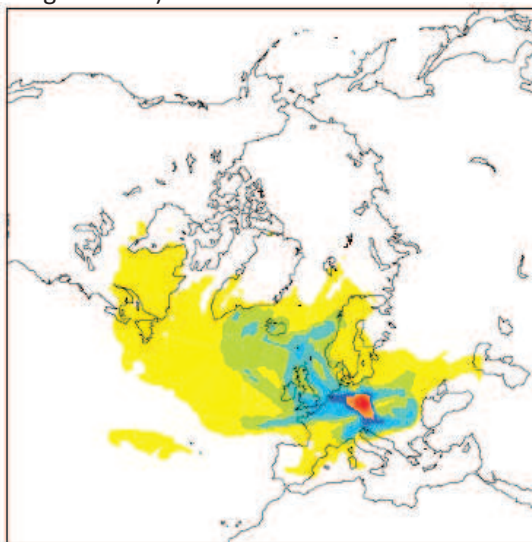
Figure S23-S24 Maps of Footprint ES (emission sensitivity) (a) and EC (emission contribution) (b) for PCB-28 for the AAS sampling period (see text) at Birkenes (23) and Košetice (24) respectively.

Figure S23a)



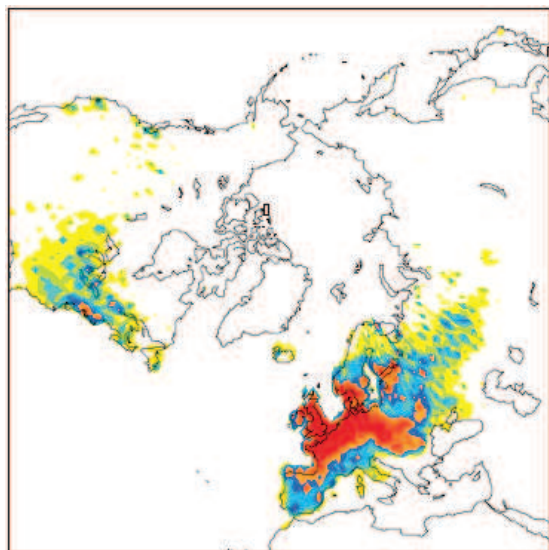
ES map [ns/m^3] Birkenes

Figure S24a)



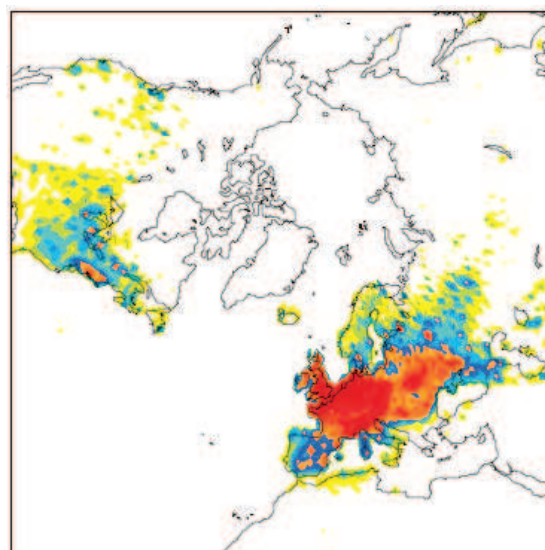
ES map [ns/m^3] Košetice

Figure S23b)

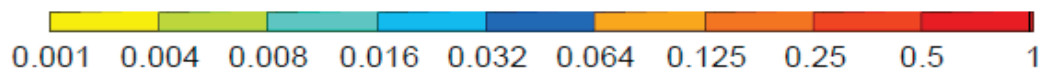


EC map $1\text{E}-12$ [pg/m^5] Birkenes

Figure S24b)



EC map $1\text{E}-12$ [pg/m^5] Košetice



Paper II



Using passive air samplers to assess local sources *versus* long range atmospheric transport of POPs†Anne Karine Halse,^a Martin Schlabach,^a Andy Sweetman,^b Kevin C. Jones^b and Knut Breivik^{*ac}

Received 14th May 2012, Accepted 24th August 2012

DOI: 10.1039/c2em30378g

Passive air samplers (PAS) are cost-efficient tools suitable for spatial mapping of atmospheric concentrations of persistent organic pollutants (POPs). The objective of this study was to use PAS to (i) determine atmospheric concentrations of selected POPs in Norwegian coastal zones with consumption advisories on seafood ($N = 22$), and (ii) evaluate a simple nested monitoring approach to assess the relative influence of local *vs.* long-range atmospheric transport (LRAT) at coastal sites. The latter was facilitated by comparison with data from a coordinated European-wide campaign in which an identical sampling and analytical approach was followed. Air concentrations were calculated based on the loss of performance reference compounds (PRCs), and results are presented for selected polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), dichlorodiphenyltrichloroethanes (DDTs) and chlordanes. Air concentrations of PCBs were generally highest at sites within larger cities and up to about an order of magnitude higher than anticipated on the basis of LRAT alone. The distribution of PAHs and HCB occasionally showed elevated concentrations at coastal sites with ongoing or former industrial activity, while an urban site was significantly influenced by banned insecticides (technical DDT and lindane). Coastal sites were also elevated in α -HCH beyond the anticipated LRAT contribution, which we attribute to volatilization from the sea. We conclude that a simple nested PAS monitoring approach provides useful information for screening efforts aiming to assess both atmospheric burdens as well as the relative significance of local sources in controlling these burdens at sites in contaminated areas.

1. Introduction

Humans may be significantly exposed to various persistent organic pollutants (POPs) through consumption of fish and

seafood from aquatic environments *e.g.* ref. 1 and 2. Any attempts to mitigate further human exposure through this pathway without changing dietary habits would ultimately call for knowledge about sources and pathways of contaminants that are affecting concentrations in fish. Several studies have indicated that the atmosphere constitutes an important pathway through which POPs enter and exchange with aquatic ecosystems. Examples include PCBs in the Great Lakes³ and the Inner Oslofjord⁴ as well as HCHs⁵ and dioxins (PCDD/Fs)^{6,7} in the Baltic Sea. This calls for further studies aimed at identifying the main sources affecting atmospheric concentrations close to contaminated aquatic environments where high levels of POPs

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† Electronic supplementary information (ESI) available: See DOI: 10.1039/c2em30378g

Environmental impact

Passive air samplers (PAS) are particularly suitable for spatial mapping of concentrations of persistent organic pollutants in air. In this study, we have applied PAS with the objective of evaluating the influence of local sources *versus* long-range atmospheric transport (LRAT) in controlling concentrations in air in contaminated areas, using Norwegian coastal zones with consumption advisories on seafood as case studies. Assessment of contributions of LRAT was facilitated by comparison with consistent data from a coordinated European-wide campaign. The study area is considered particularly interesting in the context of our objective as it is located within an urban–remote transect along an expected pollution gradient from more densely populated areas of Europe towards the Norwegian Arctic.

are of concern. Relevant cases in Norway include various coastal zones and fjords for which consumption advisories on fish and seafood exist⁸ due to elevated concentrations of PCBs, PCDD/Fs and/or PAHs.⁹

A key feature of POPs is their ability to undergo LRAT from global source regions to remote areas.^{10,11} As the population density in Norway is relatively low compared to other parts of Europe, LRAT is therefore expected to exhibit a significant influence on concentrations of POPs in air for Norway as a whole. Thus, LRAT could also play a significant role in controlling atmospheric burdens along the Norwegian coast.^{12–14} Indeed, past studies on the occurrence of POPs in air within Norway have mainly been carried out in the context of LRAT and most data are available for background sites *e.g.* ref. 15 and 16. However, the atmospheric burden in coastal zones with consumption advisories on seafood typically coincides with areas with a higher population density in Norway. Concentrations of POPs in air in these coastal zones may therefore additionally be influenced and potentially enhanced by atmospheric emissions of POPs from Local Sources (LS). Examples are emissions of PAHs and PCDD/Fs from *e.g.* industrial activities,^{17,18} and PCBs from *e.g.* building materials.^{19–22} Additionally, as our contaminated coastal zones are located within an interesting urban–remote transect along an expected pollution gradient from more densely populated areas of Europe towards the Norwegian Arctic *e.g.* ref. 15 and 16, this makes the study region an interesting area for studying LS vs. LRAT in controlling concentrations of POPs in air. Furthermore, specific topographic features in some coastal zones (*e.g.* narrow fjords surrounded by steep mountains) may cause local emissions to be “trapped” due to limited atmospheric circulation,²³ leading to locally elevated air concentrations.

Taken together, the atmospheric burden of POPs in contaminated coastal zones of Norway may thus in part be controlled by LS and in part by LRAT. So far, no study has been carried out to assess the relative importance of these two sources within these coastal zones. Yet, being able to discriminate between these two sources is of immediate relevance for the assessment of potential control strategies, including relevant monitoring efforts in support of the Stockholm Convention on POPs (SC). The relative importance of the two could furthermore be anticipated to differ, depending on the contaminant in question. As the key goal of the SC is to protect human health and the environment from these substances by reducing or eliminating releases to the environment, it becomes important to carry out further studies to help assess whether POPs are actually becoming reduced or eliminated, or whether there are sources which remain active. The Global Monitoring Plan (GMP) for POPs specifically requests comparable monitoring data to support evaluations assessing whether the goal of the SC is reached, and highlights the use of passive air samplers for spatial and temporal trends assessment.²⁴

The objective of this study was to carry out a passive air sampling campaign (PAS) to (i) determine atmospheric concentrations of selected POPs in Norwegian coastal zones and fjords where consumption advisories on seafood exist, and (ii) gain insights into the relative importance of LRAT and LS for individual sites. The latter was made possible as this campaign was coordinated in time with a comprehensive PAS campaign across European background sites,²⁵ which in turn facilitates empirical estimates of the anticipated background concentration as

attributed to LRAT alone. Finally, we conclude by discussing the merits and limitations of the PAS approach to assess LRAT *versus* LS in contaminated areas as well as remaining knowledge gaps.

2. Materials and methods

2.1. Theory

The air samples were collected by passive air samplers (PAS) using polyurethane (PUF) disks. We refer to the literature for a detailed account of this method and its application *e.g.* ref. 26–30. In brief, the PUF disk has a high ability to sorb semi-volatile organic compounds in air. During exposure, the chemicals will accumulate in the sampling material, and the amount on the PUF disk is equivalent to the rate of uptake minus the rate of loss. The uptake is airside controlled and a function of the planar area (A_{PUF}) of the disks, the mass transfer coefficient (k_A) and the concentration in air (C_A). The uptake is initially linear, but will reach equilibrium in time.²⁶ Depending on the octanol–air partition coefficient (K_{OA}) of individual compounds, the duration of the linear phase will vary and the more volatile compounds (*i.e.* low K_{OA}) will reach equilibrium faster than the less volatile compounds.²⁹ The PUF disk is placed between two stainless steel metal domes³¹ which protect the sampling media from precipitation, particle deposition, sunlight and shields against wind speed effects (*e.g.* Tuduri *et al.*³²).

2.2. Sampling

Air samples were collected using PAS deployed along the Norwegian coast for three months during late summer 2006, see Fig. 1. The 22 coastal sites were selected on the basis of advisories on the consumption of seafood caused by elevated levels of POPs,⁸ see Table S1 in the ESI.† Additionally, two samplers were deployed in a few coastal sites (Kristiansand, Bergen, Trondheim, Tromsø, Narvik and Bergen) to evaluate spatial variability within contaminated coastal zones. All PAS samplers were deployed at least 1.5 meters above the ground in close vicinity to the sea. Areas close to major roads and industrial activity were avoided, while preference was given to parks and private properties in an attempt to aim for representative “background” concentrations in each coastal zone.

During the same period, a coordinated PAS campaign was carried out at 86 background sites across 34 European countries.²⁵ Site details for the Norwegian ($N = 5$) and Swedish ($N = 7$) background sites which were included in the European campaign and used to assess contribution from LRAT in this study (see Section 2.5) are additionally listed in Table S1† (see also Fig. 1).

2.3. Sample preparation, clean-up and analysis

Details involving solvents used, sample preparation, clean-up and analysis are previously described by Halse *et al.*,²⁵ and only a brief summary is presented here. The PUF disks were pre-cleaned, spiked with performance reference compounds (PRCs),³³ wrapped in double layer of alumina foil and stored in zip-lock bags prior to deployment. After exposure, the air samples together with field and method blanks were added a mixture of internal standards and Soxhlet extracted using *n*-hexane as a solvent. The air samples were analyzed for



Fig. 1 Map showing the locations for coastal sites (this study), and Norwegian and Nordic background sites.²⁵ (1) Oslo, (2) Holmestrand, (3) Tønsberg, (4) Nøtterøy, (5) Kragerø, (6) Arendal, (7a, b) Kristiansand I, II, (8) Farsund, (9) Fedafjorden, (10) Flekkefjord, (11) Stavanger, (12) Sauda, (13a, b) Bergen I, II, (14) Sunndalsøra, (15a, b) Trondhjem I, II, (16) Hommelvik, (17) Brønnøysund, (18) Mo i Rana, (19a, b) Narvik I, II, (20) Ramsundet, (21) Harstad, (22a, b) Tromsø I, II, (I) Birkenes, (II) Hurdal, (III) Kårvatn, (IV) Tustervatn, (V) Karasjok, (VI) Vavihill, (VII) Råö, (VIII) Hoburgen, (IX) Aspöreten, (X) Bredkälen, (XI) Vindeln, (XII) Abisko.

polychlorinated biphenyls (PCBs) (PCB-28, -52, -101, -118, -138, -153, -180), polycyclic aromatic hydrocarbons (PAHs) (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)pyrene, benz(*a*)anthracene, chrysene), hexachlorocyclohexanes (HCHs) (α -, β - and γ -HCH), hexachlorobenzene (HCB), dichlorodiphenyltrichloroethanes (DDTs) (*p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT) and chlordanes (*trans*-Chlordane, *cis*-Chlordane, *trans*-nonachlor, *cis*-nonachlor). The extracts were divided into two aliquots prior to the clean-up procedures. One aliquot for the determination of the acid stable compounds (Σ_7 PCBs, Σ_3 HCHs, Σ_4 DDTs, HCB, Σ_4 Chlordanes) was treated with sulphuric acid followed by a fractionation using a silica

column. The other aliquot for the determination of PAHs was cleaned using a deactivated silica column. After the clean-up procedures, both aliquots were reduced to ~ 50 μ l by a gentle stream of nitrogen and recovery standards were added. PCBs, HCHs, DDTs, HCB and PRCs (d_6 - γ -HCH and selected PCBs, see the ESI[†]) were analyzed using gas chromatography coupled to high resolution mass spectrometry in an electron impact (EI) mode (GC/HRMS). PAHs were analyzed using gas chromatography coupled to low resolution mass spectrometry (GC/LRMS), while the chlordanes were analyzed using low resolution gas chromatography coupled to mass spectrometry in an electron capture negative ion mode (GC/ENCI-MS).²⁵

2.4. Deriving air concentrations

An estimate of the sampled volume of air is needed in order to back-calculate air concentrations for individual compounds. For these calculations, information on PUF characteristics, air temperature, measured loss of PRCs and their temperature-dependent K_{OA} values were used to calculate site specific sampling rates *e.g.* ref. 26, 28, 33 and 34. The air temperatures used for these estimations were derived from the Norwegian Meteorological Institute,³⁵ except for Birkenes and Hurdal where temperatures are measured by NILU. A detailed description of the estimation of air concentrations is given by Halse *et al.*²⁵ and references therein. The site-specific sampling rates and number of PRCs characterized by a sufficient loss for each site (>40%) are presented in Table S1.† For sites experiencing an insufficient loss of PRCs (<40%),³⁴ the default sampling rate of 3.5 m³ d⁻¹ proposed by Harner *et al.*³⁶ was used for calculating the effective volume of air sampled.

2.5. Quality assurance and quality control (QA/QC)

For assessments of the quality assurance and quality control, the analytical procedures were monitored using NS/EN ISO/IEC 17025 accredited routines. For quantification, a calibration/quantification solution was injected for every fourth sample. A standard reference material (SRM 1588) from the National Institute of Standards and Technology (NIST), containing organic compounds in cod liver oil was analyzed routinely for PCBs, HCHs, DDTs, HCB and chlordanes. For PAHs, a dilution of a PAH mixture containing 16 compounds (NE 1378) from Promochem GmGH was analyzed for each run. To furthermore verify the quantification, the retention time for the ¹²C-labeled compound should not be more than 3 seconds later than its corresponding ¹³C-labeled isomer. In addition, the 3 : 1 isotope ratio between ¹²C and ¹³C isomers must be within 20% of the theoretical value for the two monitoring masses.

2.5.1. Field and method blanks. Field ($N = 5$) and method blanks ($N = 5$) consisting of pre-cleaned spiked PUF disks were extracted and analyzed in the same way as the exposed samples. Field blanks were prepared to discover possible contamination during general handling and transport, while the method blanks focus more on laboratory conditions (*e.g.* solvents, equipment, and adsorbents). The blank values were converted into concentrations by the use of averaged values for the sampling rate (4.08 m³ d⁻¹), temperature (14 °C) and deployment time (92 days) from the deployed coastal samples.

2.5.2. Method detection limit (MDL). The method detection limits (MDLs) (Table 1) were calculated for the individual compounds as the average blank (field and method) concentration ($N = 10$) plus 3 times the standard deviation (SD) (Table 1). The field and method blanks had similar values. When the target compound was not identified in the blanks, an instrumental detection limit (IDL, signal/noise 3 : 1) divided by two was used instead to estimate a MDL.³⁴ A different approach was used for PAHs, where the lowest measured range for air samples for the instrument was 0.01–0.02 ng m⁻³. For individual PAHs only 0.01 ng m⁻³ was used, while half of this measured value was used

for samples below this value.²⁵ When the target compound was absent in the exposed samples, ½MDL was used for statistical treatment. The concentrations were not blank corrected as the blanks had both low and stable values.

2.5.3. Recoveries. Recoveries were compiled for both the internal standards and for the PRCs, where the latter were provided from the field and method blanks as detailed in the ESI (S1.1, S1.2) and Table S2.† Quantification was based on the added ¹³C or ²D-labeled internal standards, hence the sample concentrations are automatically corrected for recovery.

2.5.4. Uncertainties. There are recognized uncertainties associated with procedures used to back-calculate air concentrations from PAS *e.g.* ref. 37–39 and as also discussed by Halse *et al.*²⁵ Different factors during the chemical analysis will furthermore influence the uncertainty in the air concentrations, *e.g.* sample clean-up, accuracy in the standards and instrumental conditions. The overall uncertainty associated with the chemical analysis was estimated to be ±35%.²⁵ Internal and recovery standards were used to compensate for possible loss during sample clean-up; field blanks were furthermore included to evaluate possible contamination during transport and general handling. The method blanks were used to assess laboratory conditions. More information on the quantification of these uncertainties is provided by Halse *et al.*²⁵

2.6. Estimating the contribution from LS vs. LRAT

The availability of comparable and consistent data for European background air enables empirical estimates of the expected contribution attributed to LRAT alone. Specifically, the ratio (R) of observed concentrations at individual coastal sites divided by the anticipated “background” concentration attributed to LRAT alone provides insights into the significance of LS *versus* LRAT (eqn (1)):

$$R = \frac{C(\text{coastal site})}{C(\text{background})} \quad (1)$$

Thus, $R > 1$ would indicate the influence of LS; $R > 2$ would indicate the predominance of LS, while $R \leq 1$ would indicate the predominance of LRAT. The latter would also indicate that the LRAT contribution is overestimated for a given compound/compound group at a specific coastal site.

This approach thus requires an estimate of the background concentration attributed to LRAT alone. As both campaigns were carried out at the same time, temporal variability can be ignored. However, there is an expected and observed spatial variability in European background air,²⁵ which merit consideration. For this work, three scenarios for the background concentration were therefore explored: (i) a Norwegian background, defined as the median air concentration for the Norwegian background sites ($N = 5$, Fig. 1), (ii) a Nordic background, defined as the median air concentration for all background stations in two Nordic countries (Sweden and Norway) combined ($N = 12$, Fig. 1), and finally (iii) a European background, defined as the median air concentration from all European background sites ($N = 86$).²⁵ Consequently, three

Table 1 Concentrations of selected PCBs, HCHs, DDTs, HCB, chlordanes (pg m⁻³) and selected PAHs (ng m⁻³) in air from coastal sites in Norway

Compounds	Average \pm S.D	Median	Measured range		MDL	% above MDL	Max/min ratio (MMR)
			Deployed samples	Blanks			
PCB-28	5 \pm 3	4	1.0–10	0.09–0.3	0.4	100	10
PCB-52	6 \pm 5	5	1.2–21	0.07–0.5	0.6	100	18
PCB-101	5 \pm 5	3	0.9–19	0.06–0.6	0.7	100	21
PCB-118	1.7 \pm 1.8	1	0.2 ^a –7.3	0.04–0.3	0.4	93	>18
PCB-138	1.7 \pm 1.4	1	0.3 ^a –6.2	0.05–0.5	0.5	93	>12
PCB-153	2.5 \pm 2	2	0.5 ^a –8.7	0.08–0.8	0.9	88	>9
PCB-180	0.5 \pm 0.4	0.4	0.09 ^a –1.6	0.02–0.1	0.2	93	>9
Σ_7 PCBs	21 \pm 17	17	4.5–72				>16
Fluorene	4 \pm 6	2	0.4–32	0.006–0.03	0.04	100	74
Phenanthrene	6 \pm 7	5	0.6–41	0.01–0.07	0.1	100	72
Anthracene	0.2 \pm 0.3	0.1	0.007 ^a –1.5	0.001–0.008	0.01	96	>108
Fluoranthene	1.4 \pm 1.6	0.9	0.1–6.5	0.003–0.02	0.03	100	54
Pyrene	0.8 \pm 0.9	0.5	0.07–3.9	0.003–0.02	0.02	100	55
Benz[a]anthracene	0.03 \pm 0.03	0.02	0.005 ^a –0.2	0.005 ^c	0.01	85	>15
Chrysene	0.08 \pm 0.06	0.06	0.02–0.3	0.005 ^c	0.006	100	14
Benzo[a]pyrene	0.006 \pm 0.002	0.005	0.005 ^a –0.01	0.005 ^c	0.01	11	>1
Σ_8 PAHs	13 \pm 16	9.5	1–84				>68
α -HCH	16 \pm 3	15	11–22	0.1–0.9	1	100	2
β -HCH	0.3 \pm 0.2	0.3	0.1 ^a –0.8	0.003 ^d –0.2	0.2	70	>4
γ -HCH	18 \pm 21	15	4.5–115	0.1–1.0	1	100	26
Σ_3 HCHs	34 \pm 22	31	19–133				>7
HCB	58 \pm 50	47	42–305	0.4–1.1	1	100	7
<i>p,p'</i> -DDE	3 \pm 2	1	1.3 ^a –7.8	0.1–2.4	3	48	>3
<i>p,p'</i> -DDD	0.2 \pm 0.2	0.1	0.04 ^b –1.0	0.001 ^d –0.2	0.2	33	>4
<i>o,p'</i> -DDT	1.4 \pm 2.04	0.9	0.2 ^a –11	0.002 ^d –0.4 ^c	0.4	93	>28
<i>p,p'</i> -DDT	2.1 \pm 4.8	1.0	0.2 ^a –26	0.005 ^d –0.3	0.3	85	>86
Σ_4 DDTs	6.5 \pm 8.4	3.4	1.8–45				>26
<i>trans</i> -Chlordane	0.9 \pm 1.0	0.5	0.02 ^a –3.9	0.004 ^d –0.03	0.04	96	>91
<i>cis</i> -Chlordane	1.4 \pm 0.8	1.2	0.5–4.0	0.006–0.1	0.1	100	8
<i>trans</i> -Nonachlor	1.3 \pm 0.7	1.1	0.4–3.4	0.002 ^d –0.06	0.09	100	10
<i>cis</i> -Nonachlor	0.2 \pm 0.2	0.2	0.02 ^a –0.7	0.002 ^d –0.02	0.03	96	>20
Σ_4 Chlordanes	3.8 \pm 2.6	3.1	1.1–11				>11

^a The lower limit is 1/2MDL. ^b The lower limit was influenced by interference. ^c The component was not detected in the blanks and 1/2IDL (instrument detection limit) value was used. ^d The lower limit is 1/2IDL. ^e The upper limit was influenced by interference. ^f Lower and upper values were below IDL.

corresponding ratios were calculated: R_{NW} (Norwegian background), R_{ND} (Nordic background) and R_{EU} (Europe). Each of these background estimates has its own merits and limitations, which make it interesting to explore the impact of different predicted LRAT contributions on the overall results. In brief, while the former two estimates have a more limited empirical basis ($N = 5$ and 12) than the latter ($N = 86$), the European estimate is considered less representative for the expected “true” background air concentrations in Norway. To further assess the spatial variability in estimated background air concentrations (LRAT contributions), we used the maximum (max) and minimum (min) observed background air concentration within both the Norwegian and Nordic datasets to derive an estimate of the uncertainty in R . This approach was not considered appropriate for the European dataset due to a much larger spatial variability,²⁵ i.e. the higher concentrations observed across European background sites would typically be expected to significantly overestimate the true background in Norway. Finally, the analytical uncertainty previously estimated to be $\sim \pm 35\%$ ²⁵ was additionally incorporated by adding and subtracting 35% from the maximum and minimum background air concentrations for the three reference scenarios, respectively. Taken together, this resulted in nine different R s with median (default), maximum and minimum estimates for R_{NW} , R_{ND} and R_{EU} . Additional uncertainties associated with back-calculating

air concentrations on the basis of PAS^{37,39} were not considered as these errors were assumed to be of a more systematic rather than random character, e.g. as caused by uncertainties in K_{OA} . Finally, any data below the MDL was omitted from this analysis.

3. Results and discussion

3.1. Introductory remarks

Table 1 shows the overall results in terms of calculated air concentrations for both exposed samples from the coastal sites and the blanks (average, median, range), while Tables S3a–S6a† present results for individual compounds and compound groups at each coastal site. Three sites (Oslo, Ramsundet and Tromsø II) experienced an insufficient loss of all PRCs (<40%). The estimated air concentrations derived for these three sites critically rely on the default sampling rate and the results should therefore be interpreted with caution. Although the exact reason why these sites experienced an insufficient loss cannot be explained unequivocally, we note that the number of individual PRCs experiencing a sufficient loss tended to decrease towards the northern sites (Table S1†), which could indicate that the volatility range of our selected PRCs was less suitable at sites experiencing colder temperatures. From theoretical considerations,²⁶ we also caution that some of the more volatile substances

(fluorene > HCB > α -HCH > phenanthrene \approx γ -HCH \approx anthracene > PCB-28 and to some extent PCB-52) may have started to approach equilibrium during the 3-month deployment period as discussed in the ESI (S 1.3),† and as also can be seen from the effective air volumes derived for individual substances and compounds (Tables S3b–S6b†).

PCB-28, 52 and 101, α - and γ -HCH, HCB, *cis*-Chlordane and *trans*-nonachlor were detected in all samples. Among the PAHs, fluorene, phenanthrene, fluoranthene, pyrene together with chrysene were also detected in all samples. The spatial variability across the coastal sites is expressed by the ratio between maximum and minimum air concentrations (MMR) in Table 1. When the minimum concentration was below the MDL, the MDL value was used when calculating the MMR, which implies that only a minimum estimate of spatial variability can be provided. The estimated influence of LS at each coastal site is explored by analyzing the ratios of observed concentrations at each coastal site, divided by the different scenarios for the estimated concentration attributed to LRAT alone (R_s ; eqn (1)). Only results for selected substances and substance groups using the Norwegian background scenario (R_{NW}) are included in Fig. 2. Additional results are included in the ESI, Tables S7–S9,† which compare and contrast the predicted influence of LS for individual compounds and compound groups for each of the three background scenarios (R_{NW} (Table S7†), R_{ND} (Table S8†) and R_{EU} (Table S9†)), including median (Tables S7a, S8a and S9a†), maximum (Tables S7b, S8b and S9b†) and minimum (Tables S7c, S8c and S9c†) estimates. In Tables S7–S9,† R_s based on concentrations at coastal sites below the MDL are listed as

NQ (not quantified) while R_s using background concentrations below the MDL are tabulated as ND (not detected). Tables S10a–c† likewise summarize the number of coastal sites for which the R_s are ≥ 2 , ≥ 1 and $> \text{MDL}$ for the 9 different background scenarios. An overview of the median background air concentrations for the three background scenarios is finally included in Table 2.

3.2. PCBs

The average concentration of $\Sigma_7\text{PCBs}$ was 21 pg m^{-3} ($\text{SD} \pm 17 \text{ pg m}^{-3}$), with a range from 4.5 to 72 pg m^{-3} (Table 1). The more abundant PCBs were PCB-52, -101, -28 and -153, each of which contributed 29%, 24%, 22% and 12% to the average concentration of $\Sigma_7\text{PCBs}$, respectively. MMRs for individual PCBs varied by about an order of magnitude or more, *i.e.* >9 (PCB-153 and PCB-180) to 21 for PCB-101. The highest concentrations of $\Sigma_7\text{PCBs}$ were found in Bergen I, Kristiansand II and Oslo with 72, 59 and 51 pg m^{-3} , respectively. These sites were all located within major cities in Norway, while the lowest concentrations were observed in Narvik II, Ramsundet and Sunndalsøra with 5.8, 4.8 and 4.5 pg m^{-3} , respectively (see Table S3a†).

Fig. 2a shows the estimated contribution from LS (R_{NW}) for $\Sigma_7\text{PCBs}$ (see also Table S7a†). R_{NW} falls between 1.5 and 13.6, which strongly suggests that LS likely contributes ($R_{NW} \geq 1$) or dominates ($R_{NW} \geq 2$) the observed air concentrations of PCBs at most coastal sites. The same pattern is also evident for $R_{NW\text{max}}$ (using maximum background concentrations) but the values are lower (0.6–5.3), indicating less influence of LS (Table S7b†). Also

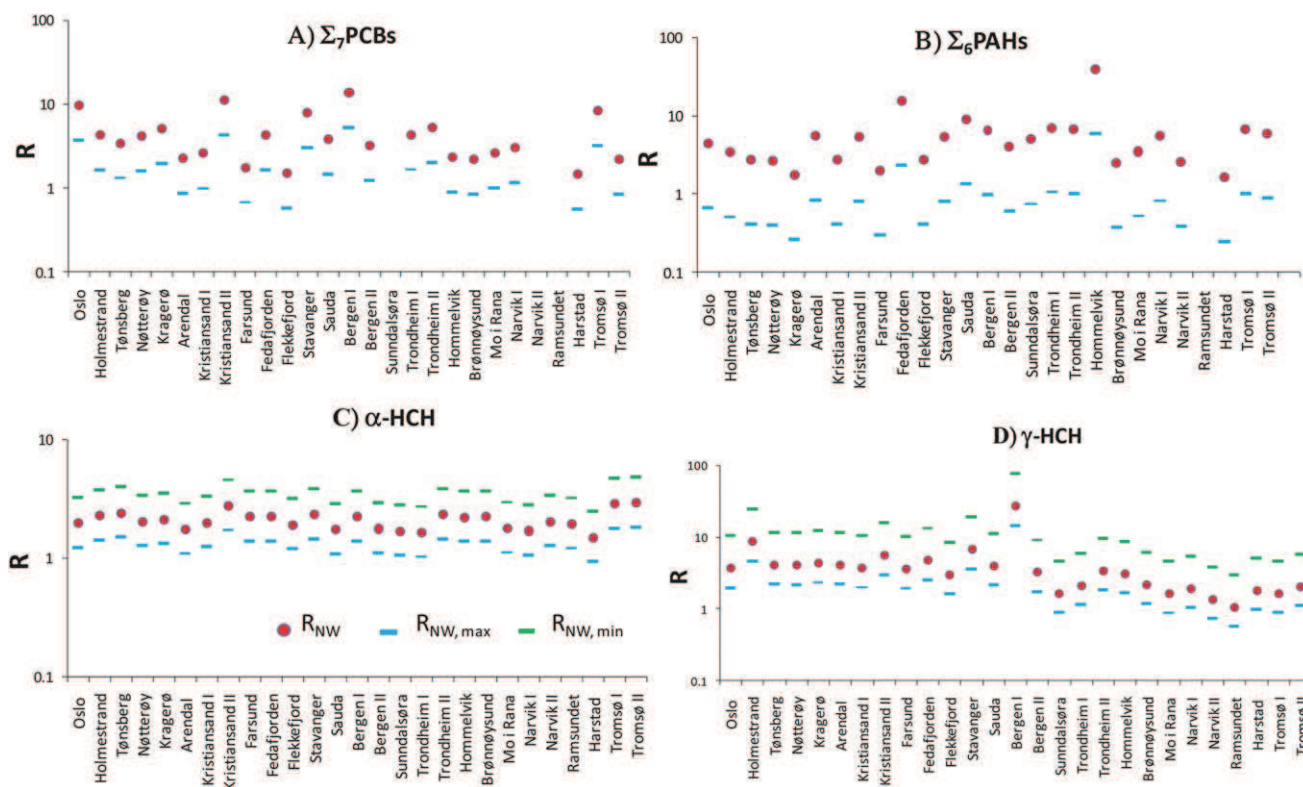


Fig. 2 (a–d) Estimated contribution from local sources, expressed as the ratio (R_{NW}) of measured air concentrations divided by the anticipated contribution from long-range atmospheric transport alone (Norwegian background scenario). The uncertainty in this ratio ($R_{NW\text{max}}$, $R_{NW\text{min}}$) is estimated as detailed in the text.

Table 2 Median background concentrations in air for the Norwegian, Nordic and European scenario for selected PCBs, HCHs, DDTs, HCB, chlordanes (pg m⁻³) and selected PAHs (ng m⁻³). All data from Halse *et al.*²⁵

Compound/groups	Norwegian background		Nordic		European median	Ratio (median values)	
	Median	Range (min–max)	Median	Range (min–max)		Nordic/Norwegian	European/Norwegian
PCB-28	1.5	0.9–2.1	1.9	0.9–4.7	3.8	1.3	2.5
PCB-52	1.6	1.1–2.3	2.1	1.1–5.7	4.2	1.3	2.6
PCB-101	1.0	0.6–1.9	1.7	0.6–8.7	2.5	1.8	2.7
PCB-118	0.3	0.2–0.6	0.5	0.2–3.3	1.0	1.6	3.0
PCB-138	0.3	0.2–1.1	0.9	0.2–4.7	1.2	2.8	3.9
PCB-153	0.5	0.3–1.6	1.4	0.3–6.8	2.0	2.9	4.2
PCB-180	0.1	0.1–0.6	0.3	0.1–2.1	0.6	2.9	5.5
Σ ₇ PCBs	5.3	3.4–10.2	8.7	3.4–32.4	15.3	1.7	2.9
Fluorene	0.7	0.3–4.5	0.7	0.3–4.5	1.0	1.06	1.3
Phenanthrene	1.2	0.6–5.0	1.5	0.5–5.0	1.9	1.3	1.6
Anthracene	0.01	0.01–0.1	0.01	N.D. ^a –0.08	0.03	1.1	1.9
Fluoranthene	0.2	0.1–0.7	0.3	0.1–1.1	0.4	1.6	2.5
Pyrene	0.1	0.1–0.2	0.1	0.1–0.5	0.2	1.5	2.76
Benzo[a]pyrene	0.005	N.D. ^a	N.D. ^a	N.D. ^a –0.06	N.D. ^a	N.D. ^a	N.D. ^a
Benz[a]anthracene	N.D. ^a	N.D. ^a –0.04	N.D. ^a	N.D. ^a –0.04	0.01	N.D. ^a	N.D. ^a
Chrysene	0.01	0.009–0.01	0.01	0.01–0.1	0.03	1.2	3.2
Σ ₆ PAH ^b	2.2	1.1–10.5	2.6	1.0–11.2	3.6	1.2	1.6
α-HCH	7.6	7.1–8.9	8.6	6.8–12.7	20.6	1.13	2.7
β-HCH	N.D. ^a	N.D. ^a –0.2	N.D. ^a	N.D. ^a –1.1	0.7	N.D. ^a	N.D. ^a
γ-HCH	4.3	2.3–5.9	5.0	2.3–11.6	19.5	1.2	4.5
Σ ₂ HCHs ^c	11.9	9.4–14.8	13.6	9.2–24.3	40.1	1.1	3.4
HCB	41.5	39.0–46.9	41.8	38.4–58.7	45.1	1.0	1.1
<i>p,p'</i> -DDE	N.D. ^a	N.D. ^a	N.D. ^a	N.D. ^a –8.0	N.D. ^a	N.D. ^a	N.D. ^a
<i>p,p'</i> -DDD	N.D. ^a	N.D. ^a	N.D. ^a	N.D. ^a –0.2	N.D. ^a	N.D. ^a	N.D. ^a
<i>o,p'</i> -DDT	N.D. ^a	N.D. ^a –0.6	0.4	N.D. ^a –2.3	1.8	N.D. ^a	N.D. ^a
<i>p,p'</i> -DDT	N.D. ^a	N.D. ^a –0.8	0.3	N.D. ^a –3.0	2.0	N.D. ^a	N.D. ^a
Σ ₂ DDTs ^d	N.D. ^a	N.D. ^a –1.4	0.7	N.D. ^a –5.3	3.8	N.D. ^a	N.D. ^a
<i>trans</i> -Chlordane	0.4	0.2–0.6	0.3	N.D. ^a –0.6	0.4	1.0	1.2
<i>cis</i> -Chlordane	0.7	0.6–1.1	0.8	0.4–1.3	1.2	1.0	1.6
<i>trans</i> -Nonachlor	0.8	0.7–1.5	0.8	0.4–1.5	1.2	1.0	1.5
<i>cis</i> -Nonachlor	0.1	0.1–0.2	0.1	N.D. ^a –0.3	0.1	0.9	1.4
Σ ₄ Chlordanes	2.0	1.6–3.4	2.0	0.9 ^e –3.7	3.0	1.0	1.5

^a Concentration <MDL.²⁵ ^b Fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene. ^c α-HCH and γ-HCH. ^d *o,p'*-DDT and *p,p'*-DDT.

^e Lower range, *trans*-Chlordane and *cis*-Chlordane < MDL.²⁵

note that R_{NWmin} is not included in Fig. 2a as a few congeners were below the MDL at Norwegian background sites.²⁵ The highest contribution from LS is estimated for sites located in larger cities, *e.g.* Bergen I (13.6: 5.3-ND), Kristiansand II (11.1: 4.3-ND) and Oslo (9.7: 3.7-ND) (Tables S7a–c†).

It is noteworthy that $R_{\text{NW}} \geq 2$ at 21 out of 24 sites, indicating that LS dominates the atmospheric burden (Table S10a†). When considering R_{NWmax} (Table S7b†), the number is reduced to 6 out of 24 for $R_{\text{NWmax}} > 2$ (Table S10b†). Still, even when applying the more conservative approach with respect to possible influence of LS (Table S7b†), as much as 15 sites experienced some influence of LS (*i.e.* $R_{\text{NWmax}} \geq 1$; Table S10b†). When comparing results for the two parallels deployed at different locations, yet within the same coastal zone, such as Bergen, Tromsø and Kristiansand (Fig. 1), it is also evident that our method and results are not applicable beyond a specific site alone. Thus, spatial variability in air concentrations of Σ₇PCBs (and hence the potential influence of LS) within a given coastal zone may differ significantly and any inferences made about the likely influence of LS in a specific coastal zone are restricted to the specific site where the sample was collected as well as when it was exposed.

When considering the Nordic background (R_{ND}) as our reference scenario (Table S8a–c†), the overall results indicate less influence of LS as the Nordic background concentrations are

higher than the Norwegian background concentrations (Table 2). This ratio ranges from 0.9–8.2 and 0.2–1.5 for Σ₇PCBs applying R_{ND} (Table S8a†) and R_{NDmax} (Table S8b†), respectively. Moreover, the number of sites which are predominantly controlled by LS ($R_{\text{ND}} \geq 2$) drops down to 13 out of 24 (Table S10a†). In other words, only about half of the coastal sites are seen as elevated by LS when assessed in the context of Nordic background concentrations. However, when applying the European background scenario (Table S9a–c†), R_{EU} falls below 1 for about half of the sites (Table S9a†) and only five sites, Bergen I (4.7: 3.5–7.3), Kristiansand II (3.9: 2.9–5.9), Oslo (3.4: 2.5–5.2), Tromsø I (2.9: 2.1–4.4) and Stavanger (2.7: 2.0–4.2) still stand out with $R_{\text{EU}} \geq 2$ (Table S10†). Clearly, whenever R_{EU} is ≥ 2 (Table S9a–c†), it strongly suggests that a significant influence of LS at a particular coastal site is likely. Hence, possible control strategies should emphasize local control measures if further reductions in atmospheric burdens of PCBs are to be achieved at these sites.

The median background air concentrations for Σ₇PCBs for the Nordic and European scenarios are, respectively, 1.7 and 2.9 times higher than that of the Norwegian background scenario (Table 2). The difference tends to increase with increasing chlorination, which is seen as a reflection of lighter PCBs being more prone to LRAT.⁴⁰ Hence, the relative influence of LRAT at

background sites may be higher for lighter PCBs compared with their heavier counterparts, which is in line with previous studies on the latitudinal distribution of PCBs in background air within Norway.⁴¹ This may explain why coastal sites seem to be increasingly controlled by LS for heavier PCBs ($R_{NW} \geq 2$; Table S10a†). Interestingly, the opposite trend across congeners is seen in comparison to the Nordic background (Table S10a†), which may be seen as a reflection of the Swedish background sites being more influenced by heavier PCBs (Table 2).

3.3. PAHs

The average concentration of Σ_8 PAHs was 13 ng m^{-3} ($SD \pm 16 \text{ ng m}^{-3}$), and ranged from 1 to 84 ng m^{-3} (Table 1). The lighter PAHs, such as phenanthrene, fluorene and fluoranthene were more abundant and each contributed 49%, 31% and 11% on average, respectively. The MMR ranged from >1 (benzo(a)pyrene) to >108 (anthracene) which illustrates a marked spatial variability for some PAHs (Table 1). At decreasing temperatures, substances with a high K_{OA} like benzo(a)pyrene may be increasingly sorbed to atmospheric particles, for which the PAS methods are not designed to capture. While the average air temperature at the coastal sites varied from 8°C to 17°C in our study (Table S1†), Klanova *et al.*³⁷ previously predicted that benzo(a)pyrene will remain 80–90% particle-bound at 22°C . In comparison, a calibration study in Toronto found that the particle-bound fraction of benzo(a)pyrene decreased from 77% at -4°C down to 23% at 16°C .⁴² Sorption onto particles may thus help in explaining why most samples were below the detection limit for this substance (Table S4a†). Sites with elevated air concentration of Σ_8 PAHs were found at Hommelvika, Fedafjorden and Sauda with 84, 33 and 19 ng m^{-3} respectively. Furthermore, Hommelvika had the highest concentrations of phenanthrene and fluorene with 41 and 32 ng m^{-3} , respectively. The lowest concentrations of Σ_8 PAHs were found at Kragerø, Harstad, Ramsundet with 3.8, 3.5 and 1.2 ng m^{-3} , respectively (Table S4a†).

As the concentration of benzo(a)pyrene and sometimes also benz(a)anthracene often were below the MDL, the following discussion will be restricted to Σ_6 PAHs. As shown in Fig. 2b, R_{NW} for Σ_6 PAHs varied between 1.6 and 38.9. The highest influence of LS was found at Hommelvika, Fedafjorden and Sauda with 38.9 (5.9-ND), 15.3 (2.3-ND) and 8.9 (1.4-ND), respectively (Table S7a–c†). Furthermore, 23 out of 26 sites had $R_{NW} \geq 2$ (Table S10a†), indicating LS to be more influential than LRAT at most of the sites. This number was reduced to 2 (out of 26) when instead applying R_{NWmax} (Table S10b†). This implies that there are significant difficulties in defining a reliable estimate of the atmospheric burden which may be attributed to LRAT alone for Σ_6 PAHs, attributed to spatial variability in background air concentrations. This, in turn, indicates that the “true” LRAT contribution may possibly overestimated using median background concentrations. Another interesting aspect is the striking variations within Σ_6 PAHs (Tables S7–S9†) as also noted from the individual MMRs (Table 1). Thus, an assessment of the R_{NW} for individual PAHs (Table S7a†) may provide clues about potential differences in sources. For example, both Fedafjorden and Saudafjorden have an industrial history and both exhibit elevated R_{NW} s for anthracene, fluoranthene, pyrene and

chrysene in excess of R_{NW} for Σ_6 PAHs (Table S7a†). This pattern is different from that of Hommelvika, a locality known to have been polluted by creosote in the past, which is seen as elevated by anthracene and fluorene in particular. For all these sites, PAHs are also among the pollutants which have caused measures on the consumption of seafood.⁴³

The median Nordic and European background air concentrations for Σ_6 PAHs were 1.2 and 1.6 higher than the Norwegian median background (Table 2). Hence, the relative influence of LS does not decrease markedly dependent on the actual background reference. For R_{ND} , 23 out of 26 sites are still implicated as predominantly controlled by LS for Σ_6 PAHs ($R_{ND} \geq 2$), while this number is reduced to 17 for R_{EU} (Table S10a†). Results from the coastal sites with duplicated PAS deployed indicate only a relatively minor difference in measured concentrations of Σ_6 PAHs, up to a factor of ~ 2 (Narvik I vs. II).

3.4. HCHs

The average concentration for Σ_3 HCHs (α , β , γ) was 34 pg m^{-3} ($SD \pm 22 \text{ pg m}^{-3}$), and varied from 19 to 133 pg m^{-3} (Table 1). The α - and γ -isomers were detected in all samples, and each contributed 46% and 53% on average, respectively. The β -isomer contributed only $\sim 1\%$ on average. β -HCH is more water-soluble than α - and γ -isomers,⁴⁴ and hence more easily washed out from the atmosphere and thus considered less prone to LRAT. The spatial variability as expressed by MMR appears limited for Σ_3 HCHs, α -HCH and β -HCH with values of >7 , 2 and >4 , respectively. This is in striking contrast to γ -HCH which has a MMR of 26. Taken together, this indicates that there are coastal sites which possibly have been affected by past or contemporary lindane usage ($>99\%$ γ -HCH) as opposed to technical HCH which contains 55–80% α -HCH, 8–15% γ -HCH and 5–14% β -HCH.⁴⁵ This result is somehow surprising given that lindane usage has been banned in Norway since 1992.⁴⁵ The highest concentration of γ -HCH was found for Bergen I with 115 pg m^{-3} . Other sites with elevated air concentrations of γ -HCH were Holmestrand and Stavanger with 37 pg m^{-3} and 28 pg m^{-3} , respectively (Table S5a†).

Fig. 2c and d display R_{NW} for individual HCHs (α and γ) evaluated against the Norwegian background (see also Tables S7a–c†). R_{NW} for α -HCH reveals a relatively uniform pattern, with estimates ranging from 1.5–2.9 (Table S7a†). The limited spatial variability in air concentrations of α -HCH in these coastal sites suggests that air concentrations are better explained by LRAT, rather than LS. At the same time, R_{NW} is ≥ 2 for 15 out of 27 sites, which in contrast suggests an influence of LS on the concentration of α -HCH measured at the coastal sites (Table S10a†). Furthermore, R_{NW} s were ≥ 1 at all sites, indicating some influence of LS (Table S10a†). Instead, when assessing R_{NWmax} (Table S7b†), the number of sites with values ≥ 2 was reduced to zero (Table S10b†). However, we believe this apparent inconsistency could have something to do with Norwegian background sites being located at some distance from the coast, which makes it appear that coastal sites have higher background air concentrations of α -HCH than inland stations. Dalla Valle *et al.*⁴⁶ have previously discussed how net ocean–land transfers of POPs *via* the atmosphere may occur in some areas, because of sharp gradients in the storage capacities of terrestrial

and aquatic environments. Thus, we hypothesize, given the fairly homogenous air concentrations observed at coastal sites, that our coastal air measurements to a large extent may reflect secondary re-emissions from the sea. Similar findings have previously been noted by *e.g.* Shen *et al.*⁴⁷ in a study on HCHs in air across Northern America, whereby passive air sampling combined with chiral analysis suggested that α -HCH was evaporating from the Labrador Current.

Fig. 2d similarly displays results for γ -HCH. R_{NW} for γ -HCH ranged from 1.0 to 26.6, and the highest influences from LS were found at Bergen I (26.6: 14.5–76.7), Holmestrand (8.5: 4.6–24.5) and Stavanger (6.6: 3.6–18.9) (Tables S7a–c†). A predominant influence of LS was estimated for 20 out of 27 sites ($R_{NW} \geq 2$) (Table S10a†). Furthermore, 10 out of 27 sites had $R_{NWmax} \geq 2$ and 21 out of 27 had $R_{NWmax} \geq 1$ (Table S10b†). These results clearly show some influence of LS, and more probably from lindane, rather than technical HCH. As γ -HCH appears less prone to re-volatilization compared to α -HCH,⁵ it is not unlikely that the sample from Bergen I might have been affected by recent usage of lindane.

R_{NW} for Σ_2 HCHs (α -HCH + γ -HCH) varied between 1.6 and 11.1. R_{NW} and R_{NWmax} were ≥ 2 for 20 out of 27 sites and 4 out of 27 sites, respectively (Tables S10a and b†). The median Nordic and European background concentrations for Σ_2 HCHs are 1.1 and 3.4 higher than the Norwegian background, respectively (Table 2). For R_{ND} , 17 out of 27 sites had ratios ≥ 2 for Σ_2 HCHs, and 27 out of 27 sites had ratios ≥ 1 , while only 1 out of 27 sites had $R_{EU} \geq 2$ (Bergen I) (Table S10a†).

3.5. HCB

This compound was detected in all samples and concentrations varied from 42 to 305 pg m^{-3} (Table 1). The average concentration was 58 pg m^{-3} with a relatively high SD ($\pm 50 \text{ pg m}^{-3}$). At the same time, the low MMR (7) illustrates a limited spatial variability. HCB is a volatile compound with a high potential for long-range atmospheric transport.⁴⁸ Fairly uniform concentrations were also seen in European background air²⁵ which in part is attributed to a significant influence of secondary emissions in controlling contemporary air concentrations.⁴⁹ Still, elevated concentrations of HCB were found at Kristiansand II and, to a lesser extent Narvik II, with 305 pg m^{-3} and 70 pg m^{-3} , respectively (Table S5a†). However, if Kristiansand II was excluded from the dataset, the MMR would be only 2.

R_{NW} varied from 1.0 to 7.3 (Table S7a†). Only 1 out of 27 sites had $R_{NW} \geq 2$ (Table S10a†), indicating that the influence of LS was dominant in the observed air concentration of HCB at Kristiansand II only (7.3: 4.8–12.0). In contrast, Kristiansand I experienced a R_{NW} of 1.2 only, which suggests that the suspected source close to Kristiansand II did not significantly affect the atmospheric burden across the coastal zone as a whole. It is particularly noteworthy that Kristiansand II really stands out as primarily controlled by LS, even in a Nordic (Table S8;† $R_{ND} = 7.3$: 3.8–12.2) and European (Table S9;† $R_{EU} = 6.8$: 5.0–10.4) context. Further monitoring efforts to potentially identify or disconfirm the suspected hot-spot at Kristiansand II might therefore be desirable.

3.6. DDTs

The average concentration for Σ_4 DDTs was 6.5 pg m^{-3} (SD $\pm 8.4 \text{ pg m}^{-3}$), and ranged from 1.8 pg m^{-3} to 45 pg m^{-3} (Table 1). p,p' -DDE was on average the major contributing isomer (44%), followed by p,p' -DDT (32%) and o,p' -DDT (22%) (Table 1). The technical mixture of DDTs contains up to 80–85% of the p,p' -DDT isomer and only small amounts of the o,p' -DDT isomer (15–20%).⁵⁰ The MMRs for individual isomers varied from >3 (p,p' -DDE) to >86 (p,p' -DDT). The high variability in detected concentrations of DDT is noteworthy since usage of technical DDT has been severely restricted in Norway after 1980 and banned since 1989.⁵¹ The highest concentration of Σ_4 DDTs was found at Bergen I, with 26 pg m^{-3} , 11 pg m^{-3} and 7.8 pg m^{-3} for the p,p' -DDT, o,p' -DDT and p,p' -DDE isomers, respectively (Table S6a†).

As median background air concentrations were below the MDL for all four isomers in Norway and for two isomers in the Nordic region (Table 2), the discussion on the relative influence of LS is restricted to Σ_2 DDTs (o,p' -DDT and p,p' -DDT) (Table S8a†). For the sum of these two isomers, R_{ND} was ≥ 2 at 18 out of 22 sites (Table S10a†). Sites that were most influenced by LS were Bergen I (55.4: 5.1–N.D.), Kristiansand II (8.7: 0.8–N.D.) and Tønsberg (7.0: 0.6–N.D.) (Table S8a–c†). R_{ND} for individual isomers for Bergen I varied from 31 (3.6–N.D.) for o,p' -DDT and 83.9 (6.3–N.D.) for p,p' -DDT. Also Kristiansand II had somewhat higher R_{ND} for the o,p' -DDT and p,p' -DDT isomers, with 7.4 (0.8–N.D.) and 10.3 (0.8–N.D.), respectively (Table S8a†). In contrast, when applying R_{NDmax} , only Bergen I remained mainly influenced by LS for Σ_2 DDTs (Table S8b†). Thus, the large spatial variability in observed background air concentrations makes it difficult to firmly conclude whether most sites or merely one (Bergen I) is mainly controlled by LS. However, it is noteworthy that it is p,p' -DDT which appears elevated at Bergen I and some other sites, which may imply the recent use of technical DDTs. Yet, a comparison of results from the two sites in Bergen reveals that only Bergen I is strongly elevated by this unknown local source(s) (Table S6a†). Even when assessed in a European background context, the atmospheric concentrations at Bergen I is seen as strikingly elevated. The corresponding R_{EU} remains ≥ 2 for Σ_2 DDTs (9.6: 7.1–14.7) o,p' -DDT (6.1: 4.6–9.5) and p,p' -DDT (12.6: 9.3–19.4) (Table S9a–c†).

3.7. Chlordanes

The average concentration of Σ_4 Chlordanes was 3.8 pg m^{-3} (SD $\pm 2.6 \text{ pg m}^{-3}$), and ranged from 1.1 pg m^{-3} to 11 pg m^{-3} (Table 1). *cis*-Chlordane and *trans*-nonachlor were the major components, each contributing 37% and 33% on average, respectively. The spatial variability expressed using MMRs varied from >91 for *trans*-Chlordane to 8 for *cis*-Chlordane (Table 1).

Table S7a† shows R_{NW} for Σ_4 Chlordanes. R_{NW} varied from 0.5 (0.2–1.0) at Harstad to 5.7 (2.5–11.2) at Nøtterøy. 9 out of 22 sites had $R_{NW} \geq 2$ (predominantly influenced by LS) and 18 out of 22 sites had $R_{NW} \geq 1$ (some influence by LS) (Table S10a†). When using R_{NWmax} , the number of sites with values ≥ 2 and ≥ 1 is reduced to 2 and 5 sites, respectively (Table S10b†) with only Nøtterøy (5.7: 2.5–11.2) and Kragerø (5.2: 2.2–10.2) still suspected of being mainly influenced by LS. The same overall

conclusion applies when considering R_{ND} (Table S8†) as the estimated Nordic and Norwegian background concentrations are virtually identical (Table 2).

When applying the European background scenario (Table S9a†), the number of sites with $R_{EU} \geq 2$ was limited to 4 (Table S10a†), *i.e.* Nøtterøy (3.8), Kragerø (3.5), Tønsberg (2.1) and Kristiansand II (2.0). Whilst all these sites are located in the south-eastern part of Norway (Fig. 1) and thus closer to regions showing elevated air concentrations in mainland Europe,²⁵ any inferences about LS should be interpreted with caution.

4. Summary and conclusions

This study has derived new data on air concentrations of selected POPs in contaminated coastal zones in Norway using passive air samplers. When compared and contrasted with different estimates of background air concentrations (as assumed attributed to LRAT alone), the results demonstrate that several legacy POPs are occasionally still elevated by local atmospheric emissions. However, the extent of influence of LS critically depends on the accuracy of the estimated contribution from LRAT alone. While the empirical basis is somehow limited for the Norwegian and Nordic background scenarios which makes it difficult to infer reliable conclusions for substances exhibiting a high spatial variability in background air (*e.g.* PAHs), the European background estimate is considered more robust, due to the enhanced number of stations ($N = 86$). While both the number of sites and extent of LS influence will vary dependent on the selection of actual background scenario, we believe that a simple nested approach could be useful for screening exercises to assess the potential influence of LS in other contaminated sites and areas.

It should also be kept in mind that the number of samplers deployed within each coastal zone was limited to one or two. Hence, more detailed follow-up studies in contaminated zones, *e.g.* by deploying a larger number of PAS may be warranted to (i) potentially confirm the presence of suspected hot-spots, and (ii) identify more specific source areas and/or sources leading to locally elevated air concentrations, *e.g.* using a denser network of samplers, and (iii) evaluate the impact of LS on contaminant burdens on the surroundings, including additional environmental surface media and contaminant exchange with the marine environment.

While the samples reported herein were all deployed during summer, we caution that there might be seasonal variability in both local emissions and influence of LRAT for some substances (*e.g.* PAHs from domestic heating). Hence, the relative influence of LS and LRAT may also vary seasonally. We finally caution that our method is not able to discriminate between primary anthropogenic emissions and secondary emissions from environmental compartments as contaminated in the past. An interesting finding in this context is the observation that coastal sites seem to be elevated in α -HCH in comparison to the estimated background concentrations, which we hypothesize could be due to volatilization from coastal waters.

Acknowledgements

The authors would like to thank the Research Council of Norway for funding (183437 and 173428). We also thank our

colleagues (A. Borgen, S. Manø, H. Gundersen, M. Ghebremeskel and A. Hjellbrekke) at NILU for support and R.R. Fjeldberg, C. Miljeteig and T.W. Rogstad for contributing to the field work.

References

- 1 C. Rylander, T. M. Sandanger and M. Brustad, *J. Environ. Monit.*, 2009, **11**, 370–376.
- 2 K. C. Cheung, H. M. Leung, K. Y. Kong and M. H. Wong, *Chemosphere*, 2007, **66**, 460–468.
- 3 K. Hornbuckle, D. Carlson, D. Swackhamer, J. Baker and S. Eisenreich, in *Persistent Organic Pollutants in the Great Lakes*, ed. R. Hites, Springer, Berlin, Heidelberg, edn, 2006, vol. 5N, pp. 13–70.
- 4 K. Breivik, B. Bjerkeng, F. Wania, A. Helland and J. Magnusson, *Environ. Toxicol. Chem.*, 2004, **23**, 2386–2395.
- 5 K. Breivik and F. Wania, *Environ. Sci. Technol.*, 2002, **36**, 1024–1032.
- 6 K. L. Sundqvist, M. Tysklind, P. Geladi, P. K. Hopke and K. Wiberg, *Environ. Sci. Technol.*, 2010, **44**, 1690–1697.
- 7 J. M. Armitage, M. S. McLachlan, K. Wiberg and P. Jonsson, *Sci. Total Environ.*, 2009, **407**, 3784–3792.
- 8 Mattilsynet, *Kostholdsråd i norske havner og fjorder (Consumption measures in Norwegian harbours and fjords)*, VKM, Klif, 2005.
- 9 VKM, *Et helhetssyn på fisk og annen sjomat i norsk kosthold (A holistic view on fish and additional seafood as part of the Norwegian diet)*, 2006.
- 10 H. Hung, R. Kallenborn, K. Breivik, Y. S. Su, E. Brorstrom-Lunden, K. Olafsdottir, J. M. Thorlacius, S. Leppanen, R. Bossi, H. Skov, S. Mano, G. W. Patton, G. Stern, E. Sverko and P. Fellin, *Sci. Total Environ.*, 2010, **408**, 2854–2873.
- 11 F. Wania and D. Mackay, *Ambio*, 1993, **22**, 10–18.
- 12 J. E. Haugen, F. Wania, N. Ritter and M. Schlabach, *Environ. Sci. Technol.*, 1998, **32**, 217–224.
- 13 S. Eckhardt, K. Breivik, Y. F. Li, S. Mano and A. Stohl, *Atmos. Chem. Phys.*, 2009, **9**, 6597–6610.
- 14 F. M. Jaward, S. N. Meijer, E. Steinnes, G. O. Thomas and K. C. Jones, *Environ. Sci. Technol.*, 2004, **38**, 2523–2530.
- 15 W. A. Ockenden, A. J. Sweetman, H. F. Prest, E. Steinnes and K. C. Jones, *Environ. Sci. Technol.*, 1998, **32**, 2795–2803.
- 16 J. K. Schuster, R. Gioia, K. Breivik, E. Steinnes, M. Scheringer and K. C. Jones, *Environ. Sci. Technol.*, 2010, **44**, 6760–6766.
- 17 R. Ishaq, N. J. Persson, Y. Zebuhr, D. Broman and K. Naes, *Environ. Sci. Technol.*, 2009, **43**, 3442–3447.
- 18 K. Næs, PhD Thesis, University of Oslo, 1998.
- 19 M. Jartun, R. T. Ottesen, E. Steinnes and T. Volden, *Environ. Pollut.*, 2009, **157**, 295–302.
- 20 M. Andersson, R. Ottesen and I. Volden, *Sci. Total Environ.*, 2004, **325**, 139–144.
- 21 A. Ruus, N. W. Green, A. Maage and J. Skei, *Mar. Pollut. Bull.*, 2006, **52**, 100–103.
- 22 M. L. Diamond, L. Melymuk, S. A. Csiszar and M. Robson, *Environ. Sci. Technol.*, 2010, **44**, 2777–2783.
- 23 F. Wania, *Environ. Sci. Pollut. Res.*, 1999, **6**, 11–19.
- 24 UNEP, *Guidance on the global monitoring Plan for persistent Organic pollutants. Preliminary version, February 2007*, Amended in May 2007.
- 25 A. K. Halse, M. Schlabach, S. Eckhardt, A. Sweetman, K. C. Jones and K. Breivik, *Atmos. Chem. Phys.*, 2011, **11**, 1549–1564.
- 26 M. Shoeib and T. Harner, *Environ. Sci. Technol.*, 2002, **36**, 4142–4151.
- 27 F. M. Jaward, N. J. Farrar, T. Harner, A. J. Sweetman and K. C. Jones, *Environ. Sci. Technol.*, 2004, **38**, 34–41.
- 28 K. Pozo, T. Harner, M. Shoeib, R. Urrutia, R. Barra, O. Parra and S. Focardi, *Environ. Sci. Technol.*, 2004, **38**, 6529–6537.
- 29 T. Harner, M. Shoeib, M. Diamond, G. Stern and B. Rosenberg, *Environ. Sci. Technol.*, 2004, **38**, 4474–4483.
- 30 T. Harner, K. Pozo, T. Gouin, A. M. Macdonald, H. Hung, J. Caaney and A. Peters, *Environ. Pollut.*, 2006, **144**, 445–452.
- 31 B. H. Wilford, T. Harner, J. P. Zhu, M. Shoeib and K. C. Jones, *Environ. Sci. Technol.*, 2004, **38**, 5312–5318.
- 32 L. Tuduri, T. Harner and H. Hung, *Environ. Pollut.*, 2006, **144**, 377–383.

- 33 J. N. Huckins, J. D. Petty, J. A. Lebo, F. V. Almeida, K. Booij, D. A. Alvarez, R. C. Clark and B. B. Mogensen, *Environ. Sci. Technol.*, 2002, **36**, 85–91.
- 34 K. Pozo, T. Harner, S. C. Lee, F. Wania, D. C. G. Muir and K. C. Jones, *Environ. Sci. Technol.*, 2009, **43**, 796–803.
- 35 klima, Norwegian Metereological Institute, 2010.
- 36 T. Harner, M. Shoeib, M. Diamond, M. Ikonou and G. Stern, *Chemosphere*, 2006, **64**, 262–267.
- 37 J. Klanova, P. Eupr, J. Kohoutek and T. Harner, *Environ. Sci. Technol.*, 2008, **42**, 550–555.
- 38 K. Kennedy, D. W. Hawker, M. E. Bartkow, S. Carter, Y. Ishikawa and J. F. Mueller, *Environ. Pollut.*, 2010, **158**, 142–147.
- 39 T. Harner, M. Bartkow, I. Holoubek, J. Klanova, F. Wania, R. Gioia, C. Moeckel, A. J. Sweetman and K. C. Jones, *Environ. Pollut.*, 2006, **144**, 361–364.
- 40 F. Wania and G. L. Daly, *Atmos. Environ.*, 2002, **36**, 5581–5593.
- 41 W. A. Ockenden, E. Steinnes, C. Parker and K. C. Jones, *Environ. Sci. Technol.*, 1998, **32**, 2721–2726.
- 42 L. Melymuk, M. Robson, P. A. Helm and M. L. Diamond, *Atmos. Environ.*, 2011, **45**, 1867–1875.
- 43 KLIF, *Organiske miljøgifter i kystområder (Organic contaminants in coastal areas)*, http://www.miljostatus.no/Tema/Hav-og-vann/Pavirkninger-pa-livet-i-vann/Miljogifter_vann/Miljogifter_marint/Organiske-miljogifter-i-kystomrader/.
- 44 Y. F. Li, R. W. Macdonald, L. M. M. Jantunen, T. Harner, T. F. Bidleman and W. M. J. Strachan, *Sci. Total Environ.*, 2002, **291**, 229–246.
- 45 K. Breivik, J. M. Pacyna and J. Munch, *Sci. Total Environ.*, 1999, **239**, 151–163.
- 46 M. Dalla Valle, E. Jurado, J. Dachs, A. J. Sweetman and K. C. Jones, *Environ. Pollut.*, 2005, **134**, 153–164.
- 47 L. Shen, F. Wania, Y. D. Lei, C. Teixeira, D. C. G. Muir and T. F. Bidleman, *Environ. Sci. Technol.*, 2004, **38**, 965–975.
- 48 F. Wania and D. Mackay, *Environ. Sci. Technol.*, 1996, **30**, A390–A396.
- 49 R. E. Bailey, *Chemosphere*, 2001, **43**, 167–182.
- 50 A. Motelay-Massei, T. Harner, M. Shoeib, M. Diamond, G. Stern and B. Rosenberg, *Environ. Sci. Technol.*, 2005, **39**, 5763–5773.
- 51 J. M. Pacyna, K. Breivik, J. Munch and J. Fudala, *Atmos. Environ.*, 2011, **37**(suppl. 1), S119–S131.

Supporting information

for

Using passive air samplers to assess local sources versus long range atmospheric transport of
POPs.

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Tables

Table S1: Site description and details.

Country	Number	Name	Latitude	Longitude	Start	End	Average sampling rate (m ³ day ⁻¹)	PRCs ¹⁾	Deployment days	Temperature (°C)
Norway	1.	Oslo ⁴⁾	N 59°55	E 10°44	03.07	03.10	3.50 ²⁾	-	92	17
Norway	2.	Holmestrand	N 59°28	E 10°19	08.07	09.10	3.52	6	93	16
Norway	3.	Tønsberg	N 59°15	E 10°23	08.07	09.10	4.85	6	93	16
Norway	4.	Nøtterøy	N 59°10	E 10°23	08.07	09.10	3.49	6	93	16
Norway	5.	Kragerø	N 58°51	E 09°25	09.07	10.10	4.33	6	93	15
Norway	6.	Arendal	N 58°29	E 08°50	09.07	10.10	4.26	3	93	15
Norway	7a.	Kristiansand I	N 58°08	E 08°04	10.07	10.10	4.56	5	92	16
Norway	7b.	Kristiansand II	N 58°08	E 07°58	10.07	10.10	4.25	4	92	16
Norway	8.	Farsund	N 58°09	E 06°48	10.07	11.10	3.21	4	93	16
Norway	9.	Fedafjorden	N 58°16	E 06°52	10.07	11.10	3.19	5	93	16
Norway	10.	Flekkefjord	N 58°16	E 06°38	10.07	11.10	3.46	3	93	16
Norway	11.	Stavanger	N 58°58	E 05°44	11.07	11.10	3.86	5	92	16
Norway	12.	Sauda	N 59°38	E 06°19	13.07	12.10	3.95	3	91	15
Norway	13a.	Bergen I	N 60°24	E 05°18	14.07	13.10	3.78	4	91	16
Norway	13b.	Bergen II	N 60°23	E 05°07	14.07	13.10	4.41	3	91	15
Norway	14.	Sunnalsøra	N 62°43	E 08°26	15.07	14.10	3.04	3	91	15
Norway	15a.	Trondheim I	N 63°26	E 10°21	16.07	16.10	3.31	2	92	14
Norway	15b.	Trondheim II	N 63°26	E 10°25	16.07	16.10	3.48	4	92	14
Norway	16.	Hommelvik	N 63°25	E 10°48	16.07	17.10	3.50	3	93	14
Norway	17.	Brønnøysund	N 65°28	E 12°11	18.07	17.10	6.08	3	91	13
Norway	18.	Mo i Rana	N 66°19	E 14°05	19.07	18.10	3.99	2	91	12
Norway	19a.	Narvik I	N 68°24	E 17°24	20.07	19.10	4.50	3	91	10
Norway	19b.	Narvik II	N 68°22	E 17°35	20.07	19.10	2.72	2	91	10
Norway	20.	Ramsundet	N 68°30	E 16°26	21.07	20.10	3.50 ²⁾	-	91	10
Norway	21.	Harstad	N 68°48	E 16°32	21.07	20.10	7.66	1	91	10

Country	Number	Name	Latitude	Longitude	Start	End	Average sampling rate (m ³ day ⁻¹)	PRCs ¹⁾	Deployment days	Temperature (°C)
Norway	22a.	Tromsø I	N 69°39	E 18°56	04.07	04.10	5.56	3	92	8
Norway	22b.	Tromsø II	N 69°40	E 18°57	04.07	04.10	3.50 ²⁾	-	92	8
Norway	I.	Birkenes ^{3), 4)}	N 58°23	E 08°15	02.07	01.10	3.83	5/6	91	14
Norway	II.	Hurdal ⁴⁾	N 60°22	E 11°04	01.07	02.10	3.93	5	93	13
Norway	III.	Kårvatn ⁴⁾	N 62°47	E 08°53	29.06	10.10	2.92	6	103	15
Norway	IV.	Tustervatn ⁴⁾	N 65°50	E 13°55	28.06	09.10	3.39	4	103	9
Norway	V.	Karasjok ⁴⁾	N 69°28	E 25°13	26.06	29.09	4.41	6	95	10
Sweden	VI.	Vavihill ⁴⁾	N 56°01	E 13°09	11.07	08.10	3.47	5	89	16
Sweden	VII.	Råö ^{3), 4)}	N 57°24	E 11°55	04.07	02.10	7.29	6	89	17
Sweden	VIII.	Hoburgen ⁴⁾	N 56°55	E 18°09	30.06	03.10	6.71	6	95	17
Sweden	IX.	Aspvreten ⁴⁾	N 58°48	E 17°23	06.07	06.10	1.66	2	92	16
Sweden	X.	Bredkälén ⁴⁾	N 63°51	E 15°20	06.06	06.09	2.56	3	92	13
Sweden	XI.	Vindeln ⁴⁾	N 64°15	E 19°46	28.06	28.09	3.41	6	92	15
Sweden	XII.	Abisko ⁴⁾	N 68°21	E 18°49	06.07	11.10	6.11	6	97	5

¹⁾ Number of PRCs with more than 40 % loss during deployment

²⁾ No significant loss of PRCs, default value used

³⁾ Two samplers co-deployed at this site

⁴⁾ Part of the European campaign, and is a background site ¹

Table S2: Range in recoveries for the internal standards for exposed samples, field and method blanks, as well as PRCs for field and method blanks respectively in %.

Internal standards	RANGE		
	Exposed samples	Field blank	Method blank
¹³ C-PeCB	25-48	33-45	27-37
¹³ C-PCB (28)	59-97	74-91	67-79
¹³ C-PCB (52)	55-92	75-82	69-82
¹³ C-PCB (101)	62-114	86-106	80-95
¹³ C-PCB (105)	67-127	101-122	106-115
¹³ C-PCB (114)	67-128	98-120	101-110
¹³ C-PCB (118)	68-131	99-123	93-109
¹³ C-PCB (123)	69-132	100-121	101-111
¹³ C-PCB (153)	66-124	100-130	97-114
¹³ C-PCB (138)	71-137	106-121	107-115
¹³ C-PCB (167)	73-135	111-136	114-127
¹³ C-PCB (156)	74-130	116-141	115-129
¹³ C-PCB (157)	72-134	117-134	117-130
¹³ C-PCB (180)	71-120	108-131	105-125
¹³ C-PCB (189)	75-147	119-147	121-128
¹³ C-PCB (209)	63-131	116-126	110-127
2-Methylnaftalene-d ₁₀	19-52	34-48	32-40
Acenaphtene-d ₁₀	23-65	40-55	39-61
Antracene-d ₁₀	29-96	45-62	53-60
Pyrene-d ₁₀	35-110	56-78	71-76
Benz(a)antrachene-d ₁₂	40-122	70-93	88-111
Benz(e)pyrene-d ₁₂	39-128	66-92	80-91
Benzo(ghi)perylene-d ₁₂	45-116	64-94	82-96
¹³ C-α-HCH	36-117	59-65	41-67
¹³ C-β-HCH	45-150	75-83	65-88
¹³ C-γ-HCH	54-120	69-78	69-81

Internal standards	RANGE		
	Exposed samples	Field blank	Method blank
¹³ C-HCB	37-62	42-57	38-47
¹³ C- <i>p,p'</i> -DDE	60-136	92-101	68-103
¹³ C- <i>p,p'</i> -DDT	64-197 ¹⁾	95-119	83-119
¹³ C-trans-chlordane	29-105	64-111	71-105
¹³ C-trans-nonachlor	20-117	53-108	64-102
¹³ C Mirex	12-124	51-113	73-131
PRCs			
d6-γ-HCH	-	92-116	82-106
PCB-12	-	83-101	80-107
PCB-14	-	77-91	74-100
PCB-23	-	83-106	86-103
PCB-30	-	70-84	67-90
PCB-32	-	82-110	86-105
PCB-107	-	92-112	87-110
PCB-198	-	80-117	90-116

¹⁾ One of the samples experienced an elevated % recovery, due to an instrumental problem.

Table S3a): Concentrations of PCBs at coastal sites (pg/m³).

Sites	PCB-28	PCB-52	PCB-101	PCB-118	PCB-138	PCB-153	PCB-180	Σ ₇ PCBs
Oslo	9.8	16.5	13.1	3.7	3.1	4.7	0.8	51.5
Holmestrand	4.9	6.1	4.5	1.8	1.8	2.5	0.6	22.3
Tønsberg	3.9	5.0	3.7	1.2	1.5	2.3	0.6	18.1
Nøtterøy	3.9	6.1	4.8	2.1	2.1	2.7	0.5	22.2
Kragerø	7.8	7.5	4.2	1.4	1.9	2.9	0.9	26.7
Arendal	3.3	3.1	2.1	0.7	0.9	1.7	0.4	12.1
Kristiansand I	2.8	3.9	2.8	1.0	1.1	1.6	0.4	13.6
Kristiansand II	8.5	14.6	15.2	7.3	5.1	6.6	1.3	58.7
Farsund	2.0	2.4	1.9	0.6	0.8	1.4	0.3	9.3
Fedafjorden	10.1	5.7	3.1	0.9	1.0	1.6	0.4	22.9
Flekkefjord	1.9	2.2	1.7	0.4	0.6	1.0	0.2	7.9
Stavanger	6.8	12.2	10.1	3.5	3.4	4.9	1.0	41.9
Sauda	2.8	5.2	5.5	2.6	1.7	2.1	0.3	20.1
Bergen I	9.2	21.1	19.0	6.7	6.2	8.6	1.5	72.3
Bergen II	3.5	6.8	3.1	1.1	0.9	1.3	0.3	17.0
Sunnøysund	1.3	1.2	0.9	0.2	0.3	0.5	0.1	4.5
Trondheim I	2.8	7.0	6.4	1.9	1.8	2.5	0.5	22.9
Trondheim II	7.7	6.9	5.5	1.8	2.0	3.0	0.7	27.6
Hommelvik	2.6	2.7	2.3	0.8	1.4	2.0	0.5	12.3
Brønnøysund	2.4	2.5	2.3	0.7	1.1	2.0	0.5	11.5
Mo i Rana	5.1	3.3	2.1	0.8	0.9	1.3	0.3	13.7
Narvik I	4.4	4.6	3.3	1.1	1.0	1.4	0.2	16.0
Narvik II	1.5	1.7	1.3	0.4	0.3	0.5	0.1	5.8
Ramsundet	1.0	1.2	1.1	0.2	0.6	0.5	0.2	4.8
Harstad	1.7	2.2	1.4	0.5	0.7	1.0	0.2	7.7
Tromsø I	8.7	9.7	12.2	2.3	3.8	6.0	1.3	44.0
Tromsø II	2.9	3.4	2.6	0.7	0.7	1.2	0.2	11.6

Numbers in bold red: Less than MDL. Number given is ½ MDL.

Table S3b): Effective air volumes for the PCBs (m³).

Sites	PCB-28	PCB-52	PCB-101	PCB-118	PCB-138	PCB-153	PCB-180
Oslo	261	282	309	318	319	318	321
Holmestrand	268	289	315	324	325	323	326
Tønsberg	344	381	428	444	446	443	449
Nøtterøy	267	287	313	321	322	321	324
Kragerø	320	349	385	397	399	397	401
Arendal	313	342	378	391	392	390	395
Kristiansand I	325	357	399	413	415	413	418
Kristiansand II	308	337	373	385	387	385	389
Farsund	249	266	288	295	296	295	298
Fedafjorden	247	265	286	294	294	293	296
Flekkefjord	264	285	310	318	319	318	321
Stavanger	286	310	340	351	352	350	354
Sauda	290	314	345	355	356	355	358
Bergen I	278	301	330	339	341	339	343
Bergen II	317	346	383	396	397	396	400
Sunndalsøra	236	251	269	274	275	274	276
Trondheim I	257	274	294	301	302	301	303
Trondheim II	268	286	309	317	317	316	319
Hommelvik	272	291	314	322	323	322	324
Brønnøysund	418	464	524	544	547	544	551
Mo i Rana	306	327	352	360	361	360	362
Narvik I	345	369	397	406	407	406	409
Narvik II	223	232	243	246	247	246	247
Ramsundet	279	293	311	316	317	316	318
Harstad	524	584	660	686	689	685	694
Tromsø I	421	453	493	506	507	505	510
Tromsø II	284	298	315	320	321	320	322

Values in *italics*: volumes are based on the default value (3.5 m³/day)

Table S4a): Concentrations of PAHs at coastal sites (ng/m³).

Sites	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benz[a]anthracene	Chrysene	Benzo[a]pyrene	Σ ₈ PAH
Oslo	2.3	6.3	0.07	0.6	0.3	0.01	0.05	0.005	9.5
Holmestrand	2.2	3.7	0.07	0.8	0.5	0.01	0.05	0.005	7.2
Tønsberg	1.7	3.0	0.07	0.6	0.4	0.02	0.06	0.005	5.8
Nøtterøy	1.8	3.0	0.05	0.5	0.3	0.01	0.04	0.005	5.7
Kragerø	1.2	1.9	0.05	0.4	0.2	0.01	0.03	0.005	3.8
Arendal	5.4	4.4	0.5	0.9	0.6	0.04	0.07	0.005	12.0
Kristiansand I	1.6	3.0	0.06	0.7	0.4	0.02	0.09	0.005	5.9
Kristiansand II	3.4	5.2	0.2	1.5	1.0	0.06	0.2	0.01	11.6
Farsund	1.2	2.1	0.03	0.6	0.3	0.01	0.07	0.005	4.3
Fedafjorden	5.7	15.9	0.8	6.5	3.9	0.1	0.3	0.01	33.1
Flekkefjord	2.2	2.9	0.03	0.5	0.2	0.01	0.04	0.005	5.9
Stavanger	2.3	5.8	0.1	1.9	1.2	0.04	0.2	0.005	11.6
Sauda	5.2	7.6	0.3	3.6	2.2	0.05	0.2	0.005	19.2
Bergen I	3.6	7.3	0.2	1.5	1.0	0.04	0.1	0.005	13.8
Bergen II	2.6	4.7	0.06	0.8	0.4	0.01	0.05	0.005	8.6
Sunndalsøra	3.9	5.7	0.08	0.6	0.2	0.01	0.02	0.005	10.6
Trondheim I	4.2	8.0	0.3	1.7	0.8	0.02	0.06	0.005	15.1
Trondheim II	3.8	7.6	0.2	1.6	0.9	0.03	0.09	0.005	14.2
Hommelvik	32.5	40.9	1.5	6.3	2.6	0.04	0.08	0.005	83.8
Brønnøysund	1.3	2.9	0.09	0.7	0.4	0.02	0.05	0.005	5.4
Mo I Rana	1.5	4.1	0.1	1.0	0.6	0.03	0.07	0.01	7.5
Narvik I	3.9	5.6	0.3	1.1	0.7	0.03	0.05	0.005	11.7
Narvik II	1.6	2.9	0.1	0.6	0.4	0.02	0.04	0.005	5.5
Ramsundet	0.4	0.6	0.01	0.1	0.07	0.01	0.02	0.005	1.2
Harstad	1.4	1.5	0.07	0.3	0.2	0.01	0.02	0.005	3.5
Tromsø I	4.6	7.1	0.3	1.3	1.1	0.05	0.1	0.005	14.6
Tromsø II	4.0	6.3	0.4	1.0	0.9	0.03	0.07	0.005	12.8

Numbers in bold red: Less than MDL. Number given is ½ MDL.

Table S4b): Effective air volumes for the PAHs (m³).

Sites	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo[a]pyrene	Benz[a]anthracene	Chrysene
Oslo	<i>113</i>	<i>219</i>	<i>230</i>	<i>297</i>	<i>297</i>	<i>321</i>	<i>318</i>	<i>320</i>
Holmestrand	120	227	237	303	304	327	324	326
Tønsberg	127	276	292	406	407	450	444	448
Nøtterøy	120	226	236	301	301	324	321	323
Kragerø	131	264	277	369	369	402	398	401
Arendal	126	257	270	361	362	395	391	394
Kristiansand I	124	264	278	380	380	419	413	417
Kristiansand II	123	253	266	356	357	390	386	389
Farsund	117	213	222	278	278	298	295	297
Fedafjorden	117	212	221	277	277	296	294	296
Flekkefjord	119	224	234	298	299	322	318	321
Stavanger	121	238	249	326	327	355	351	353
Sauda	124	243	254	331	331	359	355	358
Bergen I	120	233	244	317	317	343	340	342
Bergen II	127	260	274	366	367	401	396	399
Sunndalsøra	119	206	213	260	261	277	275	276
Trondheim I	127	223	231	285	285	304	301	303
Trondheim II	129	231	239	299	299	319	317	319
Hommelvik	130	233	242	304	304	325	322	324
Brønnøysund	153	334	352	497	497	552	545	550
Mo i Rana	153	266	274	341	341	363	360	362
Narvik I	174	300	309	385	384	409	406	409
Narvik II	142	204	208	239	238	248	246	247
Ramsundet	<i>159</i>	<i>249</i>	<i>255</i>	<i>304</i>	<i>303</i>	<i>318</i>	<i>316</i>	<i>318</i>
Harstad	193	419	438	627	625	696	687	694
Tromsø I	198	360	371	477	475	510	506	510
Tromsø II	<i>169</i>	<i>257</i>	<i>262</i>	<i>308</i>	<i>307</i>	<i>322</i>	<i>320</i>	<i>321</i>

Values in *italics*: volumes are based on the default value (3.5 m³/day)

Table S5a): Concentrations of HCB and HCHs at coastal sites (pg/m³).

Sites	HCB	α -HCH	β -HCH	γ -HCH	Σ_3 HCHs
Oslo	43	14.9	0.3	16	31
Holmestrand	49	17.3	0.5	37	55
Tønsberg	42	18.1	0.5	18	36
Nøtterøy	44	15.4	0.6	17	33
Kragerø	50	16.0	0.6	18	35
Arendal	42	13.2	0.4	17	31
Kristiansand I	51	15.1	0.4	16	31
Kristiansand II	305	20.9	0.8	24	45
Farsund	47	16.9	0.5	15	33
Fedafjorden	47	16.9	0.4	20	37
Flekkefjord	44	14.4	0.3	13	27
Stavanger	42	17.6	0.6	28	47
Sauda	42	13.2	0.2	17	30
Bergen I	56	16.9	0.4	115	133
Bergen II	42	13.4	0.2	14	27
Sunndalsøra	44	12.8	0.1	7	20
Trondheim I	45	12.4	0.1	9	21
Trondheim II	55	17.5	0.3	15	32
Hommelvik	52	16.7	0.3	13	30
Brønnøysund	47	16.9	0.3	9	26
Mo i Rana	54	13.5	0.1	7	20
Narvik I	50	12.9	0.1	8	21
Narvik II	70	15.4	0.1	6	21
Ramsundet	53	14.7	0.1	4	19
Harstad	46	11.3	0.1	8	19
Tromsø I	60	21.6	0.2	7	29
Tromsø II	57	22.1	0.1	9	31

Numbers in bold red: Less than MDL. Number given is ½ MDL.

Table S5b): Effective air volumes for HCB and HCHs (m³).

Starion name	HCB	α -HCH	β -HCH	γ -HCH
Oslo	<i>184</i>	<i>216</i>	<i>306</i>	<i>243</i>
Holmestrand	190	223	312	250
Tønsberg	220	269	422	313
Nøtterøy	189	222	310	249
Kragerø	215	258	381	295
Arendal	209	251	374	288
Kristiansand I	212	258	394	298
Kristiansand II	206	248	369	283
Farsund	181	209	286	233
Fedafjorden	180	208	284	232
Flekkefjord	188	220	307	247
Stavanger	197	234	337	265
Sauda	201	238	342	269
Bergen I	194	229	327	258
Bergen II	212	255	379	291
Sunndalsøra	176	202	267	222
Trondheim I	189	218	292	241
Trondheim II	194	226	307	251
Hommelvik	196	228	312	254
Brønnøysund	258	322	519	378
Mo i Rana	221	258	350	287
Narvik I	247	290	395	323
Narvik II	180	200	242	214
Ramsundet	<i>213</i>	<i>242</i>	<i>310</i>	<i>264</i>
Harstad	311	396	656	470
Tromsø I	286	344	491	389
Tromsø II	<i>220</i>	<i>249</i>	<i>314</i>	<i>271</i>

Values in *italics*: volumes are based on the default value (3.5 m³/day)

Table S6a): Concentrations of DDTs and Chlordanes at coastal sites (pg/m³).

Sites	<i>p,p'</i> -DDE	<i>p,p'</i> -DDD	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	Σ ₄ DDTs	trans-Chlordane	cis-Chlordane	trans-Nonachlor	cis-Nonachlor	Σ ₄ Chlordanes
Oslo	3.1	0.1	1.3	1.6	6.1	N.A	N.A	N.A	N.A	N.A
Holmestrand	6.5	0.2	1.8	2.2	10.6	1.2	1.7	1.4	0.2	4.6
Tønsberg	6.2	0.3	2.2	2.5	11.1	1.6	2.4	1.8	0.3	6.2
Nøtterøy	4.6	0.1	2.1	2.5	9.2	3.9	3.4	3.4	0.7	11.4
Kragerø	3.5	0.1	1.5	1.7	6.7	3.4	4.0	2.6	0.4	10.4
Arendal	1.3	0.1	0.9	1.1	3.4	1.3	1.4	1.2	0.2	4.0
Kristiansand I	4.0	0.1	1.0	1.1	6.3	1.3	1.8	1.6	0.4	5.1
Kristiansand II	5.7	0.3	2.6	3.1	11.7	1.8	2.1	1.9	0.3	6.1
Farsund	4.7	0.1	1.5	1.7	8.0	0.5	1.2	1.2	0.2	3.0
Fedafjorden	3.2	0.1	1.4	1.4	6.2	0.4	1.2	1.1	0.2	2.9
Flekkefjord	2.8	0.1	1.2	1.5	5.7	0.7	1.2	1.2	0.6	3.6
Stavanger	4.7	0.1	1.9	2.4	9.2	0.8	1.5	1.7	0.4	4.5
Sauda	1.3	0.1	0.7	0.7	2.8	0.3	0.7	0.8	0.1	1.9
Bergen I	7.8	1.0	11.1	25.7	45.5	1.1	1.6	1.2	0.2	4.2
Bergen II	1.3	0.1	0.9	1.1	3.4	0.4	0.9	0.9	0.1	2.4
Sunndalsøra	1.3	0.06	0.5	0.4	2.3	N.A	N.A	N.A	N.A	N.A
Trondheim I	1.3	0.1	0.6	0.7	2.7	0.3	0.9	0.6	0.09	1.9
Trondheim II	2.8	0.1	1.0	1.0	4.9	0.6	1.2	1.1	0.2	3.1
Hommelvik	1.3	0.1	0.8	0.6	2.8	0.4	1.2	1.0	0.2	2.8
Brønnøysund	1.3	0.1	0.7	0.6	2.7	0.4	1.5	1.1	0.2	3.2
Mo i Rana	1.3	0.1	0.2	0.1	1.7	0.4	1.0	0.8	0.2	2.2
Narvik I	1.3	0.1	0.2	0.1	1.7	0.2	0.6	0.5	0.08	1.5
Narvik II	1.3	0.1	0.4	0.1	2.0	0.2	0.8	0.6	0.1	1.7
Ramsundet	1.3	0.1	0.4	0.3	2.1	0.2	1.0	0.7	0.1	2.0
Harstad	1.3	0.1	0.2	0.1	1.7	0.15	0.5	0.3	0.05	1.1
Tromsø I	1.3	0.04	0.5	0.5	2.3	0.5	0.9	1.6	0.3	3.4
Tromsø II	1.3	0.11	0.7	0.6	2.7	0.02	0.5	0.9	0.02	1.4

Numbers in bold red: Less than MDL. Number given is ½ MDL.

Values in italics: ionic ratio: NO and values could be influenced by a interference

N.A: no results available

Table S6b): Effective air volumes for the DDTs and Chlordanes (m³).

Starion name	p,p'-DDE	p,p'-DDD	o,p'-DDT	p,p'-DDT	trans-Chlordane	cis-Chlordane	trans-Nonachlor	cis-Nonachlor
Oslo	317	319	315	318	306	307	314	317
Holmestrand	323	325	321	323	312	313	320	323
Tønsberg	443	446	438	444	423	425	437	443
Nøtterøy	320	322	318	321	310	311	317	320
Kragerø	397	399	393	397	382	383	392	396
Arendal	390	392	386	390	374	376	385	389
Kristiansand I	412	415	408	413	394	396	407	412
Kristiansand II	384	387	381	385	369	371	380	384
Farsund	295	296	293	295	286	287	292	295
Fedafjorden	293	295	291	293	284	285	290	293
Flekkefjord	318	319	315	318	307	308	315	318
Stavanger	350	352	347	350	337	338	346	350
Sauda	354	356	351	355	342	343	351	354
Bergen I	339	341	336	339	327	328	335	339
Bergen II	395	398	391	396	379	381	391	395
Sunnalsøra	274	275	272	274	267	268	272	274
Trondheim I	301	302	299	301	293	293	298	301
Trondheim II	316	317	314	316	307	308	313	316
Hommelvik	321	323	319	322	312	313	319	321
Brønnøysund	543	547	537	544	519	522	537	543
Mo i Rana	360	361	357	360	350	351	357	359
Narvik I	406	407	403	406	395	397	403	405
Narvik II	246	247	245	246	242	243	245	246
Ramsundet	316	317	314	316	310	311	314	316
Harstad	685	689	678	686	656	660	678	685
Tromsø I	505	507	502	506	491	493	502	505
Tromsø II	320	321	318	320	314	315	318	320

Values in *italics*: volumes are based on the default value (3.5 m³/day)

Table S7a) Concentrations in coastal zones divided by median Norwegian background concentrations (R_{NW}).

Compounds	Coastal sites																										
	Oslo	Holmestrand	Tønsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedaifjorden	Flekkefjord	Stavanger	Sauda	Bergen I	Bergen II	Sundalsøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ramsundet	Harstad	Tromsø I	Tromsø II
PCB-28	6.5	3.3	2.5	2.6	5.2	2.2	1.9	5.6	1.3	6.7	1.2	4.5	1.8	6.1	2.3	0.9	1.8	5.1	1.7	1.6	3.3	2.9	1.0	0.7	1.1	5.8	1.9
PCB-52	10.1	3.8	3.1	3.7	4.6	1.9	2.4	9.0	1.5	3.5	1.3	7.5	3.2	12.9	4.2	0.8	4.3	4.2	1.6	1.6	2.0	2.8	1.1	0.7	1.3	5.9	2.1
PCB-101	13.7	4.8	3.9	5.0	4.5	2.2	2.9	16.0	2.0	3.2	1.7	10.6	5.8	20.0	3.2	0.9	6.8	5.8	2.4	2.4	2.2	3.4	1.3	1.2	1.5	12.8	2.8
PCB-118	10.8	5.3	3.5	6.2	4.1	1.9	2.8	21.6	1.7	2.8	1.3	10.4	7.6	19.7	3.3	NQ	5.5	5.3	2.3	2.1	2.4	3.2	1.3	NQ	1.4	6.8	2.1
PCB-138	10.0	5.9	4.8	6.8	6.3	3.0	3.5	16.6	2.7	3.3	1.9	10.9	5.5	20.1	2.8	NQ	5.8	6.6	4.6	3.7	3.0	3.2	NQ	1.9	2.2	12.3	2.2
PCB-153	10.1	5.5	4.9	5.8	6.3	3.6	3.5	14.3	3.0	3.4	2.1	10.5	4.4	18.6	2.8	NQ	5.5	6.4	4.4	4.1	2.7	3.1	NQ	NQ	2.2	12.9	2.3
PCB-180	7.3	5.5	5.9	5.0	8.3	4.0	3.9	12.4	2.9	3.8	2.0	9.6	2.8	15.0	3.1	NQ	4.4	6.3	5.0	4.9	3.3	2.2	NQ	1.8	2.3	12.4	2.0
$\Sigma_7\text{PCBs}^{1)}$	9.7	4.2	3.4	4.2	5.0	2.3	2.6	11.1	1.8	4.3	1.5	7.9	3.8	13.6	3.2	NQ	4.3	5.2	2.3	2.2	2.6	3.0	NQ	NQ	1.5	8.3	2.2
Fluorene	3.1	3.0	2.3	2.5	1.6	7.5	2.1	4.6	1.7	7.8	3.0	3.2	7.2	4.9	3.5	5.4	5.8	5.2	44.6	1.8	2.1	5.4	2.2	0.6	1.9	6.3	5.5
Phenanthrene	5.4	3.2	2.6	2.6	1.6	3.8	2.6	4.5	1.8	13.6	2.5	5.0	6.5	6.3	4.0	4.9	6.8	6.5	35.0	2.4	3.5	4.8	2.4	0.5	1.3	6.1	5.4
Anthracene	4.9	4.9	5.3	3.5	3.4	33.6	4.7	15.9	2.2	56.1	2.6	7.9	21.5	14.9	4.1	5.6	19.4	15.2	112.3	6.8	10.5	20.4	8.2	NQ	4.9	21.4	29.8
Fluoranthene	3.4	4.6	3.9	3.1	2.6	5.7	4.4	9.0	3.7	39.3	3.1	11.8	22.0	9.3	5.2	3.8	10.6	9.8	38.3	4.1	6.2	6.5	3.5	0.7	1.7	7.9	6.3
Pyrene	3.8	6.9	5.5	3.9	3.2	8.1	6.0	14.1	4.2	55.5	3.5	16.7	32.0	14.6	5.4	3.1	11.7	13.0	37.3	5.7	8.3	10.5	5.1	1.0	2.8	16.5	12.9
Benzo[a]pyrene	NQ	NQ	NQ	NQ	NQ	NQ	NQ	2.2	NQ	2.5	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	2.2	NQ	NQ	NQ	NQ	NQ	NQ
Benz[a]anthracene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Chrysene	4.4	4.4	5.3	4.2	3.2	6.5	9.0	19.8	6.6	25.4	3.4	19.7	18.5	10.8	4.5	1.8	6.0	8.9	7.7	5.0	6.8	5.1	3.8	1.4	1.9	10.5	6.4
$\Sigma_6\text{PAHs}^{2)}$	4.4	3.4	2.7	2.6	1.8	5.5	2.7	5.3	2.0	15.3	2.7	5.4	8.9	6.4	4.0	4.9	7.0	6.6	38.9	2.5	3.5	5.4	2.6	NQ	1.6	6.8	5.9
$\alpha\text{-HCH}$	2.0	2.3	2.4	2.0	2.1	1.7	2.0	2.8	2.2	2.2	1.9	2.3	1.7	2.2	1.8	1.7	1.6	2.3	2.2	2.2	1.8	1.7	2.0	1.9	1.5	2.8	2.9
$\beta\text{-HCH}$	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
$\gamma\text{-HCH}$	3.6	8.5	4.1	4.0	4.3	4.0	3.6	5.4	3.5	4.6	2.9	6.6	3.9	26.6	3.2	1.6	2.1	3.4	3.0	2.1	1.6	1.9	1.3	1.0	1.8	1.6	2.0
$\Sigma_3\text{HCHs}^{3)}$	2.6	4.5	3.0	2.7	2.9	2.6	2.6	3.7	2.7	3.1	2.3	3.9	2.5	11.1	2.3	1.7	1.8	2.7	2.5	2.2	1.7	1.8	1.8	1.6	1.6	2.4	2.6

Compounds	Coastal sites																										
	Oslo	Holmestrand	Tønsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedafjorden	Flekkelfjord	Stavanger	Sauda	Bergen I	Bergen II	Sumdalsøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ramsundet	Harstad	Tromsø I	Tromsø II
HCB	1.0	1.2	1.0	1.1	1.2	1.0	1.2	7.3	1.1	1.1	1.1	1.0	1.0	1.3	1.0	1.1	1.1	1.3	1.3	1.1	1.3	1.2	1.7	1.3	1.1	1.4	1.4
p,p'-DDE	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
p,p'-DDD	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
o,p'-DDT	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
p,p'-DDT	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Σ ₇ DDTs ⁴⁾	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
trans-Chlordane	NQ	3.3	4.5	10.9	9.5	3.5	3.6	5.1	1.3	1.2	1.9	2.2	0.8	3.1	1.2	NQ	0.8	1.5	1.1	1.0	1.1	0.7	0.7	0.6	0.4	1.3	NQ
cis-Chlordane	NQ	2.3	3.2	4.6	5.3	1.9	2.4	2.8	1.6	1.6	1.6	2.0	1.0	2.2	1.3	NQ	1.2	1.6	1.6	2.0	1.3	0.9	1.1	1.3	0.7	1.3	0.7
trans-Nonachlor	NQ	1.8	2.3	4.3	3.2	1.5	2.0	2.4	1.5	1.4	1.5	2.2	1.0	1.5	1.1	NQ	0.8	1.4	1.3	1.4	1.0	0.6	0.7	0.9	0.4	2.0	1.1
cis-Nonachlor	NQ	2.1	3.0	6.5	3.9	1.6	3.6	2.9	1.6	1.6	5.8	4.0	1.1	2.0	1.4	NQ	0.9	1.7	1.7	1.7	1.5	0.8	1.0	1.2	0.5	3.2	NQ
Σ ₄ Chlordanes	NQ	2.3	3.1	5.7	5.2	2.0	2.5	3.0	1.5	1.5	1.8	2.2	NQ	2.1	NQ	NQ	0.9	1.5	1.4	1.6	1.1	0.7	0.9	1.0	0.5	1.7	NQ

N.Q (not quantified): coastal site concentration < MDL (this study)

N.D (not detected): background concentration < MDL¹

¹⁾ Sum of seven PCBs

²⁾ Sum of six PAHs (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene)

³⁾ Sum of two HCHs (α and γ -HCH)

⁴⁾ Sum of two DDTs (*o,p'* and *p,p'*-DDT)

Table S7b) Concentrations in coastal zones divided by the maximum Norwegian background concentrations (R_{NWmax})

Compounds	Coastal sites																										
	Oslo	Holmestrand	Tønsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedafjorden	Flekkefjord	Stavanger	Sauda	Bergen I	Bergen II	Sundalsøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ramsundet	Harstad	Tromsø I	Tromsø II
PCB-28	3.5	1.8	1.4	1.4	2.8	1.2	1.0	3.1	0.7	3.7	0.7	2.4	1.0	3.3	1.3	0.5	1.0	2.8	0.9	0.8	1.8	1.6	0.5	0.4	0.6	3.2	1.0
PCB-52	5.2	1.9	1.6	1.9	2.4	1.0	1.2	4.6	0.7	1.8	0.7	3.9	1.7	6.6	2.1	0.4	2.2	2.2	0.8	0.8	1.0	1.4	0.5	0.4	0.7	3.1	1.1
PCB-101	5.1	1.8	1.5	1.9	1.6	0.8	1.1	5.9	0.7	1.2	0.6	3.9	2.1	7.4	1.2	0.3	2.5	2.1	0.9	0.9	0.8	1.3	0.5	0.4	0.6	4.7	1.0
PCB-118	4.6	2.2	1.5	2.6	1.7	0.8	1.2	9.1	0.7	1.2	0.5	4.4	3.2	8.3	1.4	NQ	2.3	2.3	1.0	0.9	1.0	1.4	0.5	NQ	0.6	2.9	0.9
PCB-138	2.1	1.2	1.0	1.4	1.3	0.6	0.7	3.4	0.6	0.7	0.4	2.3	1.1	4.2	0.6	NQ	1.2	1.4	0.9	0.8	0.6	0.7	NQ	0.4	0.5	2.5	0.5
PCB-153	2.2	1.2	1.0	1.2	1.3	0.8	0.7	3.0	0.6	0.7	0.4	2.2	0.9	4.0	0.6	NQ	1.2	1.4	0.9	0.9	0.6	0.7	NQ	NQ	0.5	2.7	0.5
PCB-180	1.0	0.8	0.8	0.7	1.1	0.5	0.5	1.7	0.4	0.5	0.3	1.3	0.4	2.1	0.4	NQ	0.6	0.9	0.7	0.7	0.5	0.3	NQ	0.3	0.3	1.7	0.3
$\Sigma_7PCBs^{1)}$	3.7	1.6	1.3	1.6	1.9	0.9	1.0	4.3	0.7	1.7	0.6	3.0	1.5	5.3	1.2	NQ	1.7	2.0	0.9	0.8	1.0	1.2	NQ	NQ	0.6	3.2	0.8
Fluorene	0.4	0.4	0.3	0.3	0.2	0.9	0.3	0.6	0.2	0.9	0.4	0.4	0.9	0.6	0.4	0.6	0.7	0.6	5.3	0.2	0.3	0.6	0.3	0.1	0.2	0.8	0.7
Phenanthrene	0.9	0.5	0.4	0.4	0.3	0.7	0.4	0.8	0.3	2.3	0.4	0.9	1.1	1.1	0.7	0.8	1.2	1.1	6.0	0.4	0.6	0.8	0.4	0.1	0.2	1.0	0.9
Anthracene	0.6	0.6	0.7	0.4	0.4	4.2	0.6	2.0	0.3	7.0	0.3	1.0	2.7	1.8	0.5	0.7	2.4	1.9	13.9	0.8	1.3	2.5	1.0	NQ	0.6	2.7	3.7
Fluoranthene	0.6	0.8	0.7	0.5	0.5	1.0	0.8	1.6	0.7	7.1	0.6	2.1	3.9	1.7	0.9	0.7	1.9	1.8	6.9	0.7	1.1	1.2	0.6	0.1	0.3	1.4	1.1
Pyrene	1.1	1.9	1.6	1.1	0.9	2.3	1.7	4.0	1.2	15.7	1.0	4.7	9.1	4.1	1.5	0.9	3.3	3.7	10.6	1.6	2.3	3.0	1.5	0.3	0.8	4.7	3.6
Benzo[a]pyrene	NQ	NQ	NQ	NQ	NQ	NQ	NQ	1.4	NQ	1.5	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	1.4	NQ	NQ	NQ	NQ	NQ	NQ
Benz[a]anthracene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Chrysene	2.6	2.6	3.1	2.5	1.9	3.8	5.3	11.6	3.9	14.9	2.0	11.5	10.8	6.3	2.6	1.0	3.5	5.2	4.5	2.9	4.0	3.0	2.2	0.8	1.1	6.1	3.7
$\Sigma_6PAHs^{2)}$	0.7	0.5	0.4	0.4	0.3	0.8	0.4	0.8	0.3	2.3	0.4	0.8	1.4	1.0	0.6	0.7	1.1	1.0	5.9	0.4	0.5	0.8	0.4	NQ	0.2	1.0	0.9
α -HCH	1.2	1.4	1.5	1.3	1.3	1.1	1.3	1.7	1.4	1.4	1.2	1.5	1.1	1.4	1.1	1.1	1.0	1.5	1.4	1.4	1.1	1.1	1.3	1.2	0.9	1.8	1.8
β -HCH	1.4	2.3	2.5	2.5	2.7	1.7	1.9	3.4	2.2	1.8	1.4	2.8	0.9	1.8	1.1	NQ	NQ	1.5	1.5	1.2	NQ	NQ	NQ	NQ	NQ	1.1	NQ
γ -HCH	2.0	4.6	2.2	2.2	2.3	2.2	2.0	3.0	1.9	2.5	1.6	3.6	2.1	14.5	1.7	0.9	1.1	1.8	1.7	1.2	0.9	1.0	0.7	0.6	1.0	0.9	1.1
$\Sigma_2HCHs^{3)}$	1.5	2.7	1.8	1.6	1.7	1.5	1.5	2.2	1.6	1.8	1.4	2.3	1.5	6.6	1.4	1.0	1.1	1.6	1.5	1.3	1.0	1.1	1.1	1.0	0.9	1.4	1.5
HCB	0.7	0.8	0.7	0.7	0.8	0.7	0.8	4.8	0.7	0.7	0.7	0.7	0.7	0.9	0.7	0.7	0.7	0.9	0.8	0.7	0.8	0.8	1.1	0.8	0.7	0.9	0.9
<i>p,p'</i> -DDE	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
<i>p,p'</i> -DDD	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D

Compounds	Coastal sites																										
	Oslo	Holmestrand	Tønsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedaflorden	Flekkefjord	Stavanger	Sauda	Bergen I	Bergen II	Sundalsøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ramsundet	Harstad	Tromsø I	Tromsø II
<i>o,p'</i> -DDT	1.6	2.2	2.7	2.5	1.8	1.1	1.3	3.3	1.9	1.7	1.5	2.4	0.9	13.7	1.2	0.7	0.8	1.3	1.0	0.8	NQ	NQ	0.6	0.5	NQ	0.6	0.9
<i>p,p'</i> -DDT	1.5	2.0	2.3	2.3	1.6	1.0	1.1	2.9	1.6	1.3	1.4	2.3	0.6	23.9	1.0	0.4	0.6	0.9	0.6	0.5	NQ	NQ	NQ	0.3	NQ	0.4	0.6
Σ ₂ DDTs ⁴⁾	1.5	2.1	2.5	2.4	1.7	1.1	1.2	3.1	1.7	1.5	1.5	2.3	0.7	19.5	1.1	0.5	0.7	1.1	0.8	0.7	NQ	NQ	NQ	0.4	NQ	0.5	NQ
trans-Chlordane	NQ	1.5	2.0	4.8	4.2	1.6	1.6	2.3	0.6	0.5	0.8	1.0	0.3	1.4	0.5	NQ	0.4	0.7	0.5	0.5	0.5	0.3	0.3	0.3	0.2	0.6	NQ
cis-Chlordane	NQ	1.2	1.6	2.3	2.7	1.0	1.2	1.4	0.8	0.8	0.8	1.0	0.5	1.1	0.6	NQ	0.6	0.8	0.8	1.0	0.7	0.4	0.5	0.7	0.3	0.6	0.3
trans-Nonachlor	NQ	0.7	0.9	1.7	1.3	0.6	0.8	1.0	0.6	0.5	0.6	0.9	0.4	0.6	0.4	NQ	0.3	0.5	0.5	0.6	0.4	0.2	0.3	0.4	0.2	0.8	0.4
cis-Nonachlor	NQ	0.7	1.0	2.1	1.3	0.5	1.2	1.0	0.5	0.5	1.9	1.3	0.4	0.7	0.4	NQ	0.3	0.6	0.6	0.6	0.5	0.3	0.3	0.4	0.2	1.0	NQ
Σ ₄ Chlordanes	NQ	1.0	1.3	2.5	2.2	0.9	1.1	1.3	0.6	0.6	0.8	1.0	NQ	0.9	NQ	NQ	0.4	0.7	0.6	0.7	0.5	0.3	0.4	0.4	0.2	0.7	NQ

N.Q (not quantified): coastal site concentration < MDL (this study)

N.D (not detected): background concentration < MDL¹

¹⁾ Sum of seven PCBs

²⁾ Sum of six PAHs (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene)

³⁾ Sum of two HCHs (α and γ -HCH)

⁴⁾ Sum of two DDTs (*o,p'*- and *p,p'*-DDT)

Table S7c) Concentrations in coastal zones divided by the minimum Norwegian background concentrations (R_{NWmin}).

Compounds	Coastal sites																										
	Oslo	Holmestrand	Tønsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedafjorden	Flekkefjord	Stavanger	Sauda	Bergen I	Bergen II	Sundalsøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ramsundet	Hartstad	Tromsø I	Tromsø II
PCB-28	17.6	8.9	6.9	7.1	14.1	5.9	5.1	15.3	3.5	18.2	3.4	12.1	4.9	16.5	6.4	2.4	5.0	13.8	4.6	4.2	9.1	7.9	2.7	1.9	3.0	15.7	5.2
PCB-52	22.9	8.5	6.9	8.5	10.4	4.3	5.5	20.3	3.3	8.0	3.0	17.0	7.3	29.3	9.4	1.7	9.7	9.6	3.7	3.5	4.5	6.4	2.4	1.7	3.0	13.5	4.8
PCB-101	32.2	11.2	9.3	11.8	10.5	5.1	6.9	37.6	4.7	7.6	4.1	24.9	13.7	46.9	7.6	2.2	15.9	13.6	5.7	5.7	5.2	8.1	3.1	2.8	3.5	30.0	6.5
PCB-118	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
PCB-138	21.8	12.9	10.5	14.8	13.8	6.7	7.6	36.4	5.9	7.3	4.2	24.0	11.9	43.9	6.1	NQ	12.8	14.5	10.0	8.1	6.6	7.0	NQ	4.2	4.8	27.0	4.8
PCB-153	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
PCB-180	13.9	10.5	11.3	9.6	15.8	7.6	7.5	23.7	5.5	7.2	3.9	18.4	5.4	28.6	5.9	NQ	8.5	12.1	9.6	9.3	6.4	4.3	NQ	3.5	4.5	23.8	3.8
Σ ₇ PCBs ¹⁾	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Fluorene	11.9	11.4	8.8	9.5	6.3	28.7	8.2	17.7	6.4	29.8	11.5	12.2	27.4	18.8	13.5	20.7	22.1	20.0	170.7	6.8	8.1	20.6	8.3	2.3	7.3	24.3	21.1
Phenanthrene	16.0	9.4	7.7	7.7	4.8	11.3	7.7	13.4	5.3	40.6	7.4	14.8	19.4	18.7	11.9	14.6	20.4	19.3	104.4	7.3	10.4	14.4	7.3	1.4	4.0	18.1	16.2
Anthracene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Fluoranthene	7.2	9.7	8.2	6.4	5.4	12.1	9.2	19.0	7.7	82.7	6.6	24.8	46.2	19.6	10.9	8.1	22.3	20.6	80.6	8.6	13.1	13.6	7.3	1.5	3.5	16.6	13.3
Pyrene	7.4	13.5	10.8	7.6	6.3	15.9	11.7	27.6	8.3	109.0	6.8	32.8	62.8	28.6	10.6	6.0	23.0	25.6	73.2	11.3	16.2	20.7	10.1	2.0	5.5	32.4	25.3
Benzo[a]pyrene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Benz[a]anthracene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Chrysene	7.7	7.8	9.4	7.5	5.7	11.4	15.9	35.0	11.7	44.9	6.1	34.7	32.6	19.0	7.9	3.2	10.6	15.8	13.6	8.8	12.0	9.0	6.8	2.5	3.4	18.5	11.2
Σ ₆ PAHs ²⁾	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
α-HCH	3.2	3.8	3.9	3.3	3.5	2.9	3.3	4.6	3.7	3.7	3.1	3.8	2.9	3.7	2.9	2.8	2.7	3.8	3.6	3.7	2.9	2.8	3.3	3.2	2.5	4.7	4.8
β-HCH	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
γ-HCH	10.4	24.5	11.7	11.4	12.2	11.6	10.4	15.6	10.1	13.3	8.5	18.9	11.3	76.7	9.1	4.6	5.9	9.7	8.8	6.2	4.6	5.4	3.9	3.0	5.1	4.6	5.8
Σ ₂ HCHs ³⁾	5.0	8.9	5.9	5.3	5.7	5.0	5.0	7.3	5.3	6.1	4.5	7.5	4.9	21.7	4.4	3.2	3.5	5.3	4.9	4.3	3.3	3.5	3.5	3.1	3.1	4.7	5.0
HCB	1.7	1.9	1.7	1.8	2.0	1.7	2.0	12.0	1.9	1.9	1.7	1.7	1.6	2.2	1.7	1.7	1.8	2.2	2.1	1.8	2.1	2.0	2.8	2.1	1.8	2.4	2.2
p,p'-DDE	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
p,p'-DDD	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D

Compounds	Coastal sites																										
	Oslo	Holmestrand	Tønsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedafljorden	Flekkefjord	Stavanger	Sauda	Bergen I	Bergen II	Sundalsøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ransundet	Harstad	Tromsø I	Tromsø II
<i>o,p'</i> -DDT	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
<i>p,p'</i> -DDT	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Σ ₂ DDTs ⁴⁾	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
trans-Chlordane	NQ	9.6	12.9	31.7	27.6	10.2	10.5	14.8	3.7	3.6	5.6	6.5	2.3	8.9	3.5	NQ	2.4	4.5	3.3	3.0	3.1	2.0	2.0	1.6	1.2	3.9	NQ
cis-Chlordane	NQ	4.1	5.8	8.1	9.5	3.4	4.2	4.9	2.8	2.9	2.8	3.6	1.8	3.9	2.3	NQ	2.1	2.9	2.9	3.6	2.3	1.5	1.9	2.3	1.2	2.2	1.2
trans-Nonachlor	NQ	3.3	4.3	8.0	6.0	2.7	3.8	4.5	2.7	2.6	2.7	4.0	1.8	2.8	2.0	NQ	1.4	2.6	2.4	2.6	1.8	1.2	1.4	1.7	0.8	3.8	2.0
cis-Nonachlor	NQ	4.7	6.6	14.5	8.6	3.5	8.0	6.5	3.6	3.5	12.9	8.9	2.5	4.5	3.0	NQ	2.0	3.9	3.7	3.8	3.3	1.7	2.3	2.6	1.0	7.0	NQ
Σ ₄ Chlordanes	NQ	4.5	6.0	11.2	10.2	4.0	5.0	6.0	2.9	2.9	3.6	4.4	NQ	4.1	NQ	NQ	1.9	3.0	2.8	3.1	2.2	1.4	1.7	2.0	1.0	3.3	NQ

N.Q (not quantified): coastal site concentration < MDL (this study)

N.D (not detected): background concentration < MDL¹

¹⁾ Sum of seven PCBs

²⁾ Sum of six PAHs (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene)

³⁾ Sum of two HCHs (α and γ -HCH)

⁴⁾ Sum of two DDTs (*o,p'* and *p,p'*-DDT)

Table S8a) Concentrations in coastal zones divided by the median Nordic background concentrations (R_{ND}).

Compounds	Coastal sites																											
	Oslo	Holmestrand	Tønsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedafjorden	Flekkefjord	Stavanger	Sauda	Bergen I	Bergen II	Sundalsøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ramsundet	Harstad	Tromsø I	Tromsø II	
PCB-28	5.1	2.6	2.0	2.1	4.1	1.7	1.5	4.5	1.0	5.3	1.0	3.6	1.4	4.8	1.9	0.7	1.5	4.0	1.4	1.2	2.7	2.3	0.8	0.5	0.9	4.6	1.5	
PCB-52	7.8	2.9	2.4	2.9	3.6	1.5	1.9	6.9	1.1	2.7	1.0	5.8	2.5	10.0	3.2	0.6	3.3	3.3	1.3	1.2	1.5	2.2	0.8	0.6	1.0	4.6	1.6	
PCB-101	7.7	2.7	2.2	2.8	2.5	1.2	1.7	9.0	1.1	1.8	1.0	6.0	3.3	11.2	1.8	0.5	3.8	3.3	1.4	1.4	1.2	1.9	0.8	0.7	0.8	7.2	1.5	
PCB-118	6.8	3.3	2.2	3.9	2.5	1.2	1.8	13.5	1.1	1.7	0.8	6.5	4.8	12.4	2.1	NQ	3.5	3.4	1.5	1.3	1.5	2.0	0.8	NQ	0.9	4.3	1.3	
PCB-138	3.6	2.1	1.7	2.4	2.3	1.1	1.2	5.9	1.0	1.2	0.7	3.9	2.0	7.2	1.0	NQ	2.1	2.4	1.6	1.3	1.1	1.1	NQ	0.7	0.8	4.4	0.8	
PCB-153	3.5	1.9	1.7	2.0	2.2	1.2	1.2	4.9	1.0	1.2	0.7	3.6	1.5	6.3	1.0	NQ	1.9	2.2	1.5	1.4	0.9	1.1	NQ	NQ	0.8	4.4	0.8	
PCB-180	2.5	1.9	2.0	1.7	2.8	1.4	1.4	4.3	1.0	1.3	0.7	3.3	1.0	5.1	1.1	NQ	1.5	2.2	1.7	1.7	1.1	0.8	NQ	0.6	0.8	4.3	0.7	
Σ ₇ PCBs ¹⁾	5.9	2.5	2.1	2.5	3.0	1.4	1.6	6.7	1.1	2.6	0.9	4.8	2.3	8.2	1.9	NQ	2.6	3.1	1.4	1.3	1.6	1.8	NQ	NQ	0.9	5.0	1.3	
Fluorene	3.3	3.2	2.4	2.6	1.8	8.0	2.3	4.9	1.8	8.3	3.2	3.4	7.6	5.2	3.7	5.8	6.1	5.6	47.5	1.9	2.3	5.7	2.3	0.6	2.0	6.8	5.9	
Phenanthrene	4.2	2.5	2.0	2.0	1.3	3.0	2.0	3.5	1.4	10.8	2.0	3.9	5.2	5.0	3.2	3.9	5.4	5.1	27.7	1.9	2.8	3.8	1.9	0.4	1.0	4.8	4.3	
Anthracene	4.4	4.4	4.8	3.2	3.1	30.0	4.2	14.2	1.9	50.2	2.3	7.1	19.2	13.3	3.7	5.0	17.4	13.6	100.4	6.1	9.4	18.2	7.3	NQ	4.4	19.1	26.7	
Fluoranthene	2.1	2.9	2.4	1.9	1.6	3.6	2.7	5.6	2.3	24.4	1.9	7.3	13.6	5.8	3.2	2.4	6.6	6.1	23.7	2.5	3.8	4.0	2.1	0.4	1.0	4.9	3.9	
Pyrene	2.5	4.6	3.7	2.6	2.2	5.4	4.0	9.4	2.8	37.2	2.3	11.2	21.4	9.7	3.6	2.1	7.9	8.7	25.0	3.8	5.5	7.0	3.4	0.7	1.9	11.1	8.6	
Benzo[a]pyrene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	
Benz[a]anthracene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	
Chrysene	3.7	3.8	4.6	3.6	2.7	5.5	7.7	16.9	5.7	21.7	2.9	16.8	15.8	9.2	3.8	1.5	5.1	7.6	6.6	4.2	5.8	4.4	3.3	1.2	1.6	9.0	5.4	
Σ ₆ PAHs ²⁾	3.7	2.8	2.3	2.2	1.5	4.7	2.3	4.5	1.7	12.9	2.3	4.5	7.5	5.4	3.3	4.1	5.9	5.6	32.8	2.1	2.9	4.6	2.2	NQ	1.4	5.7	5.0	
α-HCH	1.7	2.0	2.1	1.8	1.9	1.5	1.8	2.4	2.0	2.0	1.7	2.0	1.5	2.0	1.6	1.5	1.4	2.0	1.9	2.0	1.6	1.5	1.8	1.7	1.3	2.5	2.6	
β-HCH	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	
γ-HCH	3.1	7.4	3.5	3.4	3.7	3.5	3.1	4.7	3.0	4.0	2.6	5.7	3.4	23.1	2.7	1.4	1.8	2.9	2.6	1.9	1.4	1.6	1.2	0.9	1.5	1.4	1.7	
Σ ₂ HCHs ³⁾	2.2	4.0	2.6	2.4	2.5	2.3	2.3	3.3	2.4	2.7	2.0	3.4	2.2	9.7	2.0	1.4	1.6	2.4	2.2	1.9	1.5	1.5	1.6	1.4	1.4	2.1	2.3	
HCB	1.0	1.2	1.0	1.1	1.2	1.0	1.2	7.3	1.1	1.1	1.1	1.0	1.0	1.3	1.0	1.1	1.1	1.3	1.2	1.1	1.3	1.2	1.7	1.3	1.1	1.4	1.4	
p,p'-DDE	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	
p,p'-DDD	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	

Compounds	Coastal sites																										
	Oslo	Holmestrand	Tønsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedafløden	Flekkefjord	Stavanger	Sauda	Bergen I	Bergen II	Sumdalsøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ramsundet	Harstad	Tronsø I	Tromsø II
<i>o,p'</i> -DDT	3.6	4.9	6.1	5.7	4.2	2.6	2.9	7.4	4.3	3.9	3.5	5.4	2.0	31.0	2.6	1.5	1.8	2.9	2.2	1.9	NQ	NQ	1.3	1.2	NQ	1.3	2.0
<i>p,p'</i> -DDT	5.2	7.1	8.1	8.1	5.5	3.6	3.7	10.3	5.4	4.7	5.0	8.0	2.2	83.9	3.4	1.4	2.3	3.2	2.1	1.9	NQ	NQ	NQ	1.0	NQ	1.5	2.1
Σ ₂ DDTs ⁴⁾	4.4	5.9	7.0	6.8	4.8	3.1	3.3	8.7	4.8	4.3	4.2	6.6	2.1	55.4	3.0	1.5	2.0	3.0	2.2	1.9	NQ	NQ	NQ	1.1	NQ	1.4	NQ
trans-Chlordane	NQ	3.5	4.7	11.4	10.0	3.7	3.8	5.3	1.3	1.3	2.0	2.3	0.8	3.2	1.3	NQ	0.9	1.6	1.2	1.1	1.1	0.7	0.7	0.6	0.4	1.4	NQ
cis-Chlordane	NQ	2.3	3.1	4.4	5.1	1.9	2.3	2.7	1.5	1.6	1.5	2.0	1.0	2.1	1.2	NQ	1.1	1.6	1.6	2.0	1.3	0.8	1.0	1.3	0.7	1.2	0.7
trans-Nonachlor	NQ	1.8	2.3	4.3	3.2	1.5	2.0	2.4	1.5	1.4	1.5	2.2	1.0	1.5	1.1	NQ	0.8	1.4	1.3	1.4	1.0	0.6	0.7	0.9	0.4	2.0	1.1
cis-Nonachlor	NQ	2.4	3.3	7.2	4.3	1.8	4.0	3.3	1.8	1.7	6.4	4.5	1.3	2.3	1.5	NQ	1.0	1.9	1.9	1.9	1.6	0.8	1.1	1.3	0.5	3.5	NQ
Σ ₄ Chlordanes	NQ	2.3	3.1	5.7	5.2	2.0	2.5	3.1	1.5	1.5	1.8	2.2	NQ	2.1	NQ	NQ	0.9	1.5	1.4	1.6	1.1	0.7	0.9	1.0	0.5	1.7	NQ

N.Q (not quantified): coastal site concentration < MDL (this study)

N.D (not detected): background concentration < MDL ¹

¹⁾ Sum of seven PCBs

²⁾ Sum of six PAHs (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene)

³⁾ Sum of two HCHs (α and γ -HCH)

⁴⁾ Sum of two DDTs (*o,p'*- and *p,p'*-DDT)

Table S8b) Concentrations in coastal zones divided by the maximum Nordic background concentrations (R_{NDmax}).

Compounds	Coastal sites																										
	Oslo	Holmestrand	Tønsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedafjorden	Flekkfjord	Stavanger	Sauda	Bergen I	Bergen II	Sundalsøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ramsundet	Harstad	Tromsø I	Tromsø II
PCB-28	1.5	0.8	0.6	0.6	1.2	0.5	0.4	1.3	0.3	1.6	0.3	1.1	0.4	1.5	0.6	0.2	0.4	1.2	0.4	0.4	0.8	0.7	0.2	0.2	0.3	1.4	0.5
PCB-52	2.1	0.8	0.6	0.8	1.0	0.4	0.5	1.9	0.3	0.7	0.3	1.6	0.7	2.7	0.9	0.2	0.9	0.9	0.3	0.3	0.4	0.6	0.2	0.2	0.3	1.3	0.4
PCB-101	1.1	0.4	0.3	0.4	0.4	0.2	0.2	1.3	0.2	0.3	0.1	0.9	0.5	1.6	0.3	0.1	0.5	0.5	0.2	0.2	0.2	0.3	0.1	0.1	0.1	1.0	0.2
PCB-118	0.8	0.4	0.3	0.5	0.3	0.1	0.2	1.7	0.1	0.2	0.1	0.8	0.6	1.5	0.3	NQ	0.4	0.4	0.2	0.2	0.2	0.2	0.1	NQ	0.1	0.5	0.2
PCB-138	0.5	0.3	0.2	0.3	0.3	0.1	0.2	0.8	0.1	0.2	0.1	0.5	0.3	1.0	0.1	NQ	0.3	0.3	0.2	0.2	0.1	0.2	NQ	0.1	0.1	0.6	0.1
PCB-153	0.5	0.3	0.2	0.3	0.3	0.2	0.2	0.7	0.1	0.2	0.1	0.5	0.2	0.9	0.1	NQ	0.3	0.3	0.2	0.2	0.1	0.2	NQ	NQ	0.1	0.7	0.1
PCB-180	0.3	0.2	0.2	0.2	0.3	0.1	0.1	0.4	0.1	0.1	0.1	0.3	0.1	0.5	0.1	NQ	0.2	0.2	0.2	0.2	0.1	0.1	NQ	0.1	0.1	0.4	0.1
$\Sigma_7\text{PCBs}^{1)}$	1.1	0.5	0.4	0.5	0.5	0.2	0.3	1.2	0.2	0.5	0.2	0.9	0.4	1.5	0.3	NQ	0.5	0.6	0.3	0.2	0.3	0.3	NQ	NQ	0.2	0.9	0.2
Fluorene	0.4	0.4	0.3	0.3	0.2	0.9	0.3	0.6	0.2	0.9	0.4	0.4	0.9	0.6	0.4	0.6	0.7	0.6	5.3	0.2	0.3	0.6	0.3	0.1	0.2	0.8	0.7
Phenanthrene	0.9	0.5	0.4	0.4	0.3	0.7	0.4	0.8	0.3	2.3	0.4	0.9	1.1	1.1	0.7	0.8	1.2	1.1	6.0	0.4	0.6	0.8	0.4	0.1	0.2	1.0	0.9
Anthracene	0.6	0.6	0.7	0.4	0.4	4.2	0.6	2.0	0.3	7.0	0.3	1.0	2.7	1.8	0.5	0.7	2.4	1.9	13.9	0.8	1.3	2.5	1.0	NQ	0.6	2.7	3.7
Fluoranthene	0.4	0.5	0.5	0.4	0.3	0.7	0.5	1.0	0.4	4.5	0.4	1.4	2.5	1.1	0.6	0.4	1.2	1.1	4.4	0.5	0.7	0.7	0.4	0.1	0.2	0.9	0.7
Pyrene	0.4	0.8	0.6	0.4	0.4	0.9	0.7	1.6	0.5	6.3	0.4	1.9	3.6	1.6	0.6	0.3	1.3	1.5	4.2	0.6	0.9	1.2	0.6	0.1	0.3	1.9	1.5
Benzo[a]pyrene	NQ	NQ	NQ	NQ	NQ	NQ	NQ	0.2	NQ	0.2	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	0.2	NQ	NQ	NQ	NQ	NQ	NQ
Benz[a]anthracene	NQ	0.2	0.3	0.2	NQ	0.6	0.4	1.0	0.2	2.4	0.2	0.6	0.9	0.6	0.2	NQ	0.3	0.5	0.6	0.4	0.5	0.4	0.3	NQ	NQ	0.8	0.5
Chrysene	0.3	0.3	0.4	0.3	0.3	0.5	0.7	1.6	0.5	2.0	0.3	1.6	1.5	0.8	0.4	0.1	0.5	0.7	0.6	0.4	0.5	0.4	0.3	0.1	0.2	0.8	0.5
$\Sigma_6\text{PAHs}^{2)}$	0.6	0.5	0.4	0.4	0.3	0.8	0.4	0.8	0.3	2.2	0.4	0.8	1.3	0.9	0.6	0.7	1.0	0.9	5.5	0.4	0.5	0.8	0.4	NQ	0.2	1.0	0.8
α -HCH	0.9	1.0	1.1	0.9	0.9	0.8	0.9	1.2	1.0	1.0	0.8	1.0	0.8	1.0	0.8	0.7	0.7	1.0	1.0	1.0	0.8	0.7	0.9	0.9	0.7	1.3	1.3
β -HCH	0.2	0.3	0.4	0.4	0.4	0.3	0.3	0.5	0.3	0.3	0.2	0.4	0.1	0.3	0.2	NQ	NQ	0.2	0.2	0.2	NQ	NQ	NQ	NQ	NQ	0.2	NQ
γ -HCH	1.0	2.4	1.1	1.1	1.2	1.1	1.0	1.5	1.0	1.3	0.8	1.8	1.1	7.4	0.9	0.4	0.6	0.9	0.8	0.6	0.4	0.5	0.4	0.3	0.5	0.4	0.6
$\Sigma_2\text{HCHs}^{3)}$	0.9	1.6	1.1	1.0	1.1	0.9	0.9	1.4	1.0	1.1	0.8	1.4	0.9	4.0	0.8	0.6	0.7	1.0	0.9	0.8	0.6	0.6	0.6	0.6	0.6	0.9	0.9
HCB	0.5	0.6	0.5	0.6	0.6	0.5	0.6	3.8	0.6	0.6	0.6	0.5	0.5	0.7	0.5	0.6	0.6	0.7	0.7	0.6	0.7	0.6	0.9	0.7	0.6	0.8	0.7
p,p' -DDE	0.3	0.6	0.6	0.4	0.3	NQ	0.4	0.5	0.4	0.3	0.3	0.4	NQ	0.7	NQ	NQ	NQ	0.3	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
p,p' -DDD	NQ	NQ	0.8	NQ	NQ	NQ	NQ	0.9	NQ	NQ	NQ	NQ	NQ	3.1	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ

Compounds	Coastal sites																										
	Oslo	Holmestrand	Tønsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedafljorden	Flekkelfjord	Stavanger	Sauda	Bergen I	Bergen II	Sundalsøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ramsundet	Harstad	Tromsø I	Tromsø II
<i>o,p'</i> -DDT	0.4	0.6	0.7	0.7	0.5	0.3	0.3	0.8	0.5	0.5	0.4	0.6	0.2	3.6	0.3	0.2	0.2	0.3	0.3	0.2	NQ	NQ	0.1	0.1	NQ	0.2	0.2
<i>p,p'</i> -DDT	0.4	0.5	0.6	0.6	0.4	0.3	0.3	0.8	0.4	0.4	0.4	0.6	0.2	6.3	0.3	0.1	0.2	0.2	0.2	0.1	NQ	NQ	NQ	0.1	NQ	0.1	0.2
Σ_2 DDTs ⁴⁾	0.4	0.5	0.6	0.6	0.4	0.3	0.3	0.8	0.4	0.4	0.4	0.6	0.2	5.1	0.3	0.1	0.2	0.3	0.2	0.2	NQ	NQ	NQ	0.1	NQ	0.1	NQ
trans-Chlordane	NQ	1.5	2.0	4.8	4.2	1.6	1.6	2.3	0.6	0.5	0.8	1.0	0.3	1.4	0.5	NQ	0.4	0.7	0.5	0.5	0.5	0.3	0.3	0.3	0.2	0.6	NQ
cis-Chlordane	NQ	1.0	1.4	1.9	2.2	0.8	1.0	1.2	0.7	0.7	0.7	0.8	0.4	0.9	0.5	NQ	0.5	0.7	0.7	0.9	0.5	0.4	0.4	0.6	0.3	0.5	0.3
trans-Nonachlor	NQ	0.7	0.9	1.7	1.3	0.6	0.8	1.0	0.6	0.5	0.6	0.9	0.4	0.6	0.4	NQ	0.3	0.5	0.5	0.6	0.4	0.2	0.3	0.4	0.2	0.8	0.4
cis-Nonachlor	NQ	0.5	0.8	1.7	1.0	0.4	0.9	0.7	0.4	0.4	1.5	1.0	0.3	0.5	0.3	NQ	0.2	0.4	0.4	0.4	0.4	0.2	0.3	0.3	0.1	0.8	NQ
Σ_4 Chlordanes	NQ	0.9	1.2	2.3	2.1	0.8	1.0	1.2	0.6	0.6	0.7	0.9	NQ	0.8	NQ	NQ	0.4	0.6	0.6	0.6	0.5	0.3	0.3	0.4	0.2	0.7	NQ

N.Q (not quantified): coastal site concentration < MDL (this study)

¹⁾ Sum of seven PCBs

²⁾ Sum of six PAHs (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene)

³⁾ Sum of two HCHs (α and γ -HCH)

⁴⁾ Sum of two DDTs (*o,p'* and *p,p'*-DDT)

Table S8c) Concentrations in coastal zones divided by the minimum Nordic background concentrations (R_{NDmin}).

Compounds	Coastal sites																										
	Oslo	Holmestrand	Tønsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedafjorden	Flekkefjord	Stavanger	Sauda	Bergen I	Bergen II	Sunnalsøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ramsundet	Hartstad	Tromsø I	Tromsø II
PCB-28	17.6	8.9	6.9	7.1	14.1	5.9	5.1	15.3	3.5	18.2	3.4	12.1	4.9	16.5	6.4	2.4	5.0	13.8	4.6	4.2	9.1	7.9	2.7	1.9	3.0	15.7	5.2
PCB-52	22.9	8.5	6.9	8.5	10.4	4.3	5.5	20.3	3.3	8.0	3.0	17.0	7.3	29.3	9.4	1.7	9.7	9.6	3.7	3.5	4.5	6.4	2.4	1.7	3.0	13.5	4.8
PCB-101	32.2	11.2	9.3	11.8	10.5	5.1	6.9	37.6	4.7	7.6	4.1	24.9	13.7	46.9	7.6	2.2	15.9	13.6	5.7	5.7	5.2	8.1	3.1	2.8	3.5	30.0	6.5
PCB-118	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
PCB-138	21.8	12.9	10.5	14.8	13.8	6.7	7.6	36.4	5.9	7.3	4.2	24.0	11.9	43.9	6.1	NQ	12.8	14.5	10.0	8.1	6.6	7.0	NQ	4.2	4.8	27.0	4.8
PCB-153	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
PCB-180	13.9	10.5	11.3	9.6	15.8	7.6	7.5	23.7	5.5	7.2	3.9	18.4	5.4	28.6	5.9	NQ	8.5	12.1	9.6	9.3	6.4	4.3	NQ	3.5	4.5	23.8	3.8
Σ ₇ PCBs ¹⁾	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Fluorene	12.1	11.6	8.9	9.7	6.4	29.1	8.3	18.0	6.5	30.3	11.7	12.4	27.9	19.1	13.7	21.1	22.4	20.3	173.5	6.9	8.3	20.9	8.4	2.3	7.5	24.7	21.4
Phenanthrene	18.6	11.0	8.9	8.9	5.5	13.2	8.9	15.6	6.2	47.1	8.6	17.2	22.6	21.7	13.8	16.9	23.7	22.5	121.3	8.5	12.1	16.7	8.5	1.7	4.6	21.0	18.9
Anthracene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Fluoranthene	7.3	9.9	8.4	6.6	5.5	12.3	9.5	19.4	7.9	84.6	6.7	25.4	47.2	20.0	11.1	8.2	22.8	21.1	82.4	8.8	13.4	13.9	7.4	1.5	3.6	16.9	13.6
Pyrene	8.0	14.5	11.7	8.2	6.8	17.1	12.6	29.7	9.0	117.4	7.3	35.3	67.7	30.8	11.4	6.5	24.8	27.5	78.9	12.1	17.5	22.3	10.9	2.2	6.0	35.0	27.2
Benzo[a]pyrene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Benz[a]anthracene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Chrysene	7.9	8.0	9.6	7.6	5.8	11.7	16.3	35.9	12.0	46.0	6.2	35.6	33.4	19.5	8.1	3.2	10.9	16.2	14.0	9.0	12.3	9.2	6.9	2.6	3.5	19.0	11.5
Σ ₆ PAHs ²⁾	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
α-HCH	3.4	3.9	4.1	3.5	3.6	3.0	3.4	4.7	3.8	3.8	3.2	3.9	3.0	3.8	3.0	2.9	2.8	3.9	3.8	3.8	3.0	2.9	3.5	3.3	2.5	4.9	5.0
β-HCH	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
γ-HCH	10.4	24.5	11.7	11.4	12.2	11.6	10.4	15.6	10.1	13.3	8.5	18.9	11.3	76.7	9.1	4.6	5.9	9.7	8.8	6.2	4.6	5.4	3.9	3.0	5.1	4.6	5.8
Σ ₂ HCHs ³⁾	5.1	9.1	6.0	5.5	5.8	5.2	5.2	7.5	5.4	6.2	4.6	7.7	5.1	22.2	4.6	3.3	3.6	5.4	5.0	4.4	3.4	3.5	3.6	3.2	3.2	4.8	5.2
HCB	1.7	2.0	1.7	1.8	2.0	1.7	2.1	12.2	1.9	1.9	1.8	1.7	1.7	2.2	1.7	1.8	1.8	2.2	2.1	1.9	2.1	2.0	2.8	2.1	1.9	2.4	2.3
p,p'-DDE	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
p,p'-DDD	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D

	Coastal sites																										
	Oslo	Holmestrand	Tønsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedafljorden	Flekkefjord	Stavanger	Sauda	Bergen I	Bergen II	Sundalsøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ransundet	Harstad	Tromsø I	Tromsø II
Compounds																											
<i>o,p'</i> -DDT	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
<i>p,p'</i> -DDT	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Σ_2 DDTs ⁴⁾	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
trans-Chlordane	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
cis-Chlordane	NQ	6.1	8.5	12.0	14.0	5.1	6.3	7.3	4.2	4.3	4.1	5.3	2.6	5.8	3.3	NQ	3.1	4.3	4.3	5.3	3.4	2.3	2.8	3.5	1.8	3.3	1.8
trans-Nonachlor	NQ	4.9	6.4	11.8	8.9	4.1	5.6	6.7	4.0	3.8	4.1	6.0	2.7	4.2	3.0	NQ	2.1	3.8	3.6	3.9	2.7	1.7	2.1	2.5	1.2	5.6	3.0
cis-Nonachlor	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Σ_4 Chlordanes	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D

N.Q (not quantified): coastal site concentration < MDL (this study)

N.D (not detected): background concentration < MDL ¹

¹⁾ Sum of seven PCBs

²⁾ Sum of six PAHs (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene)

³⁾ Sum of two HCHs (α and γ -HCH)

⁴⁾ Sum of two DDTs (*o,p'*- and *p,p'*-DDT)

Table S9a) Concentrations in coastal zones divided by the median European background concentrations (R_{EU}).

Compounds	Coastal sites																											
	Oslo	Holmestrand	Tønsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedaifjorden	Flekkefjord	Stavanger	Sauda	Bergen I	Bergen II	Sundalsøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ramsundet	Harstad	Tromsø I	Tromsø II	
PCB-28	2.6	1.3	1.0	1.0	2.1	0.9	0.7	2.2	0.5	2.7	0.5	1.8	0.7	2.4	0.9	0.3	0.7	2.0	0.7	0.6	1.3	1.2	0.4	0.3	0.4	2.3	0.8	
PCB-52	4.0	1.5	1.2	1.5	1.8	0.7	0.9	3.5	0.6	1.4	0.5	2.9	1.3	5.1	1.6	0.3	1.7	1.7	0.6	0.6	0.8	1.1	0.4	0.3	0.5	2.3	0.8	
PCB-101	5.2	1.8	1.5	1.9	1.7	0.8	1.1	6.0	0.7	1.2	0.7	4.0	2.2	7.5	1.2	0.4	2.5	2.2	0.9	0.9	0.8	1.3	0.5	0.4	0.6	4.8	1.0	
PCB-118	3.6	1.8	1.2	2.1	1.4	0.6	1.0	7.2	0.6	0.9	0.4	3.5	2.5	6.6	1.1	NQ	1.8	1.8	0.8	0.7	0.8	1.1	0.4	NQ	0.5	2.3	0.7	
PCB-138	2.6	1.5	1.2	1.7	1.6	0.8	0.9	4.3	0.7	0.9	0.5	2.8	1.4	5.2	0.7	NQ	1.5	1.7	1.2	0.9	0.8	0.8	NQ	0.5	0.6	3.2	0.6	
PCB-153	2.4	1.3	1.2	1.4	1.5	0.8	0.8	3.4	0.7	0.8	0.5	2.5	1.1	4.4	0.7	NQ	1.3	1.5	1.0	1.0	0.6	0.7	NQ	NQ	0.5	3.1	0.5	
PCB-180	1.3	1.0	1.1	0.9	1.5	0.7	0.7	2.3	0.5	0.7	0.4	1.8	0.5	2.7	0.6	NQ	0.8	1.2	0.9	0.9	0.6	0.4	NQ	0.3	0.4	2.3	0.4	
Σ ₇ PCBs ¹⁾	3.4	1.5	1.2	1.5	1.8	0.8	0.9	3.9	0.6	1.5	0.5	2.7	1.3	4.7	1.1	NQ	1.5	1.8	0.8	0.8	0.9	1.1	NQ	NQ	0.5	2.9	0.8	
Fluorene	2.3	2.2	1.7	1.9	1.2	5.6	1.6	3.5	1.2	5.8	2.3	2.4	5.4	3.7	2.6	4.1	4.3	3.9	33.4	1.3	1.6	4.0	1.6	0.5	1.4	4.8	4.1	
Phenanthrene	3.3	1.9	1.6	1.6	1.0	2.3	1.6	2.7	1.1	8.3	1.5	3.0	4.0	3.8	2.4	3.0	4.2	4.0	21.4	1.5	2.1	2.9	1.5	0.3	0.8	3.7	3.3	
Anthracene	2.6	2.6	2.8	1.9	1.8	17.6	2.5	8.4	1.1	29.5	1.3	4.1	11.3	7.8	2.2	2.9	10.2	8.0	59.0	3.6	5.5	10.7	4.3	NQ	2.6	11.2	15.7	
Fluoranthene	1.3	1.8	1.5	1.2	1.0	2.3	1.7	3.6	1.4	15.5	1.2	4.7	8.6	3.7	2.0	1.5	4.2	3.9	15.1	1.6	2.4	2.6	1.4	0.3	0.7	3.1	2.5	
Pyrene	1.4	2.5	2.0	1.4	1.2	2.9	2.2	5.1	1.5	20.1	1.3	6.1	11.6	5.3	2.0	1.1	4.3	4.7	13.5	2.1	3.0	3.8	1.9	0.4	1.0	6.0	4.7	
Benzo[a]pyrene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	
Benz[a]anthracene	NQ	1.3	1.6	1.1	NQ	3.6	2.4	5.7	1.2	14.3	1.4	3.8	5.2	3.6	1.1	NQ	2.0	3.0	3.5	2.4	3.2	2.5	1.7	NQ	NQ	4.6	3.1	
Chrysene	1.4	1.4	1.6	1.3	1.0	2.0	2.8	6.1	2.1	7.9	1.1	6.1	5.7	3.3	1.4	0.6	1.9	2.8	2.4	1.5	2.1	1.6	1.2	0.4	0.6	3.2	2.0	
Σ ₆ PAHs ²⁾	2.7	2.0	1.6	1.6	1.1	3.4	1.6	3.2	1.2	9.3	1.7	3.2	5.4	3.9	2.4	3.0	4.2	4.0	23.6	1.5	2.1	3.3	1.6	NQ	1.0	4.1	3.6	
α-HCH	0.7	0.8	0.9	0.7	0.8	0.6	0.7	1.0	0.8	0.8	0.7	0.9	0.6	0.8	0.7	0.6	0.6	0.9	0.8	0.8	0.7	0.6	0.7	0.7	0.5	1.0	1.1	
β-HCH	0.4	0.7	0.8	0.8	0.9	0.6	0.6	1.1	0.7	0.6	0.5	0.9	0.3	0.6	0.4	NQ	NQ	0.5	0.5	0.4	NQ	NQ	NQ	NQ	NQ	0.4	NQ	
γ-HCH	0.8	1.9	0.9	0.9	0.9	0.9	0.8	1.2	0.8	1.0	0.7	1.5	0.9	5.9	0.7	0.4	0.5	0.7	0.7	0.5	0.4	0.4	0.3	0.2	0.4	0.4	0.4	
Σ ₂ HCHs ³⁾	0.8	1.3	0.9	0.8	0.9	0.8	0.8	1.1	0.8	0.9	0.7	1.1	0.8	3.3	0.7	0.5	0.5	0.8	0.7	0.7	0.5	0.5	0.5	0.5	0.5	0.7	0.8	
HCB	1.0	1.1	0.9	1.0	1.1	0.9	1.1	6.8	1.0	1.0	1.0	0.9	0.9	1.2	0.9	1.0	1.0	1.2	1.2	1.0	1.2	1.1	1.6	1.2	1.0	1.3	1.3	
p,p'-DDE	0.5	1.1	1.0	0.8	0.6	NQ	0.7	0.9	0.8	0.5	0.5	0.8	NQ	1.3	NQ	NQ	NQ	0.5	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	
p,p'-DDD	NQ	NQ	1.6	NQ	NQ	NQ	NQ	1.6	NQ	NQ	NQ	NQ	NQ	5.9	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	
o,p'-DDT	0.7	1.0	1.2	1.1	0.8	0.5	0.6	1.5	0.8	0.8	0.7	1.1	0.4	6.1	0.5	0.3	0.4	0.6	0.4	0.4	NQ	NQ	0.2	0.2	NQ	0.3	0.4	

Compounds	Coastal sites																										
	Oslo	Holmestrand	Tønsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedafljorden	Flekkefjord	Stavanger	Sauda	Bergen I	Bergen II	Sumdalsøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ramsundet	Harstad	Tromsø I	Tromsø II
<i>p,p'</i> -DDT	0.8	1.1	1.2	1.2	0.8	0.5	0.6	1.5	0.8	0.7	0.8	1.2	0.3	12.6	0.5	0.2	0.3	0.5	0.3	0.3	NQ	NQ	NQ	0.1	NQ	0.2	0.3
Σ_7 DDTs ⁴⁾	0.8	1.0	1.2	1.2	0.8	0.5	0.6	1.5	0.8	0.7	0.7	1.1	0.4	9.6	0.5	0.3	0.3	0.5	0.4	0.3	NQ	NQ	NQ	0.2	NQ	0.2	NQ
trans-Chlordane	NQ	2.7	3.6	8.8	7.7	2.8	2.9	4.1	1.0	1.0	1.5	1.8	0.6	2.5	1.0	NQ	0.7	1.2	0.9	0.8	0.9	0.6	0.5	0.5	0.3	1.1	NQ
cis-Chlordane	NQ	1.5	2.0	2.9	3.3	1.2	1.5	1.7	1.0	1.0	1.0	1.3	0.6	1.4	0.8	NQ	0.7	1.0	1.0	1.3	0.8	0.5	0.7	0.8	0.4	0.8	0.4
trans-Nonachlor	NQ	1.2	1.5	2.8	2.1	1.0	1.3	1.6	1.0	0.9	1.0	1.4	0.6	1.0	0.7	NQ	0.5	0.9	0.9	0.9	0.7	0.4	0.5	0.6	0.3	1.3	0.7
cis-Nonachlor	NQ	1.5	2.1	4.6	2.7	1.1	2.5	2.1	1.1	1.1	4.1	2.8	0.8	1.4	1.0	NQ	0.6	1.2	1.2	1.2	1.0	0.5	0.7	0.8	0.3	2.2	NQ
Σ_4 Chlordanes	NQ	1.5	2.1	3.8	3.5	1.4	1.7	2.0	1.0	1.0	1.2	1.5	NQ	1.4	NQ	NQ	0.6	1.0	1.0	1.1	0.8	0.5	0.6	0.7	0.4	1.1	NQ

N.Q (not quantified): coastal site concentration < MDL (this study)

N.D (not detected): background concentration < MDL¹

¹⁾ Sum of seven PCBs

²⁾ Sum of six PAHs (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene)

³⁾ Sum of two HCHs (α and γ -HCH)

⁴⁾ Sum of two DDTs (*o,p'* and *p,p'*-DDT)

Table S9b) Concentrations in coastal zones divided by the maximum European background concentrations (R_{EUmax}).

Compounds	Coastal sites																										
	Oslo	Holmestrand	Tønsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedaifjorden	Flekkefjord	Stavanger	Sauda	Bergen I	Bergen II	Sunnalsøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ramsundet	Harstad	Tromsø I	Tromsø II
PCB-28	1.9	1.0	0.7	0.8	1.5	0.6	0.6	1.7	0.4	2.0	0.4	1.3	0.5	1.8	0.7	0.3	0.5	1.5	0.5	0.5	1.0	0.9	0.3	0.2	0.3	1.7	0.6
PCB-52	2.9	1.1	0.9	1.1	1.3	0.6	0.7	2.6	0.4	1.0	0.4	2.2	0.9	3.8	1.2	0.2	1.2	1.2	0.5	0.5	0.6	0.8	0.3	0.2	0.4	1.7	0.6
PCB-101	3.8	1.3	1.1	1.4	1.2	0.6	0.8	4.4	0.6	0.9	0.5	3.0	1.6	5.5	0.9	0.3	1.9	1.6	0.7	0.7	0.6	1.0	0.4	0.3	0.4	3.6	0.8
PCB-118	2.7	1.3	0.9	1.5	1.0	0.5	0.7	5.3	0.4	0.7	0.3	2.6	1.9	4.9	0.8	NQ	1.4	1.3	0.6	0.5	0.6	0.8	0.3	NQ	0.3	1.7	0.5
PCB-138	1.9	1.1	0.9	1.3	1.2	0.6	0.7	3.2	0.5	0.6	0.4	2.1	1.0	3.8	0.5	NQ	1.1	1.3	0.9	0.7	0.6	0.6	NQ	0.4	0.4	2.3	0.4
PCB-153	1.8	1.0	0.9	1.0	1.1	0.6	0.6	2.5	0.5	0.6	0.4	1.9	0.8	3.3	0.5	NQ	1.0	1.1	0.8	0.7	0.5	0.5	NQ	NQ	0.4	2.3	0.4
PCB-180	1.0	0.7	0.8	0.7	1.1	0.5	0.5	1.7	0.4	0.5	0.3	1.3	0.4	2.0	0.4	NQ	0.6	0.9	0.7	0.7	0.4	0.3	NQ	0.2	0.3	1.7	0.3
Σ ₇ PCBs ¹⁾	2.5	1.1	0.9	1.1	1.3	0.6	0.7	2.9	0.5	1.1	0.4	2.0	1.0	3.5	0.8	NQ	1.1	1.3	0.6	0.6	0.7	0.8	NQ	NQ	0.4	2.1	0.6
Fluorene	1.7	1.7	1.3	1.4	0.9	4.2	1.2	2.6	0.9	4.3	1.7	1.8	4.0	2.7	2.0	3.0	3.2	2.9	24.7	1.0	1.2	3.0	1.2	0.3	1.1	3.5	3.1
Phenanthrene	2.4	1.4	1.2	1.2	0.7	1.7	1.2	2.0	0.8	6.2	1.1	2.2	2.9	2.8	1.8	2.2	3.1	2.9	15.8	1.1	1.6	2.2	1.1	0.2	0.6	2.7	2.5
Anthracene	1.9	1.9	2.1	1.4	1.3	13.1	1.8	6.2	0.8	21.8	1.0	3.1	8.4	5.8	1.6	2.2	7.6	5.9	43.7	2.6	4.1	7.9	3.2	NQ	1.9	8.3	11.6
Fluoranthene	1.0	1.3	1.1	0.9	0.7	1.7	1.3	2.6	1.1	11.5	0.9	3.4	6.4	2.7	1.5	1.1	3.1	2.9	11.2	1.2	1.8	1.9	1.0	0.2	0.5	2.3	1.8
Pyrene	1.0	1.8	1.5	1.0	0.9	2.2	1.6	3.8	1.1	14.9	0.9	4.5	8.6	3.9	1.5	0.8	3.1	3.5	10.0	1.5	2.2	2.8	1.4	0.3	0.8	4.4	3.5
Benzo[a]pyrene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Benz[a]anthracene	NQ	1.0	1.2	0.8	NQ	2.7	1.8	4.2	0.9	10.6	1.0	2.8	3.8	2.6	0.8	NQ	1.4	2.2	2.6	1.8	2.3	1.9	1.3	NQ	NQ	3.4	2.3
Chrysene	1.0	1.0	1.2	1.0	0.7	1.5	2.1	4.5	1.5	5.8	0.8	4.5	4.2	2.5	1.0	0.4	1.4	2.0	1.8	1.1	1.6	1.2	0.9	0.3	0.4	2.4	1.5
Σ ₆ PAHs ²⁾	2.0	1.5	1.2	1.2	0.8	2.5	1.2	2.4	0.9	6.9	1.2	2.4	4.0	2.9	1.8	2.2	3.1	3.0	17.5	1.1	1.6	2.4	1.1	NQ	0.7	3.0	2.7
α-HCH	0.5	0.6	0.7	0.6	0.6	0.5	0.5	0.8	0.6	0.6	0.5	0.6	0.5	0.6	0.5	0.5	0.4	0.6	0.6	0.6	0.5	0.5	0.6	0.5	0.4	0.8	0.8
β-HCH	0.3	0.5	0.6	0.6	0.6	0.4	0.4	0.8	0.5	0.4	0.3	0.7	0.2	0.4	0.3	NQ	NQ	0.3	0.4	0.3	NQ	NQ	NQ	NQ	NQ	0.3	NQ
γ-HCH	0.6	1.4	0.7	0.7	0.7	0.7	0.6	0.9	0.6	0.8	0.5	1.1	0.6	4.4	0.5	0.3	0.3	0.6	0.5	0.4	0.3	0.3	0.2	0.2	0.3	0.3	0.3
Σ ₂ HCHs ³⁾	0.6	1.0	0.7	0.6	0.6	0.6	0.6	0.8	0.6	0.7	0.5	0.8	0.6	2.4	0.5	0.4	0.4	0.6	0.6	0.5	0.4	0.4	0.4	0.4	0.4	0.5	0.6
HCB	0.7	0.8	0.7	0.7	0.8	0.7	0.8	5.0	0.8	0.8	0.7	0.7	0.7	0.9	0.7	0.7	0.7	0.9	0.9	0.8	0.9	0.8	1.1	0.9	0.8	1.0	0.9
p,p'-DDE	0.4	0.8	0.8	0.6	0.4	NQ	0.5	0.7	0.6	0.4	0.3	0.6	NQ	1.0	NQ	NQ	NQ	0.3	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
p,p'-DDD	NQ	NQ	1.2	NQ	NQ	NQ	NQ	1.2	NQ	NQ	NQ	NQ	NQ	4.4	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
o,p'-DDT	0.5	0.7	0.9	0.8	0.6	0.4	0.4	1.1	0.6	0.6	0.5	0.8	0.3	4.6	0.4	0.2	0.3	0.4	0.3	0.3	NQ	NQ	0.2	0.2	NQ	0.2	0.3

Compounds	Coastal sites																										
	Oslo	Holmestrand	Tønsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedaifjorden	Flekkefjord	Stavanger	Sauda	Bergen I	Bergen II	Sundalsøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ramsundet	Harstad	Tromsø I	Tromsø II
<i>p,p'</i> -DDT	0.6	0.8	0.9	0.9	0.6	0.4	0.4	1.1	0.6	0.5	0.6	0.9	0.2	9.3	0.4	0.2	0.3	0.4	0.2	0.2	NQ	NQ	NQ	0.1	NQ	0.2	0.2
Σ_7 DDTs ⁴⁾	0.6	0.8	0.9	0.9	0.6	0.4	0.4	1.1	0.6	0.5	0.5	0.8	0.3	7.1	0.4	0.2	0.3	0.4	0.3	0.2	NQ	NQ	NQ	0.1	NQ	0.2	NQ
trans-Chlordane	NQ	2.0	2.7	6.5	5.7	2.1	2.2	3.1	0.8	0.7	1.1	1.3	0.5	1.8	0.7	NQ	0.5	0.9	0.7	0.6	0.6	0.4	0.4	0.3	0.2	0.8	NQ
cis-Chlordane	NQ	1.1	1.5	2.1	2.5	0.9	1.1	1.3	0.7	0.8	0.7	0.9	0.5	1.0	0.6	NQ	0.5	0.8	0.8	0.9	0.6	0.4	0.5	0.6	0.3	0.6	0.3
trans-Nonachlor	NQ	0.9	1.1	2.1	1.6	0.7	1.0	1.2	0.7	0.7	0.7	1.1	0.5	0.7	0.5	NQ	0.4	0.7	0.6	0.7	0.5	0.3	0.4	0.4	0.2	1.0	0.5
cis-Nonachlor	NQ	1.1	1.5	3.4	2.0	0.8	1.9	1.5	0.9	0.8	3.0	2.1	0.6	1.1	0.7	NQ	0.5	0.9	0.9	0.9	0.8	0.4	0.5	0.6	0.2	1.7	NQ
Σ_4 Chlordanes	NQ	1.1	1.5	2.8	2.6	1.0	1.3	1.5	0.7	0.7	0.9	1.1	NQ	1.0	NQ	NQ	0.5	0.8	0.7	0.8	0.6	0.4	0.4	0.5	0.3	0.8	NQ

N.Q (not quantified): coastal site concentration < MDL (this study)

N.D (not detected): background concentration < MDL¹

¹⁾ Sum of seven PCBs

²⁾ Sum of six PAHs (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene)

³⁾ Sum of two HCHs (α and γ -HCH)

⁴⁾ Sum of two DDTs (*o,p'* and *p,p'*-DDT)

Table S9c) Concentrations in coastal zones divided by the minimum European background concentrations (R_{EUmin}).

Compounds	Coastal sites																										
	Oslo	Holmestrand	Tonsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedaifjorden	Flekkefjord	Stavanger	Sauda	Bergen I	Bergen II	Sundalsøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ramsundet	Harstad	Tromsø I	Tromsø II
PCB-28	3.9	2.0	1.6	1.6	3.2	1.3	1.1	3.4	0.8	4.1	0.8	2.7	1.1	3.7	1.4	0.5	1.1	3.1	1.0	0.9	2.0	1.8	0.6	0.4	0.7	3.5	1.2
PCB-52	6.1	2.3	1.8	2.2	2.8	1.1	1.5	5.4	0.9	2.1	0.8	4.5	1.9	7.8	2.5	0.5	2.6	2.6	1.0	0.9	1.2	1.7	0.6	0.4	0.8	3.6	1.3
PCB-101	7.9	2.8	2.3	2.9	2.6	1.2	1.7	9.2	1.1	1.9	1.0	6.1	3.4	11.5	1.9	0.5	3.9	3.3	1.4	1.4	1.3	2.0	0.8	0.7	0.9	7.4	1.6
PCB-118	5.6	2.7	1.8	3.2	2.1	1.0	1.5	11.1	0.9	1.4	0.7	5.3	3.9	10.1	1.7	NQ	2.8	2.8	1.2	1.1	1.2	1.7	0.7	NQ	0.7	3.5	1.1
PCB-138	3.9	2.3	1.9	2.7	2.5	1.2	1.4	6.6	1.1	1.3	0.8	4.3	2.2	7.9	1.1	NQ	2.3	2.6	1.8	1.5	1.2	1.3	NQ	0.8	0.9	4.9	0.9
PCB-153	3.7	2.0	1.8	2.1	2.3	1.3	1.3	5.2	1.1	1.2	0.8	3.9	1.6	6.8	1.0	NQ	2.0	2.3	1.6	1.5	1.0	1.1	NQ	NQ	0.8	4.7	0.8
PCB-180	2.0	1.5	1.7	1.4	2.3	1.1	1.1	3.5	0.8	1.1	0.6	2.7	0.8	4.2	0.9	NQ	1.2	1.8	1.4	1.4	0.9	0.6	NQ	0.5	0.7	3.5	0.6
$\Sigma_7\text{PCBs}^{1)}$	5.2	2.3	1.8	2.2	2.7	1.2	1.4	5.9	0.9	2.3	0.8	4.2	2.0	7.3	1.7	NQ	2.3	2.8	1.2	1.2	1.4	1.6	NQ	NQ	0.8	4.4	1.2
Fluorene	3.6	3.4	2.6	2.9	1.9	8.6	2.5	5.3	1.9	9.0	3.5	3.7	8.3	5.7	4.1	6.2	6.6	6.0	51.4	2.0	2.5	6.2	2.5	0.7	2.2	7.3	6.4
Phenanthrene	5.0	3.0	2.4	2.4	1.5	3.6	2.4	4.2	1.7	12.8	2.3	4.7	6.1	5.9	3.8	4.6	6.4	6.1	32.9	2.3	3.3	4.5	2.3	0.5	1.2	5.7	5.1
Anthracene	4.0	4.0	4.3	2.9	2.8	27.1	3.8	12.9	1.7	45.4	2.1	6.4	17.4	12.1	3.3	4.5	15.7	12.3	90.8	5.5	8.5	16.5	6.6	NQ	4.0	17.3	24.1
Fluoranthene	2.1	2.8	2.4	1.8	1.6	3.5	2.7	5.5	2.2	23.8	1.9	7.2	13.3	5.6	3.1	2.3	6.4	5.9	23.2	2.5	3.8	3.9	2.1	0.4	1.0	4.8	3.8
Pyrene	2.1	3.8	3.1	2.2	1.8	4.5	3.3	7.8	2.4	31.0	1.9	9.3	17.8	8.1	3.0	1.7	6.5	7.3	20.8	3.2	4.6	5.9	2.9	0.6	1.6	9.2	7.2
Benzo[a]pyrene	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Benz[a]anthracene	NQ	2.0	2.4	1.7	NQ	5.6	3.6	8.8	1.8	22.0	2.1	5.8	8.0	5.5	1.7	NQ	3.0	4.6	5.4	3.7	4.9	3.9	2.7	NQ	NQ	7.1	4.7
Chrysene	2.1	2.1	2.5	2.0	1.5	3.1	4.3	9.4	3.2	12.1	1.6	9.3	8.8	5.1	2.1	0.8	2.9	4.2	3.7	2.4	3.2	2.4	1.8	0.7	0.9	5.0	3.0
$\Sigma_6\text{PAHs}^{2)}$	4.1	3.1	2.5	2.5	1.6	5.2	2.5	5.0	1.9	14.3	2.6	5.0	8.3	6.0	3.7	4.6	6.5	6.1	36.3	2.3	3.2	5.1	2.4	NQ	1.5	6.3	5.5
α -CH	1.1	1.3	1.4	1.1	1.2	1.0	1.1	1.6	1.3	1.3	1.1	1.3	1.0	1.3	1.0	1.0	0.9	1.3	1.2	1.3	1.0	1.0	1.1	1.1	0.8	1.6	1.6
β -HCH	0.7	1.1	1.2	1.2	1.3	0.9	0.9	1.7	1.1	0.9	0.7	1.4	0.5	0.9	0.5	NQ	NQ	0.7	0.8	0.6	NQ	NQ	NQ	NQ	NQ	0.5	NQ
γ -HCH	1.2	2.9	1.4	1.4	1.5	1.4	1.2	1.9	1.2	1.6	1.0	2.2	1.3	9.1	1.1	0.5	0.7	1.1	1.0	0.7	0.5	0.6	0.5	0.4	0.6	0.5	0.7
$\Sigma_2\text{HCHs}^{3)}$	1.2	2.1	1.4	1.3	1.3	1.2	1.2	1.7	1.2	1.4	1.0	1.8	1.2	5.1	1.0	0.8	0.8	1.2	1.1	1.0	0.8	0.8	0.8	0.7	0.7	1.1	1.2
HCB	1.5	1.7	1.4	1.5	1.7	1.4	1.8	10.4	1.6	1.6	1.5	1.4	1.4	1.9	1.4	1.5	1.5	1.9	1.8	1.6	1.8	1.7	2.4	1.8	1.6	2.0	1.9
p,p' -DDE	0.8	1.7	1.6	1.2	0.9	NQ	1.0	1.5	1.2	0.8	0.7	1.2	NQ	2.0	NQ	NQ	NQ	0.7	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
p,p' -DDD	NQ	NQ	2.4	NQ	NQ	NQ	NQ	2.5	NQ	NQ	NQ	NQ	NQ	9.1	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
o,p' -DDT	1.1	1.5	1.9	1.7	1.3	0.8	0.9	2.2	1.3	1.2	1.1	1.6	0.6	9.5	0.8	0.5	0.5	0.9	0.7	0.6	NQ	NQ	0.4	0.4	NQ	0.4	0.6

Compounds	Coastal sites																										
	Oslo	Holmestrand	Tønsberg	Nøtterøy	Kragerø	Arendal	Kristiansand I	Kristiansand II	Farsund	Fedafljorden	Flekkefjord	Stavanger	Sauda	Bergen I	Bergen II	Sundalsjøra	Trondheim I	Trondheim II	Hommelvik	Brønnøysund	Mo i Rana	Narvik I	Narvik II	Ramsundet	Harstad	Tromsø I	Tromsø II
<i>p,p'</i> -DDT	1.2	1.6	1.9	1.9	1.3	0.8	0.9	2.4	1.3	1.1	1.2	1.8	0.5	19.4	0.8	0.3	0.5	0.7	0.5	0.4	NQ	NQ	NQ	0.2	NQ	0.4	0.5
Σ_7 DDTs ⁴⁾	1.2	1.6	1.9	1.8	1.3	0.8	0.9	2.3	1.3	1.1	1.1	1.7	0.6	14.7	0.8	0.4	0.5	0.8	0.6	0.5	NQ	NQ	NQ	0.3	NQ	0.4	NQ
trans-Chlordane	NQ	4.1	5.6	13.6	11.9	4.4	4.5	6.3	1.6	1.5	2.4	2.8	1.0	3.8	1.5	NQ	1.0	1.9	1.4	1.3	1.3	0.9	0.8	0.7	0.5	1.7	NQ
cis-Chlordane	NQ	2.2	3.1	4.4	5.1	1.9	2.3	2.7	1.5	1.6	1.5	2.0	1.0	2.1	1.2	NQ	1.1	1.6	1.6	2.0	1.3	0.8	1.0	1.3	0.7	1.2	0.7
trans-Nonachlor	NQ	1.8	2.3	4.4	3.3	1.5	2.1	2.5	1.5	1.4	1.5	2.2	1.0	1.5	1.1	NQ	0.8	1.4	1.3	1.4	1.0	0.6	0.8	0.9	0.4	2.1	1.1
cis-Nonachlor	NQ	2.3	3.2	7.1	4.2	1.7	3.9	3.2	1.8	1.7	6.3	4.4	1.2	2.2	1.5	NQ	1.0	1.9	1.8	1.9	1.6	0.8	1.1	1.3	0.5	3.4	NQ
Σ_4 Chlordanes	NQ	2.3	3.2	5.9	5.3	2.1	2.6	3.2	1.5	1.5	1.9	2.3	NQ	2.1	NQ	NQ	1.0	1.6	1.5	1.6	1.2	0.8	0.9	1.0	0.5	1.7	NQ

N.Q (not quantified): coastal site concentration < MDL (this study)

N.D (not detected): background concentration < MDL¹

¹⁾ Sum of seven PCBs

²⁾ Sum of six PAHs (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene)

³⁾ Sum of two HCHs (α and γ -HCH)

⁴⁾ Sum of two DDTs (*o,p'* and *p,p'*-DDT)

Table S10a) Number of coastal sites with a ratio ≥ 2 , ≥ 1 and $> \text{MDL}$ for the median background scenarios.

Components/-groups	Norwegian background (R_{NW})			Nordic background (R_{ND})			European background (R_{EU})		
	≥ 1	≥ 2	$> \text{MDL}$	≥ 1	≥ 2	$> \text{MDL}$	≥ 1	≥ 2	$> \text{MDL}$
PCB-28	24	15	27	22	13	27	13	7	27
PCB-52	25	17	27	24	15	27	15	5	27
PCB-101	26	21	27	22	12	27	17	8	27
PCB-118	25	20	25	22	14	25	14	7	25
PCB-138	25	23	25	19	10	25	13	5	25
PCB-153	24	24	24	19	7	24	13	5	24
PCB-180	25	23	25	18	8	25	8	3	25
$\Sigma_7\text{PCBs}$	24	21	24	22	13	24	15	5	24
Fluorene	26	22	27	26	23	27	26	17	27
Phenanthrene	26	23	27	26	20	27	24	16	27
Anthracene	26	26	26	26	25	26	26	22	26
Fluoranthene	26	25	27	26	22	27	25	14	27
Pyrene	27	26	27	26	25	27	26	16	27
Benzo[a]pyrene	3	3	3	0	0	0	0	0	0
Benz[a]anthracene	0	0	0	0	0	0	22	14	22
Chrysene	27	24	27	27	24	27	23	11	27
$\Sigma_6\text{PAHs}^{1)}$	26	23	26	26	23	26	25	17	26
α -HCH	27	15	27	27	7	27	3	0	27
β -HCH	0	0	0	0	0	0	1	0	19
γ -HCH	27	20	27	26	17	27	5	1	27
$\Sigma_2\text{HCHs}^{2)}$	27	20	27	27	17	27	4	1	27
HCB	27	1	27	27	1	27	17	1	27
p,p' -DDE	0	0	0	0	0	0	3	0	13
p,p' -DDD	0	0	0	0	0	0	3	1	3
o,p' -DDT	0	0	0	24	16	24	5	1	24
p,p' -DDT	0	0	0	22	19	23	6	1	23
$\Sigma_2\text{DDTs}^{3)}$	0	0	0	22	18	22	6	1	22

Components/-groups	Norwegian background (R_{NW})			Nordic background (R_{ND})			European background (R_{EU})		
	≥ 1	≥ 2	> MDL	≥ 1	≥ 2	> MDL	≥ 1	≥ 2	> MDL
trans-Chlordane	18	9	24	18	10	24	13	8	24
cis-Chlordane	21	9	25	21	7	25	14	3	25
trans-Nonachlor	18	7	25	18	7	25	9	2	25
cis-Nonachlor	21	10	24	22	10	24	17	8	24
Σ_4Chlordanes	18	9	22	18	9	22	13	4	22

¹⁾ Fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene.

²⁾ α -HCH and γ -HCH

³⁾ *o,p'*-DDT and *p,p'*-DDT

Bold: Value of zero, when coastal site concentration < European MDL.

Table S10b) Number of coastal sites with a ratio ≥ 2 , ≥ 1 and $> \text{MDL}$ for the maximum background scenarios.

Components/-groups	Norwegian background (R_{NWmax})			Nordic background (R_{NDmax})			European background (R_{EUmax})		
	≥ 1	≥ 2	$> \text{MDL}$	≥ 1	≥ 2	$> \text{MDL}$	≥ 1	≥ 2	$> \text{MDL}$
PCB-28	18	8	27	8	0	27	8	0	27
PCB-52	18	9	27	5	2	27	12	4	27
PCB-101	17	8	27	4	0	27	12	5	27
PCB-118	17	10	25	2	0	25	11	4	25
PCB-138	11	5	25	0	0	25	11	4	25
PCB-153	11	5	24	0	0	24	8	3	24
PCB-180	5	1	25	0	0	25	5	1	25
$\Sigma_7\text{PCBs}$	15	6	24	3	0	24	11	5	24
Fluorene	1	1	27	1	1	27	23	12	27
Phenanthrene	7	2	27	7	2	27	23	13	27
Anthracene	13	8	26	13	8	26	24	17	26
Fluoranthene	13	4	27	8	3	27	21	9	27
Pyrene	22	13	27	11	3	27	22	13	27
Benzo[a]pyrene	3	0	3	0	0	3	0	0	0
Benz[a]anthracene	0	0	0	1	1	22	18	11	22
Chrysene	26	23	27	4	1	27	20	8	27
$\Sigma_6\text{PAHs}^{1)}$	6	2	26	3	2	26	23	13	26
α -HCH	26	0	27	7	0	27	0	0	27
β -HCH	18	7	19	0	0	19	0	0	19
γ -HCH	21	10	27	12	2	27	3	1	27
$\Sigma_2\text{HCHs}^{2)}$	24	4	27	7	1	27	1	1	27
HCB	2	1	27	1	1	27	2	1	27
p,p' -DDE	0	0	0	0	0	13	0	0	13
p,p' -DDD	0	0	0	1	1	3	3	1	3
o,p' -DDT	15	6	24	1	1	24	2	1	24
p,p' -DDT	13	6	23	1	1	23	2	1	23
$\Sigma_2\text{DDTs}^{3)}$	15	6	22	1	1	22	2	1	22

Components/-groups	Norwegian background (R_{NWmax})			Nordic background (R_{NDmax})			European background (R_{EUmax})		
	≥ 1	≥ 2	> MDL	≥ 1	≥ 2	> MDL	≥ 1	≥ 2	> MDL
trans-Chlordane	8	3	24	8	3	24	10	6	24
cis-Chlordane	9	2	25	5	1	25	7	2	25
trans-Nonachlor	2	0	25	2	0	25	5	1	25
cis-Nonachlor	6	1	24	3	0	24	10	4	24
Σ_4Chlordanes	5	2	22	5	2	22	9	2	22

¹⁾ Fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene.

²⁾ α -HCH and γ -HCH

³⁾ *o,p'*-DDT and *p,p'*-DDT

Bold: Value of zero, when coastal site concentration < European MDL.

Table S10c) Number of coastal sites with a ratio ≥ 2 , ≥ 1 and $> \text{MDL}$ for the minimum background scenarios.

Components/-groups	Norwegian background (R_{NWmin})			Nordic background (R_{NDmin})			European background (R_{EUmin})		
	≥ 1	≥ 2	$> \text{MDL}$	≥ 1	≥ 2	$> \text{MDL}$	≥ 1	≥ 2	$> \text{MDL}$
PCB-28	27	26	27	27	26	27	20	9	27
PCB-52	27	25	27	27	25	27	19	12	27
PCB-101	27	27	27	27	27	27	23	12	27
PCB-118	0	0	0	0	0	0	20	11	25
PCB-138	25	25	25	25	25	25	21	11	25
PCB-153	0	0	0	0	0	0	20	10	24
PCB-180	25	25	25	25	25	25	16	6	25
$\Sigma_7\text{PCBs}$	0	0	0	0	0	0	21	12	24
Fluorene	27	27	27	27	27	27	26	24	27
Phenanthrene	27	26	27	27	26	27	26	23	27
Anthracene	0	0	0	0	0	0	26	25	26
Fluoranthene	27	26	27	27	26	27	26	22	27
Pyrene	27	27	27	27	27	27	26	22	27
Benzo[a]pyrene	0	0	0	0	0	0	0	0	0
Benz[a]anthracene	0	0	0	0	0	0	22	19	22
Chrysene	27	27	27	27	27	27	24	21	27
$\Sigma_6\text{PAHs}^{1)}$	0	0	0	0	0	0	26	23	26
α -HCH	27	27	27	27	27	27	21	0	27
β -HCH	0	0	0	0	0	0	7	0	19
γ -HCH	27	27	27	27	27	27	17	3	27
$\Sigma_2\text{HCHs}^{2)}$	27	27	27	27	27	27	20	2	27
HCB	27	10	27	27	11	27	27	3	27
p,p' -DDE	0	0	0	0	0	0	8	0	13
p,p' -DDD	0	0	0	0	0	0	3	3	3
o,p' -DDT	0	0	0	0	0	0	11	2	24
p,p' -DDT	0	0	0	0	0	0	11	2	23
$\Sigma_2\text{DDTs}^{3)}$	0	0	0	0	0	0	11	2	22

Components/-groups	Norwegian background (R_{NWmin})			Nordic background (R_{NDmin})			European background (R_{EUmin})		
	≥ 1	≥ 2	> MDL	≥ 1	≥ 2	> MDL	≥ 1	≥ 2	> MDL
trans-Chlordane	24	20	24	0	0	0	19	10	24
cis-Chlordane	25	20	25	25	23	25	21	7	25
trans-Nonachlor	24	18	25	25	23	25	19	7	25
cis-Nonachlor	24	22	24	0	0	0	21	10	24
Σ_4Chlordanes	22	17	22	0	0	0	18	9	22

¹⁾ Fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene.

²⁾ α -HCH and γ -HCH

³⁾ *o,p'*-DDT and *p,p'*-DDT

Bold: Value of zero, when coastal site concentration < European MDL.

Table S11 Estimated log K_{OA}, t₂₅ and t₉₅ at 3 different air temperatures.

	log K _{OA}			t ₂₅ (days)			t ₉₅ (days)		
	8°C	14°C	17°C	8°C	14°C	17°C	8°C	14°C	17°C
HCB	8.01	7.71	7.57	30	20	16	312	204	166
PCB-28	8.68	8.37	8.23	81	52	42	838	536	432
PCB-52	9.08	8.76	8.61	146	92	73	1506	948	757
PCB-101	9.62	9.29	9.13	319	199	158	3302	2054	1631
PCB-118	10.30	9.96	9.79	877	528	413	9069	5466	4277
PCB-138	10.57	10.24	10.07	1296	793	625	13409	8206	6469
PCB-153	10.44	10.07	9.89	1062	623	481	10991	6442	4973
PCB-180	11.15	10.79	10.61	3016	1779	1377	31200	18401	14248
α-HCH	8.12	7.88	7.76	36	25	21	369	259	219
γ-HCH	8.35	8.13	8.02	50	36	31	520	374	319
p,p-DDT	10.58	10.27	10.12	1308	830	666	13531	8583	6885
p,p-DDE	10.55	10.24	10.09	1252	794	637	12949	8214	6589
p,p-DDD	10.88	10.57	10.42	2030	1288	1033	21005	13324	10687
trans-Chlordane	9.85	9.48	9.30	451	261	200	4667	2697	2067
cis-Chlordane	9.87	9.49	9.30	464	265	202	4796	2743	2093
Fluorene	7.59	7.29	7.14	16	11	8	170	109	88
Phenanthrene	8.36	8.07	7.94	51	33	27	526	345	282
Anthracene	8.43	8.16	8.03	56	38	31	578	391	324
Fluoranthene	9.49	9.18	9.02	267	168	134	2760	1735	1385
Pyrene	9.46	9.18	9.04	253	168	138	2615	1741	1429
Benzo(a)pyrene	11.81	11.56	11.45	7920	5556	4680	81928	57480	48411
Benz(a)anthracene	10.80	10.46	10.29	1821	1093	854	18841	11310	8832
Chrysene	11.52	11.04	10.81	5219	2583	1837	53987	26722	19007

Values in red are less than the longest deployment period in this study (Table S1).

Text

S 1.1 Internal standard recoveries

The percentage recovery for the internal standard recoveries for the exposed samples, field and method blanks were all together at the same level (Table S2), and address minimal matrix interferences. Nonetheless, the recovery was all over somewhat higher for the exposed samples than for some of the internal standards, in comparison to field and method blanks. Furthermore, a problem during the analysis for one of the exposed samples resulted in a high percentage recovery for the ^{13}C -*p,p'*-DDT isomer.

S 1.2 PRC recoveries

The second recovery values were for the added mixture of PRCs. The range in the percentage recovery was governed for each PRC (8) in the field and method blanks, and ranged from 67-117 % (Table S2). The lower value originated from PCB-30, which had to be corrected towards two internal standards (^{13}C HCB and ^{13}C PCB-28).

S 1.3 Approach towards equilibrium

During deployment, the duration of the linear phase will vary and the more volatile compounds (low K_{OA}) will reach equilibrium faster than the less volatile compounds (high K_{OA}). The uptake profiles for substances with different $\log K_{\text{OA}}$ values are usually plotted with the equivalent sample volume calculated and expressed as a function of the disk deployment time (see e.g. ²). For chemicals with $\log K_{\text{OA}}$ values larger than 8.5 to 9, the sampling rate has previously been found to remain linear over the first 100 days ². Upon prolonged exposures, the sampling rate will proceed towards the curvilinear stage and ultimately approach equilibrium³. For substances of lower K_{OA} , the PUF disk may thus become saturated in less than 100 days. In this study, the coastal samples were deployed for 91 to 93 days with average air temperatures at the different sites ranging from 8 °C to 17 °C with a mean value of 14 °C (Table S1). As K_{OA} is strongly temperature dependent, we have calculated $\log K_{\text{OA}}$ at three different relevant air temperatures (8 °C, 14 °C and 17 °C) for selected substances (Table S11). The temperature-dependent K_{OA} values were calculated using reported data on physical-chemical properties and their temperature dependencies from literature reviews ⁴⁻⁷ with the notable exception of the temperature

dependencies for the DDTs, for which an energy of phase transfer of -80 kJ mol^{-1} was assumed for each isomer. Using equations presented by Shoeib and Harner³, PUF characteristics applicable for this study¹, and applying the default uptake rate throughout ($3.5 \text{ m}^3/\text{day}$), we have furthermore estimated the times to 95% of equilibrium (t_{95}) as well as the upper bounds of the linear uptake phase (t_{25} – arbitrary defined as the time when the PUF has accumulated 25% of the equilibrium value). The results in Table S11 implies that substances with the lower $\log K_{OA}$ values are increasingly about to approach equilibrium by the end of exposure – in particular at the southernmost and warmer coastal sites - which also can be deduced from the equivalent air volumes in Tables S3b-S6b.

References

1. A. K. Halse, M. Schlabach, S. Eckhardt, A. Sweetman, K. C. Jones and K. Breivik, *Atmospheric Chemistry and Physics*, 2011, **11**, 1549-1564.
2. T. Harner, M. Shoeib, M. Diamond, G. Stern and B. Rosenberg, *Environ. Sci. Technol.*, 2004, **38**, 4474-4483.
3. M. Shoeib and T. Harner, *Environ. Sci. Technol.*, 2002, **36**, 4142-4151.
4. L. Shen and F. Wania, *Journal of Chemical and Engineering Data*, 2005, **50**, 742-768.
5. N. Q. Li, F. Wania, Y. D. Lei and G. L. Daly, *Journal of Physical and Chemical Reference Data*, 2003, **32**, 1545-1590.
6. H. Xiao, N. Q. Li and F. Wania, *Journal of Chemical and Engineering Data*, 2004, **49**, 173-185.
7. A. Beyer, F. Wania, T. Gouin, D. Mackay and M. Matthies, *Environmental Toxicology and Chemistry*, 2002, **21**, 941-953.

Paper III



Forecasting long-range atmospheric transport episodes of polychlorinated biphenyls using FLEXPART

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Abstract

The analysis of concentrations of persistent organic pollutants (POPs) in ambient air is costly and can only be done for a limited number of samples. It is thus beneficial to maximize the information content of the samples analyzed via a targeted observation strategy. Using polychlorinated biphenyls (PCBs) as an example, a forecasting system to predict and evaluate long-range atmospheric transport (LRAT) episodes of POPs at a remote site in southern Norway has been developed. The system uses the Lagrangian particle transport model FLEXPART, and can be used for triggering extra (“targeted”) sampling when LRAT episodes are predicted to occur. The system was evaluated by comparing targeted samples collected over 12 to 25 hours during individual LRAT episodes with monitoring samples regularly collected over one day per week throughout a year. Measured concentrations in all targeted samples were above the 75th percentile of the concentrations obtained from the regular monitoring program and included the highest measured values of all samples. This clearly demonstrates the success of the targeted sampling strategy.

1. Introduction

Background air measurements of persistent organic pollutants (POPs) within several existing monitoring programs (e.g. Tørseth et al., 2012; Wu et al., 2009) are typically conducted using active air sampling (AAS). However, the high cost associated with this type of sampling limits the spatial and temporal coverage of air measurements. Furthermore, sampling at many sites occurs only at fixed intervals (e.g. one day per week) without any *a priori* consideration of air mass transport (i.e., whether the air is likely to be polluted or not). While the current strategy is appropriate for the purpose of assessing long-term

trends (years, decades), the intermittent sampling approach may not effectively capture key long-range atmospheric transport (LRAT) episodes (e.g. Yao et al., 2007), which are often associated with the highest POP concentrations (Eckhardt et al., 2007; Yao et al., 2007).

The objectives of this study were to (i) develop a forecast system using the FLEXPART model to predict long-range atmospheric transport episodes of POPs using PCB-28 as a model compound, (ii) to evaluate the capability of the forecast system to capture specific LRAT episodes at a background site in southern Norway (Birkenes) through targeted sampling (i.e. when LRAT episodes are predicted), (iii) to assess whether predicted LRAT episodes for PCB-28 coincide with elevated concentrations of additional PCBs, and (iv) to identify source regions of PCBs during individual episodes.

2. Material and Methods

2.1.1 The Birkenes observatory

Sampling was carried out at the Birkenes observatory, which has been in operation since 1981. The station is located in the southern part of Norway (N 58°23, E 08°15, 190 m.a.s.l), on top of a hill and is mainly surrounded by forest. We refer to Eckhardt et al. (2009) for further details.

2.1.2 Sampling

Air sampling was carried out by use of high volume air sampling devices (DHA-80, Digitel, Hegenau, CH), where both particulate and gas phase samples were collected. The samplers consist of a glass fiber filter (collecting particles), in combination with two polyurethane foam (PUF) plugs (7.5 cm x 4.5 cm), for collection of the gaseous compounds. The glass fiber filters (weight: 53 g/m², thickness: 260 µm, particle retention: 1,2 µm) were purchased from Whatman™ GF/C, GE Healthcare, Buckinghamshire, UK. Air was pumped through the sampling material. For regular monitoring samples collected once per week, the pump was set to sample ~770 m³ (0.5 m³/minute) of air for 24 hours of sampling (Eckhardt et al., 2009). The targeted air samples were collected by use of a similar high-volume air sampling device (DHA-80, Digitel), using a different pump (SAH 155, Elmo Rietschle, Bad Neustadt, Germany). This included both an on-line control of the sampling system and the possibility to apply a higher flow rate to achieve shorter sampling periods, since LRAT episodes are often shorter than a day. The sampling volumes for the targeted LRAT samples ranged from 395 to 1443 m³ (average 0.8, range 0.6-0.9 m³/minute) and were collected over 12 to 25 hours. After sampling was completed, the exposed PUF samples were sealed in a gas tight container and glass fiber filters were wrapped in alumina foil and sealed.

2.1.3 Clean-up and analysis

Prior to sampling, the glass fiber filters were heated to 450 °C for 8 hours and wrapped in alumina foil. PUF plugs were pre-extracted with acetone and toluene for 8 hours using a Soxhlet extraction system and dried under vacuum in desiccators (Eckhardt et al., 2009). After sampling was completed, a mixture of ^{13}C -isotope labeled internal standard of PCBs was added to the sample material (both filter and PUFs) prior to extraction. Samples were extracted via Soxhlet extraction using *n*-hexane/diethyl ether 9:1 as an extraction solvent (Eckhardt et al., 2009). All extracts were pre-concentrated to approximately 2 mL and treated with sulfuric acid to remove matrix related components. The organic phase was further cleaned up using a silica column and eluted with *n*-hexane/diethyl ether. The final extracts were reduced in volume to approximately 0.1 mL using nitrogen followed by the addition of a recovery standard (Eckhardt et al., 2009). An Agilent 6890 gas chromatograph coupled to a high resolution Waters AutoSpec mass spectrometer in an electron impact mode was used for quantification and identification of the target compounds. The gas chromatograph conditions are given elsewhere (e.g. Eckhardt et al., 2009).

2.2 FLEXPART model

The atmospheric transport of PCB-28 was simulated by use of the Lagrangian particle dispersion model FLEXPART (Stohl et al., 2005; Stohl et al., 1998). The main purpose for FLEXPART model simulations was to calculate PCB-28 concentrations at the measurement station and identify the source regions of PCB-28. The model calculates the trajectories of so-called tracer particles and accounts for turbulence, convection, deposition and atmospheric reaction with hydroxyl (OH) radicals (Eckhardt et al., 2009). FLEXPART was run in backward mode for this study in order to identify possible source regions influencing the measurement site during an air pollution episode (Eckhardt et al., 2007; Seibert and Frank, 2004). Following an earlier study for Birkenes (Eckhardt et al., 2009), PCB-28 was chosen as our model compound. We used the maximum emission scenario derived by Breivik et al. (2007) as model input. Physical-chemical properties for PCB-28 were adapted from Li et al. (2003) and the atmospheric reaction rate taken from Anderson and Hites (1996) as further detailed in Eckhardt et al. (2009). FLEXPART was run daily using meteorological forecast data to predict airborne concentration of PCB-28 for the following day (further referred to as FLEXPART-forecast – *FLEXPART-f*). The FLEXPART run was initialized at the coordinates of the measurement site and at the future time and was then run backward in time incorporating first forecast meteorological data and, for past periods for which such data were already available at the time of the model calculations, analysis data. Predictions using *FLEXPART-f*

91 began in December 2008. By the end of 2010, the upper 95% percentile for simulated concentrations of
92 PCB-28 (5.7 pg/m^3) was determined and selected as a threshold limit for targeted sampling of predicted
93 LRAT episodes. During 2011, upcoming LRAT episodes were identified one day ahead by *FLEXPART-f* as
94 predicted concentrations exceeding the threshold of 5.7 pg/m^3 .

95 After all targeted sampling was completed, FLEXPART was run again for dates in which sampling
96 occurred but using meteorological analysis data (these runs will be referred to as FLEXPART-
97 retrospective – *FLEXPART-r*). In *FLEXPART-f* 40 000 particles were released over a 24 hour interval, and in
98 *FLEXPART-r* 100 000 particles were released over the exact interval of the measurement, from the
99 receptor site (Birkenes) and followed backwards in time for 20 days in order to calculate emission
100 sensitivities (ES) (Seibert and Frank, 2004; Stohl et al., 2003; Stohl et al., 2005). A larger number of
101 particles were released for the *FLEXPART-r* runs for more accurate determination of source regions
102 during the episodes which were sampled. The ES (unit nanoseconds) provides information about the
103 residence time of an air mass within a grid cell and uptake of emissions was facilitated in the so-called
104 footprint layer (0-100 m above ground) (Eckhardt et al., 2009). Multiplying the footprint ES value by
105 emission fluxes from the PCB-28 emission inventory (Breivik et al., 2007) yields the geographical
106 distribution of sources contributing to the simulated concentrations at the measurement site. Spatial
107 integration of all contributions then gives the simulated concentration at the measurement site.

108 For the forecast system (*FLEXPART-f*), FLEXPART used meteorological forecast data taken every three
109 hours (26 model levels and resolution of 1×1 globally) from the Global Forecast System (GFS) model of
110 the National Centers for Environmental Prediction (NCEP) to predict the concentration of PCB-28 one
111 day ahead. For the selected episodes which were subject to targeted sampling and analysis, FLEXPART
112 (*FLEXPART-r*) was run for retrospective simulations driven by operational analysis from the European
113 Centre for Medium-Range Weather Forecasts (ECMWF, 1995), with $1^\circ \times 1^\circ$ resolution and 91 model
114 levels. Analyses at 00:00, 06:00, 12:00 and 18:00 UTC, and 3-h forecasts at 03:00, 09:00, 15:00 and 21:00
115 UTC were used.

116 3. Results and Discussion

117 3.1. Annual averages and concentrations during the predicted episodes

118 Samples from targeted sampling (based on model results of *FLEXPART-f*) during three predicted LRAT
119 episodes (E) in 2011, which occurred in January (E1), February (E2) and late September/early October
120 (E3a ,b, c, d, e), were analyzed (Table 1). An overview of predicted and measured concentrations is
121 presented in Table A.1 in Appendix.

Figure 1 compares the modeled *FLEXPART-r* concentrations of PCB-28, and selected PCBs measured during the individual episodes (n=7, colored dots) with annual results obtained through the regular monitoring program (n=52). We show results for *FLEXPART-r* modeled PCB-28 (a) and measured concentrations for seven PCBs (PCB-28,-52,-101,-118,-138,-153,-180) (b-h). In Figure 1, the median and the percentiles were estimated based on annual results for the AAS sampler. To further facilitate interpretation of results, Table A.1 tabulates the predicted and measured concentrations (pg/m³) during each sampled episode. Table A.2 presents the annual mean and standard deviation (SD) based on results from the regular monitoring program in 2011 (n=52) and compares concentrations measured during each episode with the annual mean.

There are major uncertainties in the exact magnitude of PCB emissions with different emission scenarios varying by several orders of magnitude (Breivik et al., 2007 and references therein). Independent model evaluations using this data have therefore experienced difficulties in accurately reproducing the exact magnitude of observed concentrations (e.g. Gong et al., 2007; Macleod et al., 2005; Wania and Su, 2004). For all episodes, we start by noting that the model overestimated measured concentrations of PCB-28 during the episodes by a factor of 4.2 on average, ranging from 1.7 (E3e) to 7.7 (E2). This was anticipated based on past model evaluations using *FLEXPART* (Eckhardt et al., 2009; Halse et al., 2011) and mainly attributed to uncertainties in the maximum emission scenario used as model input (Breivik et al., 2007). Despite this uncertainty, the model was clearly successful in singling out LRAT episodes of PCB-28 as all targeted samples exceeded the 75 percentile of the regular monitoring program (Figure 1b). The measurements were elevated, ranging from mean plus 0.8 standard deviations (E1) up to mean plus 6.4 standard deviations (E3e) (Table A.2), with two samples (E3e and E3c) exceeding the highest concentration of the 52 samples collected as part of the monitoring program. However, the ranking of predicted and observed concentrations of PCB-28 did not fully match, with predictions for PCB-28 decreasing from E3c > E2 > E3b > E3d > E3a ≈ E3e > E1 and observations declining from E3e > E3c > E3b > E3d > E3a > E2 > E1 (Table A.1). Nevertheless, the overall results indicate that there is a fairly good understanding of major source regions leading to elevated concentrations of PCB-28 at Birkenes.

An obvious question to follow is whether the model predictions may work as a suitable surrogate for PCBs other than PCB-28? For all other PCB congeners, each episodically collected sample was above the 75 percentile (Figure 1c-h). Furthermore, the measurements of Σ_7 PCBs were elevated by 0.7 (E1) to 6.9 (E3e) SDs (Table A.2) above the annual mean, with all congeners being elevated by more than two SDs for the five consecutive samples collected during autumn (E3). As the ranking of observed

concentrations from high to low are identical for each PCB congener in all targeted samples ($E3e > E3c > E3b > E3d > E3a > E2 > E1$), we conclude that PCB-28 serves as a suitable surrogate to identify probable LRAT episodes for the other congeners included. This would imply that major source regions affecting concentrations of these PCBs are likely to be similar.

3.2. Source regions predicted using backwards simulation

Figures 2a and 2b shows the corresponding *FLEXPART-r* emission contribution (EC) maps for the episodes with highest modeled ($E3c$) and measured ($E3e$) concentrations of PCB-28 in air at Birkenes, respectively. Similarly, Figures A.6 and A.8 in the Appendix show the *FLEXPART-r* footprint emission sensitivity (ES) maps for these two episodes. Additional maps based on annual results as well as the other individual episodes are included in the Appendix (Figures A.1-A.8).

While $E3c$ had the highest modeled (*FLEXPART-r*) concentration of PCB-28, the highest measured concentration was found for $E3e$ (Table A.1). This may reflect inaccuracies in the spatial emission pattern used as model input. In other words, the emissions in western parts of Europe highlighted in Figure 2b (e.g. UK and/or France) might be underestimated in the emission inventory compared to those regions in more central parts of mainland Europe which are highlighted in Figure 2a. A study done by Eckhardt et al. (2009) revealed that the dominating regions for PCB-28 affecting Birkenes were Eastern and Central Europe together with the UK and Ireland. Although the data set of targeted samples is too limited to infer any reliable conclusions (as e.g. atmospheric loss processes occurring en route could have been more efficient than predicted by the model in the case of $E3c$, relatively to $E3e$), it illustrates how a combined modeling and monitoring approach has the potential to better constrain our understanding of how major source regions are affecting concentrations of PCBs at a background site.

4. Conclusions

Trajectories have been widely used to interpret air measurement of various POPs and other pollutants. However, few studies have performed targeted air sampling of organic contaminants from suspected source regions as triggered by real-time meteorological forecast models (Yao et al., 2007). To the best of our knowledge, our study represents the first attempt to both (i) use model predictions driven by *a priori* information on emissions of POPs to trigger air sampling as well as (ii) retrospectively evaluate the source regions for measurements collected during predicted episodes. The *FLEXPART-f* model was clearly successful in identifying LRAT episodes for both PCB-28 and other PCBs as the measured concentration of PCB-28 in all seven targeted samples was above the 75 percentile with two samples exceeding concentrations measured in the 52 samples collected as part of the regular monitoring

program. The *FLEXPART-r* model fails to accurately reproduce the magnitude of PCB-28 concentrations during individual episodes, but this can be mainly attributed to uncertainties in the absolute emission rates of PCB-28 used to drive simulations. We conclude that forecasting of pollution episodes has the potential to add value to relevant monitoring efforts which are normally collecting active air samples at fixed intervals in a non-continuous manner. Observations targeted at strong pollution episodes (as in this paper) or on transport from specific source regions with highly uncertain emissions (as could be done in a very similar forecasting framework) could significantly enhance our understanding of POP sources. However, in order to obtain more confidence in the forecast system and predicted source-receptor relationships (*FLEXPART-r*), the number of targeted samples which are collected and substances which are predicted and analyzed need to be increased.

Acknowledgements

This study was financed by the Research Council of Norway (183437/S30). We would also like to thank the Norwegian Climate and Pollution Agency for financing the POPs monitoring program at Birkenes, Olav Lien for support with the sampling, and Nick Warner for comments on this manuscript.

5. References

- Anderson, P.N., Hites, R.A., 1996, OH radical reactions: The major removal pathway for polychlorinated biphenyls from the atmosphere. *Environ. Sci. Technol.* 30, 1756-1763.
- Breivik, K., Sweetman, A., Pacyna, J.M., Jones, K.C., 2007, Towards a global historical emission inventory for selected PCB congeners - A mass balance approach-3. An update. *Science of the Total Environment* 377, 296-307.
- Eckhardt, S., Breivik, K., Li, Y.F., Mano, S., Stohl, A., 2009, Source regions of some persistent organic pollutants measured in the atmosphere at Birkenes, Norway. *Atmospheric Chemistry and Physics* 9, 6597-6610.
- Eckhardt, S., Breivik, K., Mano, S., Stohl, A., 2007, Record high peaks in PCB concentrations in the Arctic atmosphere due to long-range transport of biomass burning emissions. *Atmospheric Chemistry and Physics* 7, 4527-4536.
- ECMWF, E.C.f.M.-R.W.F. 1995. User guide to ECMWF products 2.1 (Reading, Meteorological Bulletin).
- Gong, S.L., Huang, P., Zhao, T.L., Sahsuvar, L., Barrie, L.A., Kaminski, J.W., Li, Y.F., Niu, T., 2007, GEM/POPs: a global 3-D dynamic model for semi-volatile persistent organic pollutants - Part 1: Model description and evaluations of air concentrations. *Atmospheric Chemistry and Physics* 7, 4001-4013.
- Halse, A.K., Schlabach, M., Eckhardt, S., Sweetman, A., Jones, K.C., Breivik, K., 2011, Spatial variability of POPs in European background air. *Atmospheric Chemistry and Physics* 11, 1549-1564.
- Li, N.Q., Wania, F., Lei, Y.D., Daly, G.L., 2003, A comprehensive and critical compilation, evaluation, and selection of physical-chemical property data for selected polychlorinated biphenyls. *Journal of Physical and Chemical Reference Data* 32, 1545-1590.
- Macleod, M., Riley, W.J., McKone, T.E., 2005, Assessing the influence of climate variability on atmospheric concentrations of polychlorinated biphenyls using a global-scale mass balance model (BETR-global). *Environ. Sci. Technol.* 39, 6749-6756.
- Seibert, P., Frank, A., 2004, Source-receptor matrix calculation with a Lagrangian particle dispersion model in backward mode. *Atmospheric Chemistry and Physics* 4, 51-63.
- Stohl, A., Forster, C., Eckhardt, S., Spichtinger, N., Huntrieser, H., Heland, J., Schlager, H., Wilhelm, S., Arnold, F., Cooper, O., 2003, A backward modeling study of intercontinental pollution transport using aircraft measurements. *J. Geophys. Res.-Atmos.* 108, 18.
- Stohl, A., Forster, C., Frank, A., Seibert, P., Wotawa, G., 2005, Technical note: The Lagrangian particle dispersion model FLEXPART version 6.2. *Atmospheric Chemistry and Physics* 5, 2461-2474.
- Stohl, A., Hittenberger, M., Wotawa, G., 1998, Validation of the Lagrangian particle dispersion model FLEXPART against large-scale tracer experiment data. *Atmospheric Environment* 32, 4245-4264.
- Tørseth, K., Aas, W., Breivik, K., Fjæraa, A.M., Fiebig, M., Hjellbrekke, A.G., Lund Myhre, C., Solberg, S., Yttri, K.E., 2012, Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972-2009. *Atmospheric Chemistry and Physics* 12, 5447-5481.
- Wania, F., Su, Y.S., 2004, Quantifying the global fractionation of polychlorinated biphenyls. *Ambio* 33, 161-168.
- Wu, R., Backus, S., Basu, I., Blanchard, P., Brice, K., Dryfhout-Clark, H., Fowlie, P., Hulting, M., Hites, R., 2009, Findings from quality assurance activities in the Integrated Atmospheric Deposition Network. *J. Environ. Monit.* 11, 277-296.
- Yao, Y., Harner, T., Ma, J.M., Tuduri, L., Blanchard, P., 2007, Sources and occurrence of dacthal in the Canadian atmosphere. *Environ. Sci. Technol.* 41, 688-694.

245 Table 1: Sampling times for targeted samples collected during predicted episodes in 2011.

Episode	Start date	Start time	End date	End time
E1	06.01	11:50	07.01	23:49
E2	24.02	17:29	25.02	05:49
E3a	29.09	08:05	29.09	21:10
E3b	29.09	21:15	30.09	15:30
E3c	30.09	15:30	01.10	05:35
E3d	01.10	05:38	02.10	07:04
E3e	02.10	07:08	02.10	18:49

246

Figure Captions:

Figure 1: Modeled (*FLEXPART-r*) PCB-28 (a) and measured PCB concentrations (b-h) in units of pg/m^3 , for both the annual sampling program and the targeted samples. The box and whisker plots show the annual results (2011) for Birkenes, southern Norway based on weekly samples. The line shows the median, while the box and whiskers delineates the 25 and 75 percentiles and the 5 and 95 percentiles, respectively. Targeted samples are represented by colored dots.

Figure 2: Maps of *FLEXPART-r* EC (emission contributions, $1\text{E-}12$ [pg/m^3]) for PCB-28 for the episodes with highest predicted (E3c) (a) and measured (E3e) (b) concentrations at Birkenes during 2011.

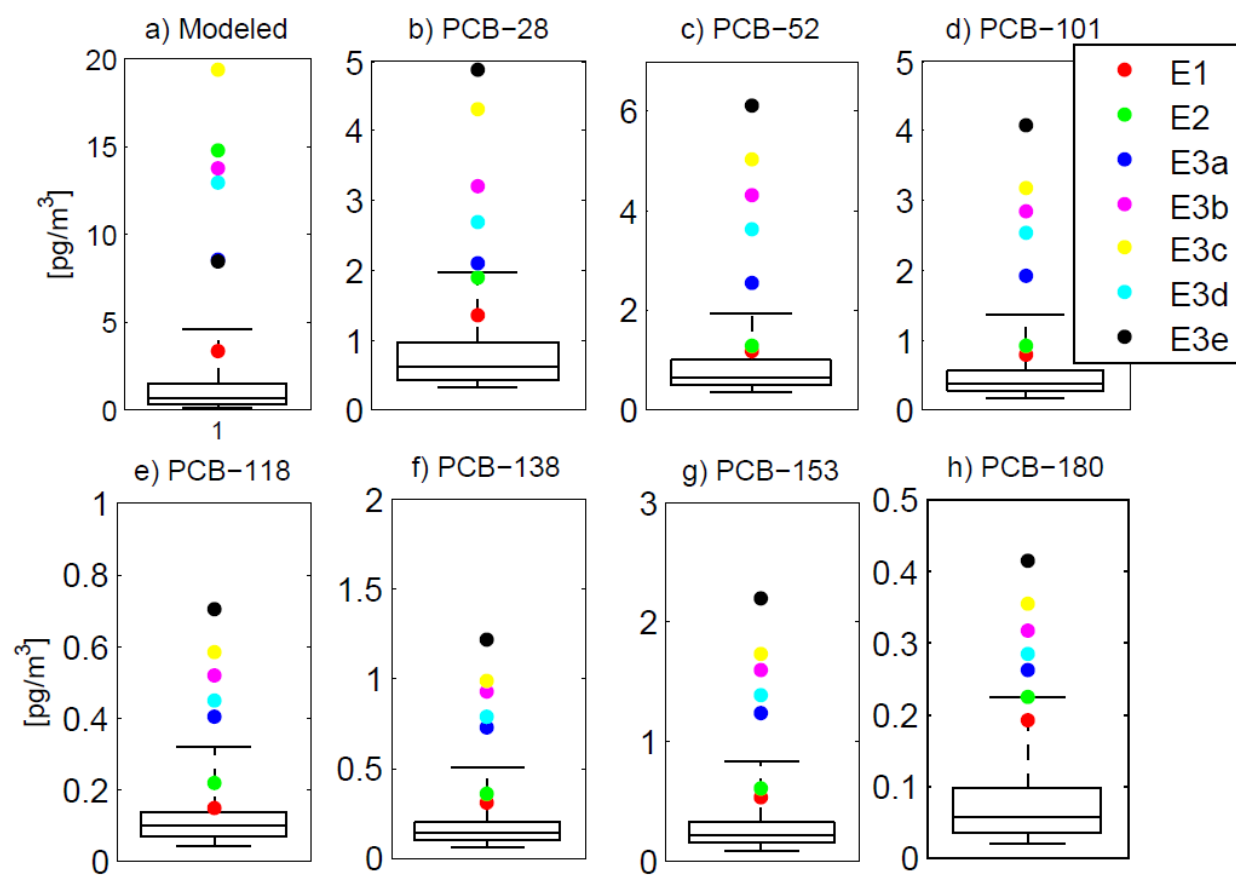


Figure 1

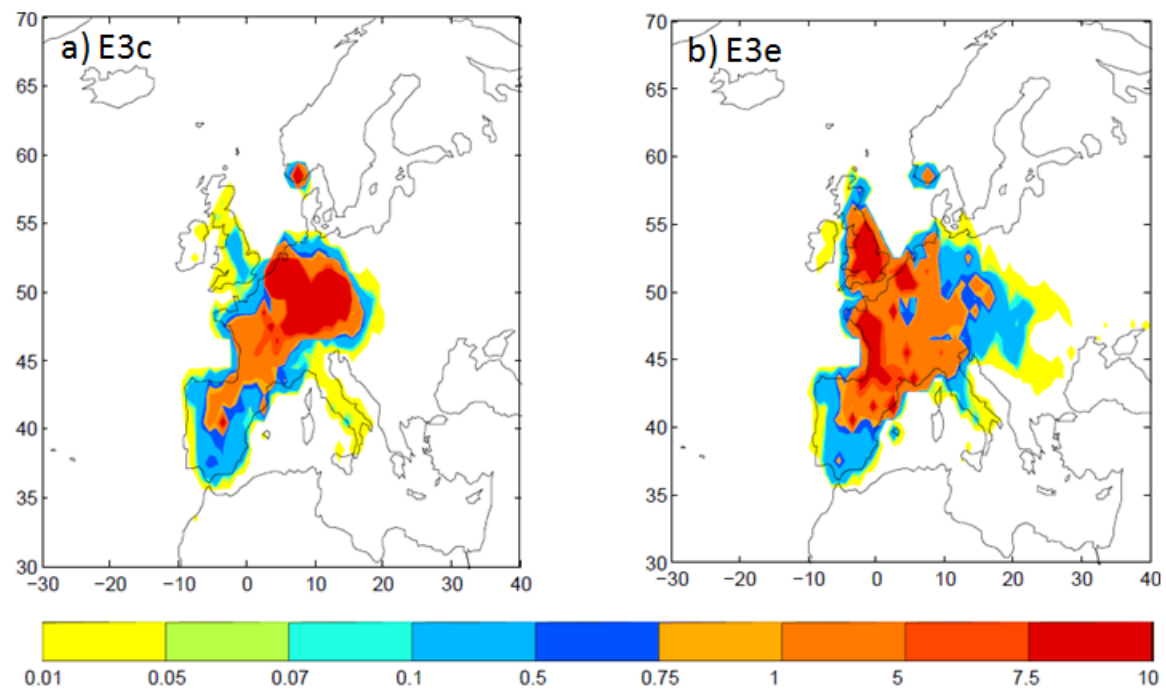


Figure 2

Supporting information

for

Forecasting long-range atmospheric episodes of polychlorinated biphenyls using FLEXPART

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Table A.1: Predicted (*FLEXPART-r*) and measured concentrations (in pg/m^3) during each episode.

Compounds	<i>E1</i>	<i>E2</i>	<i>E3a</i>	<i>E3b</i>	<i>E3c</i>	<i>E3d</i>	<i>E3e</i>
PCB-28 (model)	3.3	14.7	8.5	13.7	19.4	13.0	8.4
PCB-28	1.4	1.9	2.1	3.2	4.3	2.7	4.9
PCB-52	1.2	1.3	2.6	4.3	5	3.6	6.1
PCB-101	0.8	0.9	1.9	2.9	3.2	2.5	4.1
PCB-118	0.1	0.2	0.4	0.5	0.6	0.4	0.7
PCB-138	0.3	0.4	0.7	0.9	1	0.8	1.2
PCB-153	0.5	0.6	1.2	1.6	1.7	1.4	2.2
PCB-180	0.2	0.2	0.3	0.3	0.4	0.3	0.4
$\Sigma_7\text{PCBs}$	4.5	5.5	9.2	13.7	16.2	11.8	19.6

Table A.2: Mean and standard deviation (SD) (pg/m^3) for the AAS samples, including the number of standard deviations by which the individual concentrations were above the annual mean value.

Compounds	Annual samples		Number of standard deviations from the annual mean						
	Mean	Standard deviation (SD)	E1	E2	E3a	E3b	E3c	E3d	E3e
PCB-28	0.82	0.63	0.8	1.7	2.0	3.8	5.6	3.0	6.4
PCB-52	0.84	0.75	0.5	0.6	2.3	4.6	5.6	3.7	7.0
PCB-101	0.52	0.47	0.6	0.8	3.0	5.0	5.7	4.3	7.6
PCB-118	0.12	0.09	0.3	1.1	3.1	4.4	5.1	3.6	6.5
PCB-138	0.18	0.15	0.8	1.2	3.6	5.0	5.4	4.0	6.9
PCB-153	0.29	0.26	0.9	1.2	3.6	5.0	5.5	4.2	7.3
PCB-180	0.08	0.06	1.9	2.4	3.0	3.9	4.6	3.4	5.6
$\Sigma_7\text{PCBs}$	2.85	2.41	0.7	1.1	2.6	4.5	5.5	3.7	6.9

Figure A.1: Map of *FLEXPART-r* footprint ES (emission sensitivities) (a) and EC (emission contributions) (b) for PCB-28 for the annual average concentrations (2011) at Birkenes.

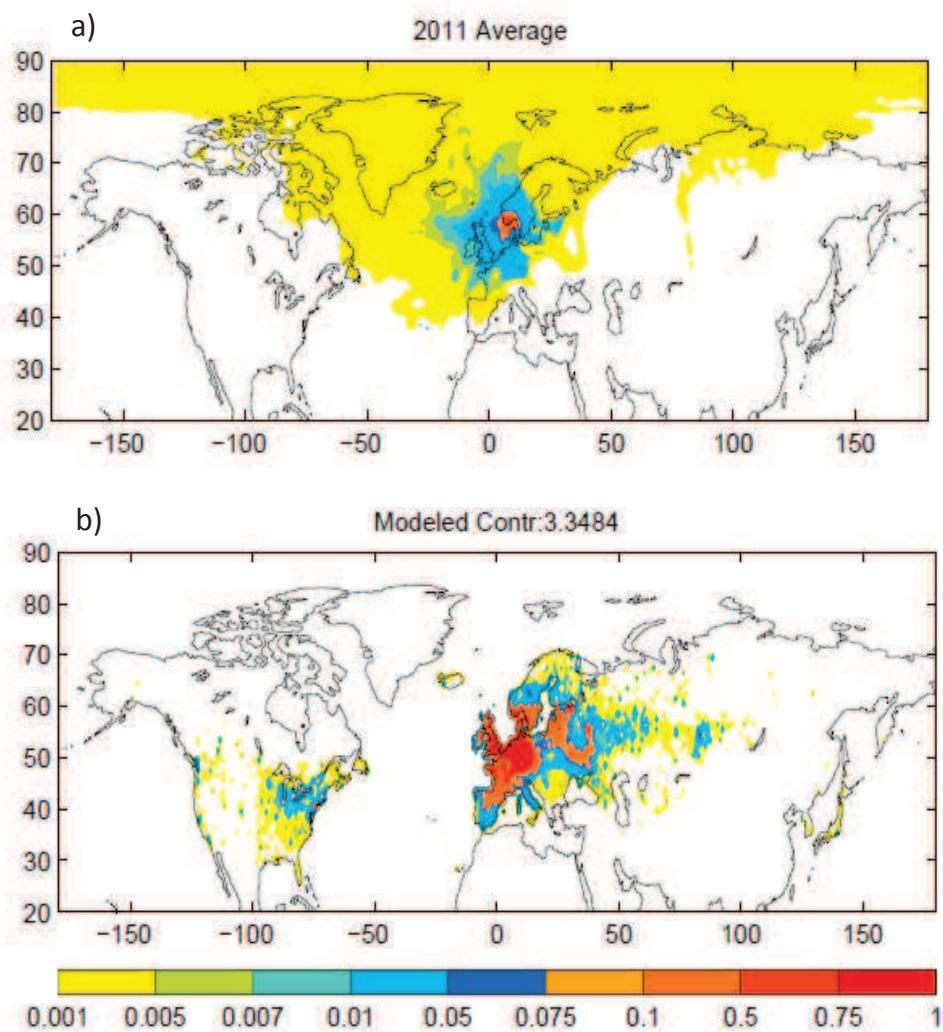


Figure A.2: Maps of *FLEXPART-r* footprint ES (a) and EC (b) for PCB-28 for the selected episode sampled in January (E1) at Birkenes.

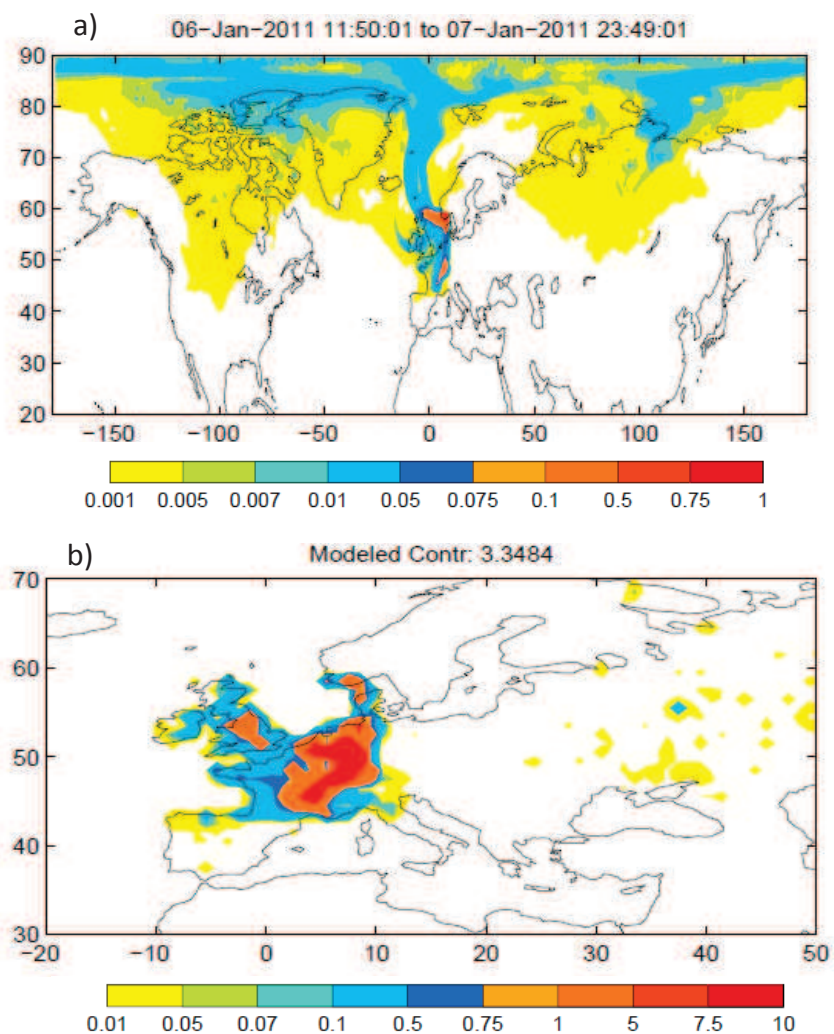


Figure A.3: Maps of *FLEXPART-r* footprint ES (a) and EC (b) for PCB-28 for the selected episode sampled at the end of February (E2) at Birkenes.

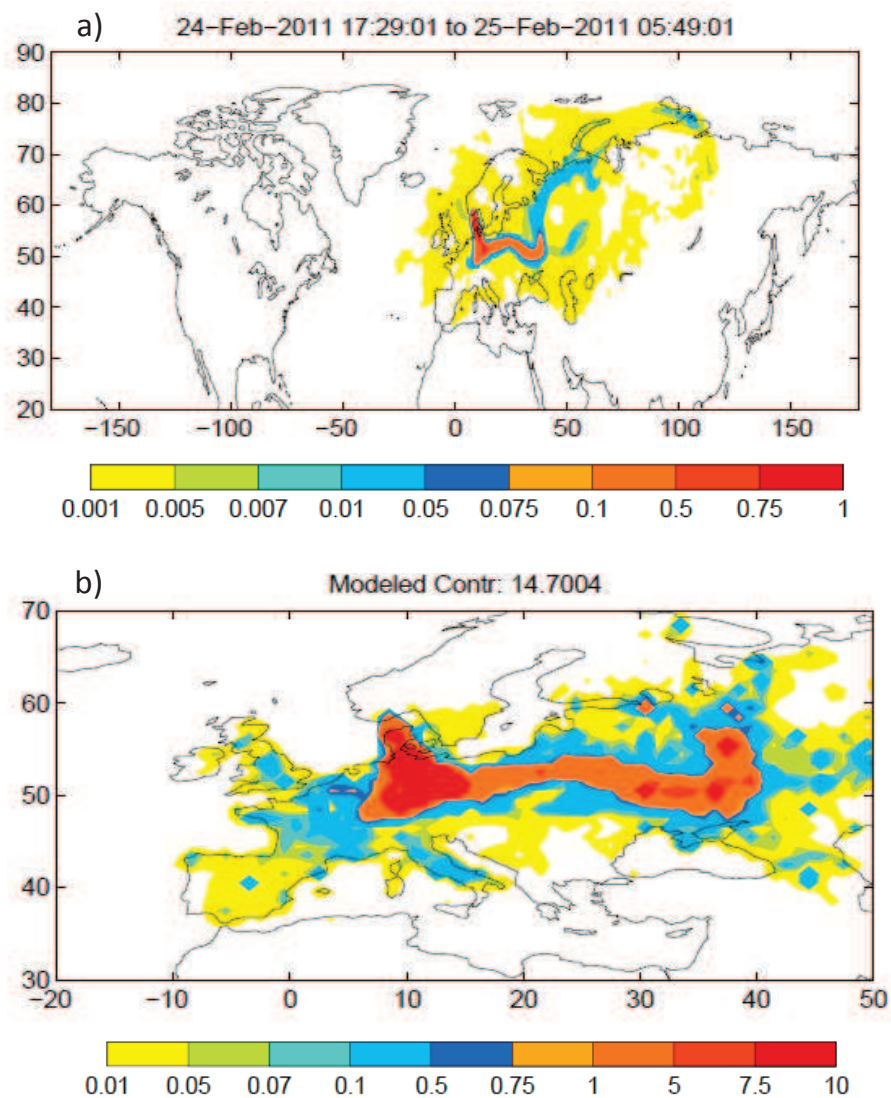


Figure A.4: Maps of *FLEXPART-r* footprint ES (a) and EC (b) for PCB-28 for the first of total five episodes sampled in late September / early October (E3a) at Birkenes.

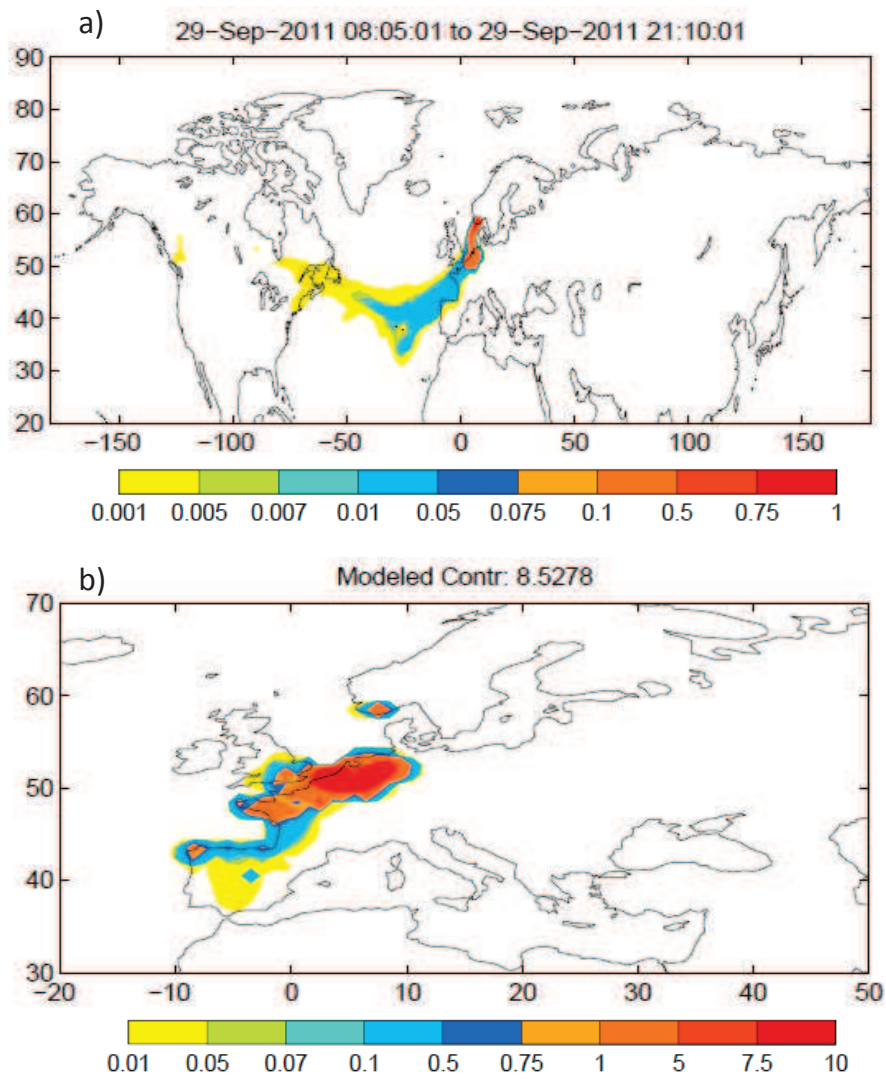


Figure A.5: Maps of *FLEXPART-r* footprint ES (a) and EC (b) for PCB-28 for the second of total five episodes sampled in late September / early October (E3b) at Birkenes.

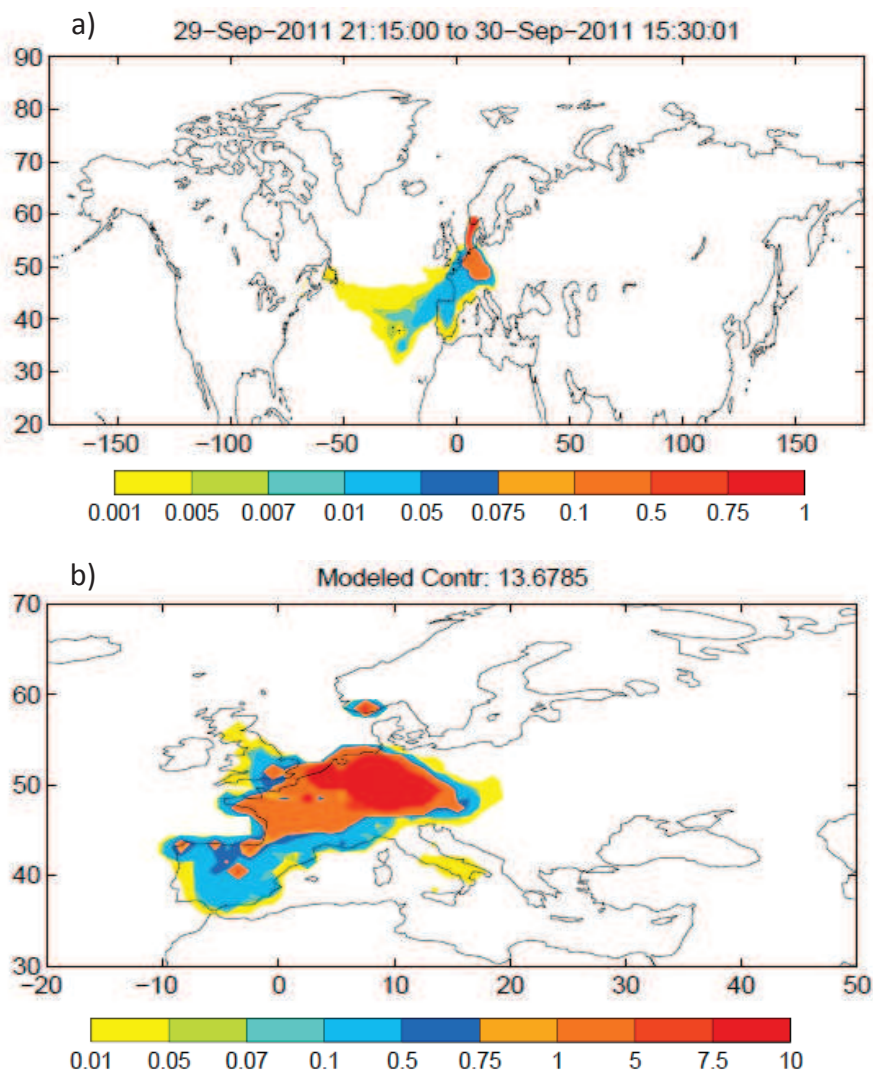


Figure A.6: Map of *FLEXPART-r* footprint ES for PCB-28 for the third of total five episodes sampled in late September / early October (E3c) at Birkenes.

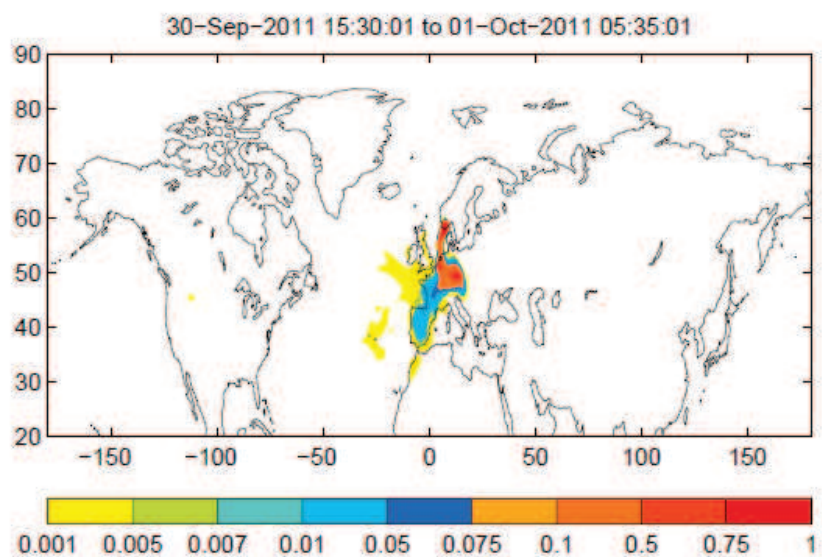


Figure A.7: Maps of *FLEXPART-r* footprint ES (a) and EC (b) for PCB-28 for the fourth of total five episodes sampled in late September / early October (E3d) at Birkenes.

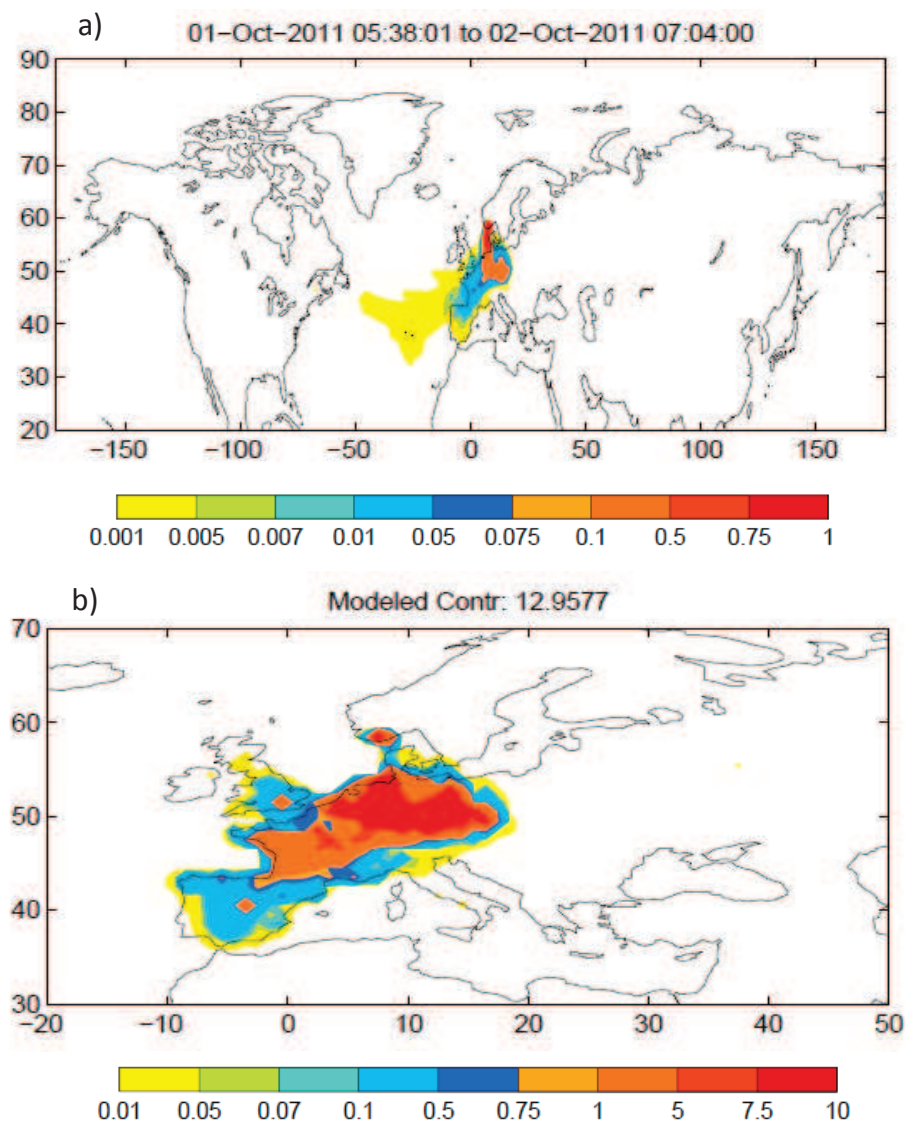
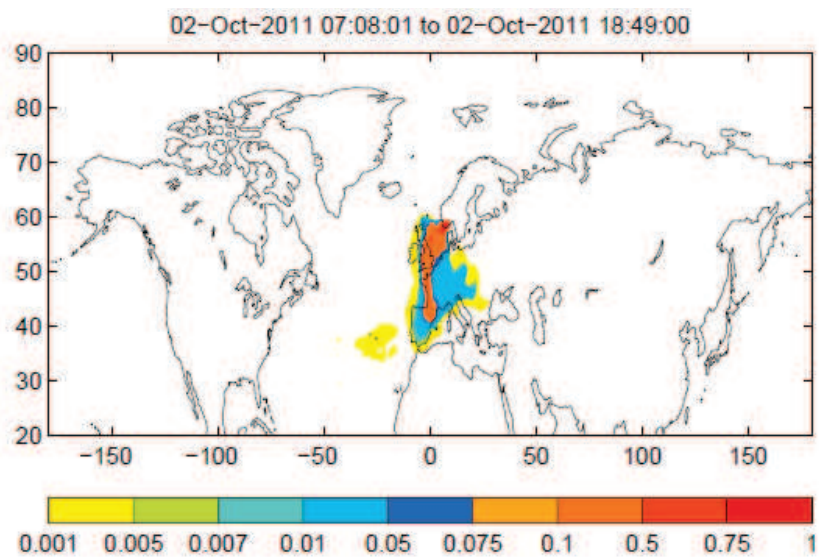


Figure A.8: Map of *FLEXPART-r* footprint ES for PCB-28 for the fifth of total five episodes sampled in late September / early October (E3e) at Birkenes.



Paper IV



Endosulfan, pentachlorobenzene and short-chain chlorinated paraffins in background soils from Western Europe

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Abstract

Soils are major reservoirs for many persistent organic pollutants (POPs). In this study, “newly” regulated POPs i.e. Σ endosulfans (α -endosulfan, β -endosulfan, endosulfan sulfate), pentachlorobenzene (PeCB), and short-chain chlorinated paraffins (SCCPs) were determined in background samples from woodland (WL) and grassland (GL) surface soil, collected along an existing latitudinal UK-Norway transect. Statistical analysis, complemented with plots showing the predicted equilibrium distribution and mobility potential, was then explored to discuss factors controlling their spatial distribution. SCCPs were detected with the highest average concentrations (35 ± 100 ng/g soil organic matter (SOM)), followed by Σ endosulfans (3 ± 3 ng/g SOM) and PeCB (1 ± 1 ng/g SOM). PeCB and Σ endosulfans share many similarities in their distribution in these background soils as well as with several legacy POPs. A steep decline in concentrations of SCCPs with increasing latitude indicates that their occurrence is dictated by proximity to source regions, while concentrations of Σ endosulfans peaked in regions experiencing elevated precipitation rates.

Capsule

Processes affecting the occurrence and latitudinal distribution of some “newly” regulated POPs in background soils.

Keywords

Short-chain chlorinated paraffins, Endosulfan, Pentachlorobenzene,
Background soils, Soil organic matter

1 Introduction

Soils have a large affinity and capacity for sorbing and storing persistent organic pollutants (POPs) (Meijer et al., 2003). Yet, the storage capacities of soils are expected and observed to vary significantly across the globe, reflecting differences in e.g. proximity to global source regions of POPs, soil organic matter content, and climatic conditions (Meijer et al., 2003). Soils from boreal regions are of particular interest, due to the low temperatures, high organic matter content, and slow decomposition associated with this type of environment (Moeckel et al., 2008). Hence, soils from boreal regions are expected to have elevated storage capacities for POPs (Dalla Valle et al., 2005).

Soils located remote from potential sources such as e.g. industrial or populated regions and agricultural areas are defined as background soils (Meijer et al., 2003). The POP contamination of background soils is mainly due to atmospheric deposition. Background soils may therefore be utilized to study potential pollution gradients as mediated by atmospheric transport, e.g. from potential source regions towards remote areas. A latitudinal transect of background soil sites, extending from southern parts of the UK towards northern Norway (UK-Norway transect), was established in 1998 (Meijer et al., 2002). Past studies from the UK-Norway transect have reported data on the occurrence and distribution of legacy POPs such as polychlorinated biphenyls (PCBs) (Meijer et al., 2002; Schuster et al., 2011), polybrominated diphenyl ethers (PBDEs) (Hassanin et al., 2004), polycyclic aromatic hydrocarbons (PAHs) (Nam et al., 2008b), polychlorinated dibenzodioxins and dibenzofurans (PCDDs/Fs) (Hassanin et al., 2005) and selected organochlorine pesticides (Schuster et al., 2011). While the UK-Norway transect has been considered a suitable “model environment” for empirical evaluation of long-range atmospheric transport (LRAT) behaviour of legacy POPs, studies of “new” (i.e. recently regulated) POPs have still been lacking. The overall goal of the study is to obtain a quantitative

and mechanistic understanding of the occurrence, fate, and distribution in background soils from North-western Europe of the following three substances/substance groups, collectively referred to as “new” POPs in this study.

(i) Endosulfan is an organochlorine pesticide, which is banned in many parts of the world. Technical mixtures of endosulfan contain two isomers, α - and β -endosulfan (α/β) in a 7/3 or 2/1 ratio, depending on the origin of the technical mixture (Weber et al., 2010). Technical endosulfan was listed under the Stockholm Convention on POPs (Annex A) in 2011 (UNEP, 2011).

(ii) Pentachlorobenzene (PeCB) has been used in production of the pesticide quintozone (pentachloronitrobenzene) and in a variety of chlorobenzene mixtures in order to reduce the viscosity of dielectric fluids. Current sources of PeCB to the environment include various combustion and industrial processes, as well as degradation of other chemicals (Bailey et al., 2009). PeCB was listed in Annex A and C under the Stockholm Convention in 2009 (UNEP, 2009), in addition to being adopted under the 1998 Aarhus protocol in 2009 (UNECE, 2010).

(iii) Short-chain chlorinated paraffins (SCCPs) are a complex mixture of polychlorinated *n*-alkanes. The alkane chain length can reach up to 13 carbons with chlorine content ranging between 30-70% (Houde et al., 2008). SCCPs have the general chemical formula $C_xCl_yH_{2x+2-y}$ where *x* is the number of carbon atoms (*x*=10-13) and *y* is the number of chlorine atoms (*y*=1-13) (Muir et al., 2000). SCCPs have been utilized in e.g. metal-cutting fluids, sealants, paints, lubricants, flame-retardants, and as softeners in different materials (UNECE ad hoc expert group on POPs, 2003; van der Gon et al., 2007). They have a potential to be released into the environment through production, storage, leaching, and/or volatilization (Muir et al., 2000). SCCPs have been adopted under the 1998 Aarhus protocol (UNECE, 2010) and are being evaluated by the Persistent Organic Pollutants Review Committee (POPRC) under the Stockholm Convention on POPs (UNEP, 2012).

There are few studies which have reported levels and distribution of these new POPs in background soils. However, endosulfans have previously been studied in forest soils in Canada and UK (Wong et al., 2009) and Tajikistan (Zhao et al., 2013), PeCB has been measured in

Estonian (Roots et al., 2010) and Antarctic soils (Borghini et al., 2005) while SCCPs have been reported in background soils from China (Wang et al., 2013).

2 Materials and methods

2.1 Sampling

Background surface soil samples were collected in 2008 (Schuster et al., 2011), along an existing transect of 39 sites (Meijer et al., 2002). This transect includes a number of United Kingdom (UK) sites (n=16) and Norwegian sites (n=23), covering remote/rural areas from 50.58-70.47° N and -6.20-27.95° E. Site descriptions are provided in Table A1 while a map is provided in Figure A1 in the Supplementary Data (SD). The soil sampling strategy together with information on soil characteristics has been presented earlier (Schuster et al., 2011), and only a brief summary is given here. The soil samples were collected to represent two types of remote soils, i.e. grassland soils (GL, n=25) and woodland (coniferous/deciduous) soils (WL, n=34). 59 surface soil samples in total were sampled and analysed. The samples were collected with a stainless steel hand-held corer and the targeted sampling depth was the upper layer (0-5 cm). Ten cores were taken to cover an area over several square meters and pooled to obtain a composite sample from each site (Meijer et al., 2002). The lumped samples were placed in zip-locked bags and stored in a freezer at ~-18 °C until further sample preparation.

2.2 Sample preparation, clean-up, and analysis

In the following section, a short overview of the sample treatment is given. More detailed information of the sample preparation, including drying, sieving, extraction, clean-up and analysis of the soil samples, is available in the SD (Sect A2.1-A2.3).

Wet soil samples were placed on aluminium foil and dried in an oven at low temperature (~27 °C), to minimize the potential for volatilization of target compounds. The time required to obtain complete dryness was approximately two weeks. Diatomaceous earth (DE) was prepared along with the soil samples, in order to address possible laboratory contamination from drying and clean-up procedures. Dried soil samples were afterwards sieved with a pre-cleaned sieve and stored cold in clean, brown glass bottles, covered with aluminium foil and a polypropylene (PP)-lid until extraction.

Extraction of the soil samples was performed by use of a Dionex Accelerated Solvent Extractor (ASE-200, 1995) unit (California, USA). An ASE cell was packed with soil samples that had been pre-mixed with DE for better extraction efficiency (see Figure A2). In addition, a mixture of internal standard was added. The extraction was carried out with acetone/*n*-hexane 1/1 (w/w). The content of soil organic matter (SOM) was determined by loss on ignition (LOI) at 550 °C (A2.6).

The soil extracts were divided into two aliquots prior to the clean-up procedures (A2.2.2), i.e. an endosulfan fraction (α -endosulfan, β -endosulfan and endosulfan sulfate), referred collectively to as Σ endosulfans, and an acid stable fraction (PeCB, SCCPs). The aliquot for the determination of Σ endosulfans was cleaned using a silica column only, while the aliquot for the determination of the acid stable compounds was treated with sulphuric acid followed by a fractionation with a silica column (A2.2.2). Subsequently, both aliquots were reduced to ~50 μ l by nitrogen and recovery standards were added (see A2.3). There were some problems with sedimentation in the endosulfan extracts, and it was necessary to centrifuge the samples (see A2.2.2) prior to instrumental analysis. Σ Endosulfans and SCCPs were determined with high resolution gas chromatography coupled to mass spectrometry in an electron capture negative ion mode (GC/HRMS(ECNI)), while PeCB was determined using gas chromatography coupled to high resolution mass spectrometry in an electron impact (EI) mode (GC/HRMS(EI)) (see Table A2). More information concerning the general method validation (QA/QC) is given in SD (A2.4 and A2.5).

2.3 Statistical analysis

Statistical analysis was performed with Microsoft Office Excel 2007 (Albuquerque, New Mexico, USA). Pearson correlation coefficients (*r*) were calculated to evaluate any linear relationships between the included variables, while the significance (*p*) was estimated by use of a Student's *t*-distribution (see A2.8). A correlation with a *p* < 0.05 was defined as statistically significant. For statistical summaries of overall results, samples with concentrations below method detection limit (MDL) (see A2.5) were assigned a value of ½ MDL. Prior to the correlation analyses, data below MDL and outliers were removed. The dataset was reviewed for possible outliers using a *z*-score test, and a *z*-score value ≥ 3 was determined as an outlier (A2.8.1). Additional parameters explored in the statistical analysis were bulk density (BD),

black carbon (BC), SOM content, and concentrations of HCB, PBDEs and PCBs which were all adapted from Schuster et al. (2011), with the exception of SOM. All data, with the exception of values for latitude and land use, were log transformed prior to the correlation analysis.

2.4 Mapping phase distribution and fate in soils

The distribution of organic compounds within environmental compartments is largely determined by their environmental partitioning behaviour which, in turn, is dictated by their physical-chemical properties (Gouin et al., 2000). Following Wong and Wania (2011), the phase distribution and mobility potential of individual substances in soils can therefore be plotted in chemical partitioning space maps (Figure 1). This simple graphical technique facilitates mechanistic insights into the likely partitioning and fate in soils and is used to complement interpretation of measurement data and results obtained based on the statistical analysis. Physical-chemical properties used to represent the various substances were adopted from the literature. Data for PCBs and PBDEs (Li et al., 2003; Wania and Dugani, 2003), HCB, PeCB, α -, β -endosulfan (Shen et al., 2005), endosulfan sulfate (U.S. EPA, 2011) and SCCPs (European Chemicals Bureau, 2008; Gawor and Wania, 2013)). The SCCPs are represented by a 38 formula groups, each representing the average properties of all isomers within each group (Krogseth et al., 2013), as well as the average property derived for SCCPs in the European Union (EU) Risk Assessment Report (RAR) (European Chemicals Bureau, 2008). For details, see SD (sect. A2.7). However, we caution that uncertainties remain with regards to the physical-chemical properties for SCCPs and refer to Gluege et al., (2013) for a detailed analysis and discussion.

3 Results and discussion

3.1 Overall results

Table 1 presents a summary of overall results for Σ endosulfans and its individual constituents as well as for PeCB and SCCPs, expressed as ng/g SOM. Table A4 shows the same results, but expressed on a ng/g dw basis, while Table A5 presents concentrations for individual compounds and sampling sites, expressed as ng/g dw and ng/g SOM. A few results were considered invalid and excluded from further analysis, either because of matrix related disturbances (Σ endosulfans; n=2, SCCPs and PeCB; n=1) or a low recovery of less than 10% (PeCB; n=5) (see also A2.4). Due to the complexity of SCCP mixture, a complete separation of

the individual congeners was not achieved (Sverko et al., 2012; Tomy et al., 1997), consequently introducing higher uncertainty into the quantified results of this compound group. The results for SCCPs should therefore be interpreted with caution. Concentrations were often below MDL for several of the studied compounds (see A2.5). Following removal of invalid data and data below MDL, one or more endosulfan constituents were detected in 56 out of the 57 samples considered valid (Table A5).

Within the group of Σ endosulfans, endosulfan sulfate was most frequently detected ($n=56$), followed by β -endosulfan ($n=17$) and α -endosulfan ($n=13$) (Table 1). PeCB was detected in 52 samples, while SCCPs were detected in 23 samples. The average concentration of SCCPs analysed ($n=58$) was by far the highest among the “new” POPs with 35 ng/g SOM ($SD\pm 100$ ng/g SOM), ranging from < MDL (0.6 ng/g SOM) to 570 ng/g SOM. The average concentration of Σ endosulfans in all background soil samples ($n=57$) was 3 ng/g SOM ($SD\pm 3$ ng/g SOM), and ranged from < MDL (0.02 ng/g SOM) to 20 ng/g SOM. The average concentration of PeCB for all sites studied ($n=53$) was 1 ng/g SOM ($SD\pm 1$ ng/g SOM), ranging from < MDL (0.08 ng/g SOM) to 6 ng/g SOM.

For comparison, Table 1 additionally includes previously published data for some legacy POPs (PCBs, PBDEs and HCB) collected during the same sampling campaign (Schuster et al., 2011). Table A4 additionally includes concentration ranges for endosulfans, PeCB and SCCPs from other localities around the world. While a direct comparison is somewhat difficult because of differences in methodologies, it is encouraging to note that the concentration ranges reported in the literature are generally similar to the levels measured in this study (Table A4). The average concentrations of SCCPs in all soil samples were highest among all compounds listed in Table 1, followed by Σ_{31} PCBs (6 ± 5 ng/g SOM). This pattern was consistent also for each subset of samples listed in Table 1 (UK, Norway, GL, and WL). Σ Endosulfans came out third for all soils combined (3 ± 3 ng/g SOM) including the Norwegian and WL sub-sets, while PeCB exceeded Σ endosulfans in the UK and GL soils. For all soils combined, HCB (1 ± 1 ng/g SOM) was more or less at the same level as PeCB (1 ± 1 ng/g SOM) which in turn exceeded that of Σ_5 PBDEs (0.6 ± 0.8 ng/g SOM). The same pattern was evident for Norwegian and WL soils, but not for UK and GL soils. PeCB exceeded both HCB and Σ_5 PBDEs in UK and GL soils (Table 1).

Table 1:

3.2 Correlation analysis

3.2.1 Removal of outliers

Outliers were removed prior to the correlation analysis. Results for PeCB (Birkenes, WL, Norway), Σ endosulfans (endosulfan sulfate, β -endosulfan) and Σ_{31} PCBs (Onsøy, WL, Norway), SCCPs (Tamokdalen, GL, Norway) and Σ_5 PBDEs (Okehampton, WL, UK) were consequently excluded (A2.8.1). Correlation analysis was then performed on the full remaining dataset (Table 2), as well as individually for UK, Norway, GL, and WL soils (Tables A6-A9).

3.2.2 Correlations between compound groups

For all soils combined, a highly significant correlation was found between the Σ endosulfans and HCB ($r=0.82$, $p<0.001$), Σ endosulfans and Σ_{31} PCBs ($r=0.73$, $p<0.001$) as well as between Σ endosulfans and PeCB ($r=0.58$, $p<0.001$) (Table 2). These results show that Σ endosulfans share some similarities in their distribution and fate in these background soils with other POPs known to be relatively volatile (i.e. $\log K_{OA} < \sim 10$, see Fig. 1a). The correlation between Σ_5 PBDEs ($\log K_{OA} > \sim 10$) and Σ endosulfans was significant, but weaker ($r=0.38$, $p<0.01$).

Significant correlations were also found between PeCB and HCB ($r=0.63$, $p<0.001$) and between PeCB and Σ_{31} PCBs ($r=0.62$, $p<0.001$) for all soils combined (Table 2), which is attributed to similarities in their predicted phase partitioning and distribution in soil (Fig. 1a). PeCB and Σ_5 PBDEs displayed a weaker correlation for all soils ($r=0.49$, $p<0.001$) (Table 2), which might be partly explained by a more divergent distribution partitioning behaviour as the Σ_5 PBDEs are less volatile (Fig. 1a, b).

SCCPs were not significantly correlated with any other POPs listed in Table 2 nor in any subsets (Tables A6-A9) with the notable exceptions of a weak and significant correlation with Σ_5 PBDEs for all soils combined ($r=0.27$, $p<0.05$) (Table 2) as well as for GL soils only ($r=0.50$, $p<0.05$) (Table A8). These results indicate that SCCPs are comparatively less prone to LRAT (see also Fig. 2c, f).

Figure 1.

3.2.3 Correlation with site variables

It is well established that POPs and SOM are typically correlated in soils (e.g. Seth et al., 1999) which is also observed in this dataset (Table 2). For all GL soils (n=24), the SOM content varied from 11 to 93 % (w/w), while the SOM content ranged from 13 to 98 % within the WL soils (n=34). A confounding factor in the correlation analysis is the strong and significant correlation between SOM and BC for all soils combined ($r=0.63$, $p<0.001$) (Table 2). BC is a by-product of incomplete combustion of fossil fuels and biomass (Schmidt and Noack, 2000), and POPs may have the potential to be emitted with BC from an emission source (Nam et al., 2008a). SOM is composed of amorphous organic matter (AOM) and carbonaceous matter such as BC (Nam et al., 2008a). The sorption capacity of carbonaceous materials (BC) is considered to be remarkably higher compared to AOM, and BC is thought to be responsible for a large part of the sorption of organic contaminants in soils (Cornelissen et al., 2005; Lohmann et al., 2005). Consequently, correlations between POPs and SOM should be evaluated with caution as high correlations between POPs and SOM may in part be due to the sorption properties of BC. Another confounding variable is bulk density (BD) which is inversely proportional to SOM; hence SOM rich soil has low BD.

Highest correlations between BC and the “new” POPs for all soils combined (Table 2) were seen with PeCB ($r=0.57$, $p<0.001$) followed by Σ endosulfans ($r=0.46$, $p<0.001$). Strong and significant correlation was also seen between SOM and Σ endosulfans ($r=0.80$, $p<0.001$) albeit weaker for SOM and PeCB ($r=0.70$, $p<0.001$). In contrast to Σ endosulfans, PeCB is known to be emitted from a variety of industrial sources and combustion processes (Bailey et al., 2009; Doring et al., 1992). As PeCB experienced the strongest correlation with BC among all POPs listed in Table 2, this indicates that PeCB and BC may to some extent be co-emitted from various combustion processes.

SCCPs showed no significant correlations ($p>0.05$) to any of the soil parameters, i.e. BD, BC and SOM, either for all soils combined nor for any sub-sets (Table 2, A6-A9). This indicates that the distribution of SCCPs in soil is probably more influenced by proximity to sources, rather than soil characteristics.

Table 2:

3.3 Σ Endosulfans, endosulfan constituents and distribution within the soil subsets

Within the Σ endosulfans, endosulfan sulfate was the dominant component and was detected in all samples except one, while the α - and the β - endosulfan isomers were detected in 13 and 17 samples, respectively (Table 1, Table A5). Endosulfan sulfate contributed with 97 % to the average concentration of Σ endosulfans, while α -and β - endosulfan isomers contributed with ~1.4 % and ~ 1.6 %, respectively.

The elevated concentration of endosulfan sulfate, compared to α and β -endosulfan, is because the former is the effective transformation product of the parent endosulfan compounds in soils (Antonious et al., 1998; Walse et al., 2003). The α/β ratio of technical mixtures are reported to be 7/2 or 2/1, depending on the mixture (Weber et al., 2010). For sites where both α - and β -endosulfan were above MDL ($n=7$), the observed ratio in soils ranged from 0.1 to 0.9. These findings clearly imply a depletion of α -endosulfan in soils, relative to in the technical mixtures. We believe this depletion in part can be explained by Figure 1, which shows that α -endosulfan is more volatile and less prone to atmospheric deposition (Fig. 1a) as well as more prone to evaporate from soils (Fig. 1b) in comparison to β -endosulfan and endosulfan sulfate, which are relatively more prone to erosion and leaching, respectively. These findings are consistent with a study by Rice and co-workers (2002) where α -endosulfan was found to be more volatile than β -endosulfan in soils. Furthermore, while strong and significant correlations are seen between Σ endosulfans and endosulfan sulfate ($r=0.99$, $p<0.001$) as well as between Σ endosulfans and β -endosulfan ($r=0.91$, $p<0.001$) in background soils, there is no statistical significance between Σ endosulfans and α -endosulfan ($r=0.49$, $p>0.05$) which indicates divergent behaviour and fate of the latter isomer (Table 2). However, as α and β -endosulfan were often below or close to MDL, the focus in the following is on Σ endosulfans.

Results for the Σ endosulfan concerning the UK and Norwegian soil revealed essentially the same distribution pattern with respect to the soil parameters, i.e. BC, BD and SOM (Table A6 and A7). Several studies have revealed that the forest may act as filter for airborne contaminants by enhancing the rate of deposition (Horstmann and McLachlan, 1998; Wania and McLachlan, 2001). The average endosulfan concentration in WL soil was about three times higher than in GL soil with 4 ng/SOM and 1 ng/g SOM, respectively (Table 1). Our data therefore suggest that Σ endosulfans are influenced by the forest filter effect, although the

partitioning properties (Fig. 1a) for β -endosulfan in particular are slightly outside the forest filter “window” (i.e. $\log K_{OA}$ and $\log K_{AW}$ around 9-10 and -2 to -3, respectively) as proposed by Wania and McLachlan (2001). A confounding factor, which might help to explain the enrichment of Σ endosulfans in WL soils compared to GL soils, is that the forest soils are higher in SOM (Table A1). The capacity of WL soils rich in SOM (average 0.66 g SOM) to retain Σ endosulfans may thus exceed that of GL soils (average 0.44 g SOM). The strong and significant correlation between Σ endosulfans and SOM is displayed in Figure 2g). Here the concentration of Σ endosulfans increased with amount of SOM both for GL and WL soil.

Figure 2a) and 2d) display the latitudinal distribution of Σ endosulfans expressed on SOM and on a dry weight basis, respectively. The concentration of Σ endosulfans for both WL and GL soil tends to increase towards 60 °N, followed by a slight decrease at higher latitudes, irrespective of the normalization. The elevated concentrations of Σ endosulfans seen at mid-latitudes (~60°N) may in part be caused by an orographic effect, which enhances wet deposition in southern parts of Norway compared to central and northern Norway (Aamot et al., 1996; Becker et al., 2011). The average concentration of Σ endosulfans for the Norwegian sites (n=32) was also more than two times higher than for the UK sites (n=24), with 3 and 2 ng/g SOM, respectively (Table 1). An orographic effect on the spatial distribution of Σ endosulfan concentrations also seems plausible as Σ endosulfans are among the more water-soluble substances in our data set (Fig. 1a). Σ Endosulfans are furthermore positively correlated with latitude in GL soils, albeit with limited significance ($r=0.47$, $p<0.05$) (Table A8), yet negatively correlated (and not significant) for the Norwegian sub-set (Table A7). It is interesting to note that α -endosulfan is slightly positively correlated with latitude ($r=0.24$), whereas β -endosulfan as the more water-soluble substance is slightly negatively correlated ($r=-0.11$) for all soils combined (Table 2). However, none of these two correlations nor any correlations between average precipitation rates and Σ endosulfans, including its constituents, were significant (Tables 2 and A6-A9).

Figure 2 (a-i)

3.4 Pentachlorobenzene (PeCB) and distribution within soil subsets

The average concentration of PeCB in UK soils (n=21) was about twice the average concentration for the Norwegian sites (n=31) with 2 ng/g SOM and 1 ng/g SOM, respectively (Table 1). The higher concentration of PeCB in UK soils may be due to proximity to past or ongoing source regions (Bailey et al., 2009; Nam et al., 2008a). It is interesting to note that this pattern is different from the one previously reported for HCB, where concentrations in Norwegian soils were found to exceed UK soils by a factor of about two (Table 1) in spite of close similarities in their partitioning behaviour (Fig. 1). Taken together with the strong association noted between PeCB and BC in soils, this provides further support for our hypothesis that PeCB may be co-emitted with BC from combustion processes. Combustion processes are also implicated as major emission sources of PeCB in the literature (Bailey et al., 2009; Tiernan et al., 1983). Studies have furthermore revealed that fly-ash from combustion processes contain PeCB (Liu et al., 2013; Nie et al., 2011). Furthermore, it is interesting to note that the correlation between PeCB and SOM was slightly stronger in Norwegian soils ($r=0.80$, $p<0.001$) (Table A7) compared to UK soils ($r=0.71$, $p<0.001$) (Table A6) which suggests that SOM may be somehow more important in controlling the occurrence in background soils in more remote regions of this transect.

The average concentration of PeCB in GL soils (n=19) was at more or less at the same level as WL soils (n=33), i.e. 1 ng/g SOM and 1 ng/g SOM (Table 1), respectively. This suggests that PeCB is not affected by the forest filter effect. PeCB showed significant correlation with BC for GL soil ($r=0.66$, $p<0.01$) (Table A8), but to a lesser extent with BC in WL soil ($r=0.41$, $p<0.05$) (Table A9). This may be explained by the lower and weaker correlation between BC and SOM in WL soil ($r=0.42$, $p<0.05$) (Table A9) compared to in GL soil ($r=0.79$, $p<0.001$) (Table A8). The latter could be due to a higher influence of fresh input of organic matter containing organic carbon in forest soils, versus carbonaceous carbon (BC) (Agarwal and Bucheli, 2011), causing a possible dilution of BC in WL soils.

Figure 2b) and 2e) present the latitudinal distribution of PeCB on a SOM and dry weight basis, respectively. Concentrations of PeCB based on ng/g SOM for both WL and GL soil were generally somewhat higher between ~ 50 - 55°N (>1.5 ng/g SOM in most samples), compared to higher latitudes (typically less than 1.0 ng/g SOM) (Fig. 2b). Nonetheless, the concentration

of PeCB is more or less uniformly distributed with exception from two sites (Fig. 2b). Figure 2h) shows the concentration of PeCB expressed on dry weight basis versus the content of SOM in all soil samples. The figure clearly illustrates how the concentrations of PeCB for both WL and GL soil increase with increasing amounts of SOM. This increase furthermore appears particularly steep at low SOM content (~30%). These findings are supported by the strong and significant correlation between PeCB and SOM seen for all soils and each sub-set (Tables 2, A6-A9).

3.5 Short-chain chlorinated paraffins (SCCPs) and distribution within soil subsets

The average concentration of SCCPs for the UK sites was approximately twice the average concentration for the Norwegian sites, with 50 ng/g SOM and 22 ng/g SOM, respectively (Table 1). The higher concentrations found in UK soil may reflect closer proximity to source regions (van der Gon et al., 2007). This is consistent with findings by Barber et al., (2005), who noted a significant temporal and spatial variability of SCCPs in UK air.

No sign of a forest filter effect could be observed as the average SCCP concentration in GL soils was 59 ng/g SOM, which is more than 3 times higher than the average concentration in WL soils (17 ng/g SOM) (Table 1).

Figures 2c) and 2f) illustrate the concentration of SCCPs as a function of latitude on an ng/g SOM and on a dry weight basis, respectively. The results show that the higher concentrations are typically seen at lower latitudes and that no sites at higher latitudes (> 62°N) experienced concentrations of SCCPs above MDL. This further suggests that SCCPs have a limited potential for LRAT as levels in soils decline relatively fast with increasing distance from suspected source regions. However, previous studies by Reth et al., (2006) and Tomy et al., (1999) show that SCCPs have been found in biota and sediments in the Arctic. Figure 2i) displays the concentrations of SCCPs on a dry weight basis versus SOM content (%) which further confirms the lack of correlation between SCCPs and SOM (Table 2, A6-A9).

4 Conclusion

The occurrence of Σ endosulfans, PeCB, and SCCPs in background surface soils from Western Europe has been evaluated by the use of statistical analyses, distribution maps and mobility

plots in soil, as well as data on concentrations of legacy POPs (PCBs, HCB and PBDEs). Overall, the statistical analysis and mobility plots showed that Σ endosulfans and PeCB share many similarities with selected old POPs in their distribution in background soils. Moreover, PeCB and Σ endosulfans were highly correlated with each other, and soil characteristics as SOM and BC were both important in explaining their occurrence and distribution. Concentrations of Σ endosulfans peaked in areas experiencing elevated precipitation rates and were strongly dominated by endosulfan sulfate (~97%). PeCB was found with higher concentrations in UK soil compared to Norwegian soil. A particularly strong association between BC and PeCB suggests that emissions of PeCB in part may be attributed to various combustion processes, and therefore retained closer to source regions. SCCPs do not share many similarities with Σ endosulfans and PeCB nor most legacy POPs in these background soils, with the exception of PBDEs. A steep decline in SCCP concentrations with increasing latitude indicates a limited potential for long-range atmospheric transport. Further, the lack of correlation between soil concentrations and key soil characteristics, such as SOM, indicate that the occurrence of SCCPs is largely dictated by proximity to source regions. This study also demonstrates that simple chemical distribution and mobility plots (chemical space maps) are useful as complementary tools to assess whether any inferences made from statistical analysis of observations are reasonable from a mechanistic standpoint.

Appendix A. Supplementary data

Supplementary data available.

Acknowledgements

This study was financed by the Research Council of Norway (183437 and 196191). The authors thank Sabine Eckhardt for valuable assistance on the ECMWF data, provided by the Norwegian MetOffice. We would also like to thank our colleagues at NILU (A. Borgen, H. Gundersen, H. Lunder, K. Davanger, I.S. Krogseth and M. Ghebremeskel) for support, together with Andy Sweetman and Rosalinda Gioia for their valuable contributions.

5 References

- Aamot, E., Steinnes, E., and Schmid, R. (1996). Polycyclic aromatic hydrocarbons in Norwegian forest soils: Impact of long range atmospheric transport. *Environmental Pollution* **92**, 275-280.
- Agarwal, T., and Bucheli, T. D. (2011). Adaptation, validation and application of the chemo-thermal oxidation method to quantify black carbon in soils. *Environmental Pollution* **159**, 532-538.
- Antonious, G. F., Byers, M. E., and Snyder, J. C. (1998). Residues and fate of endosulfan on field-grown pepper and tomato. *Pesticide Science* **54**, 61-67.
- Bailey, R. E., van Wijk, D., and Thomas, P. C. (2009). Sources and prevalence of pentachlorobenzene in the environment. *Chemosphere* **75**, 555-564.
- Barber, J. L., Sweetman, A. J., Thomas, G. O., Braekevelt, E., Stern, G. A., and Jones, K. C. (2005). Spatial and temporal variability in air concentrations of short-chain (C-10-C-13) and medium-chain (C-14-C-17) chlorinated n-alkanes measured in the UK atmosphere. *Environmental Science & Technology* **39**, 4407-4415.
- Becker, L., Scheringer, M., Schenker, U., and Hungerbuhler, K. (2011). Assessment of the environmental persistence and long-range transport of endosulfan. *Environmental Pollution* **159**, 1737-1743.
- Borghini, F., Grimalt, J. O., Sanchez-Hernandez, J. C., and Bargagli, R. (2005). Organochlorine pollutants in soils and mosses from Victoria Land (Antarctica). *Chemosphere* **58**, 271-278.
- Cornelissen, G., Gustafsson, O., Bucheli, T. D., Jonker, M. T. O., Koelmans, A. A., and Van Noort, P. C. M. (2005). Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environmental Science & Technology* **39**, 6881-6895.
- Dalla Valle, M., Jurado, E., Dachs, J., Sweetman, A. J., and Jones, K. C. (2005). The maximum reservoir capacity of soils for persistent organic pollutants: implications for global cycling. *Environmental Pollution* **134**, 153-164.
- Doring, J., Damberg, M., Gamradt, A., and Oehme, M. (1992). Screening method based on the determination of perchlorinated aromatics for surface soil contaminated by copper slag containing high-levels of polychlorinated dibenzofurans and dibenzo-p-dioxines. *Chemosphere* **25**, 755-762.
- European Chemicals Bureau (2008). "European Union Risk Assessment Report: Alkanes, C10-13, chloro, updated version." European Chemicals Bureau, Luxemburg.
- Gawor, A., and Wania, F. (2013). Using quantitative structural property relationships, chemical fate models, and the chemical partitioning space to investigate the potential for long range transport and bioaccumulation of complex halogenated chemical mixtures. *Environmental Science-Processes & Impacts* **15**, 1671-1684.
- Gluge, J., Bogdal, C., Scheringer, M., Buser, A. M., and Hungerbuhler, K. (2013). Calculation of Physicochemical Properties for Short- and Medium-Chain Chlorinated Paraffins. *Journal of Physical and Chemical Reference Data* **42**.
- Gouin, T., Mackay, D., Webster, E., and Wania, F. (2000). Screening chemicals for persistence in the environment. *Environmental Science & Technology* **34**, 881-884.
- Hassanin, A., Breivik, K., Meijer, S. N., Steinnes, E., Thomas, G. O., and Jones, K. C. (2004). PBDEs in European background soils: Levels and factors controlling their distribution. *Environmental Science & Technology* **38**, 738-745.
- Hassanin, A., Lee, R. G. M., Steinnes, E., and Jones, K. C. (2005). PCDD/Fs in Norwegian and UK soils: Implications for sources and environmental cycling. *Environmental Science & Technology* **39**, 4784-4792.
- Horstmann, M., and McLachlan, M. S. (1998). Atmospheric deposition of semivolatile organic compounds to two forest canopies. *Atmospheric Environment* **32**, 1799-1809.
- Houde, M., Muir, D. C. G., Tomy, G. T., Whittle, D. M., Teixeira, C., and Moore, S. (2008). Bioaccumulation and trophic magnification of short- and medium-chain chlorinated paraffins

- in food webs from Lake Ontario and Lake Michigan. *Environmental Science & Technology* **42**, 3893-3899.
- Krogseth, I. S., Breivik, K., Arnot, J. A., Wania, F., Borgen, A. R., and Schlabach, M. (2013). Evaluating the environmental fate of short-chain chlorinated paraffins (SCCPs) in the Nordic environment using a dynamic multimedia model. *Environmental Science-Processes & Impacts* **15**, 2240-2251.
- Li, N. Q., Wania, F., Lei, Y. D., and Daly, G. L. (2003). A comprehensive and critical compilation, evaluation, and selection of physical-chemical property data for selected polychlorinated biphenyls. *Journal of Physical and Chemical Reference Data* **32**, 1545-1590.
- Liu, G. R., Liu, W. B., Cai, Z. W., and Zheng, M. H. (2013). Concentrations, profiles, and emission factors of unintentionally produced persistent organic pollutants in fly ash from coking processes. *Journal of Hazardous Materials* **261**, 421-426.
- Lohmann, R., MacFarlane, J. K., and Gschwend, P. M. (2005). Importance of black carbon to sorption of native PAHs, PCBs, and PCDDs in Boston and New York, Harbor sediments. *Environmental Science & Technology* **39**, 141-148.
- Meijer, S. N., Ockenden, W. A., Sweetman, A., Breivik, K., Grimalt, J. O., and Jones, K. C. (2003). Global distribution and budget of PCBs and HCB in background surface soils: Implications for sources and environmental processes. *Environmental Science & Technology* **37**, 667-672.
- Meijer, S. N., Steinnes, E., Ockenden, W. A., and Jones, K. C. (2002). Influence of environmental variables on the spatial distribution of PCBs in Norwegian and UK soils: Implications for global cycling. *Environmental Science & Technology* **36**, 2146-2153.
- Moeckel, C., Nizzetto, L., Di Guardo, A., Steinnes, E., Freppaz, M., Filippa, G., Camporini, P., Benner, J., and Jones, K. C. (2008). Persistent Organic Pollutants in Boreal and Montane Soil Profiles: Distribution, Evidence of Processes and Implications for Global Cycling. *Environmental Science & Technology* **42**, 8374-8380.
- Muir, D., Stern, G., and Tomy, G. (2000). Chlorinated paraffins. In "The Handbook of Environmental Chemistry" (J. Paasivirta, ed.), Vol. 3. Springer-Verlag, Berlin, Heidelberg.
- Nam, J. J., Gustafsson, O., Kurt-Karakus, P., Breivik, K., Steinnes, E., and Jones, K. C. (2008a). Relationships between organic matter, black carbon and persistent organic pollutants in European background soils: Implications for sources and environmental fate. *Environmental Pollution* **156**, 809-817.
- Nam, J. J., Thomas, G. O., Jaward, F. M., Steinnes, E., Gustafsson, O., and Jones, K. C. (2008b). PAHs in background soils from Western Europe: Influence of atmospheric deposition and soil organic matter. *Chemosphere* **70**, 1596-1602.
- Nie, Z. Q., Zheng, M. H., Liu, W. B., Zhang, B., Liu, G. R., Su, G. J., Lv, P., and Xiao, K. (2011). Estimation and characterization of PCDD/Fs, dl-PCBs, PCNs, HxCbz and PeCBz emissions from magnesium metallurgy facilities in China. *Chemosphere* **85**, 1707-1712.
- Reth, M., Ciric, A., Christensen, G. N., Heimstad, E. S., and Oehme, M. (2006). Short- and medium-chain chlorinated paraffins in biota from the European Arctic - differences in homologue group patterns. *Science of the Total Environment* **367**, 252-260.
- Rice, C. P., Nochetto, C. B., and Zara, P. (2002). Volatilization of trifluralin, atrazine, metolachlor, chlorpyrifos, alpha-endosulfan, and beta-endosulfan from freshly tilled soil. *Journal of Agricultural and Food Chemistry* **50**, 4009-4017.
- Roots, O., Roose, A., Kull, A., Holoubek, I., Cupr, P., and Klanova, J. (2010). Distribution pattern of PCBs, HCB and PeCB using passive air and soil sampling in Estonia. *Environmental Science and Pollution Research* **17**, 740-749.
- Schmidt, M. W. I., and Noack, A. G. (2000). Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges. *Global Biogeochemical Cycles* **14**, 777-793.
- Schuster, J. K., Gioia, R., Moeckel, C., Agarwal, T., Bucheli, T. D., Breivik, K., Steinnes, E., and Jones, K. C. (2011). Has the Burden and Distribution of PCBs and PBDEs Changed in European Background Soils between 1998 and 2008? Implications for Sources and Processes. *Environmental Science & Technology* **45**, 7291-7297.

- Seth, R., Mackay, D., and Muncke, J. (1999). Estimating the organic carbon partition coefficient and its variability for hydrophobic chemicals. *Environmental Science & Technology* **33**, 2390-2394.
- Shen, L., Wania, F., Lei, Y. D., Teixeira, C., Muir, D. C. G., and Bidleman, T. F. (2005). Atmospheric distribution and long-range transport behavior of organochlorine pesticides in north America. *Environmental Science & Technology* **39**, 409-420.
- Sverko, E., Tomy, G. T., Marvin, C. H., and Muir, D. C. G. (2012). Improving the Quality of Environmental Measurements on Short Chain Chlorinated Paraffins to Support Global Regulatory Efforts. *Environmental Science & Technology* **46**, 4697-4698.
- Tiernan, T. O., Taylor, M. L., Garrett, J. H., Vanness, G. F., Solch, J. G., Deis, D. A., and Wagel, D. J. (1983). Chlorodibenzodioxines, chlorodibenzofurans and related-compounds in the effluents from combustion processes. *Chemosphere* **12**, 595-606.
- Tomy, G. T., Stern, G. A., Lockhart, W. L., and Muir, D. C. G. (1999). Occurrence of C-10-C-13 polychlorinated n-alkanes in Canadian midlatitude and arctic lake sediments. *Environmental Science & Technology* **33**, 2858-2863.
- Tomy, G. T., Stern, G. A., Muir, D. C. G., Fisk, A. T., Cymbalisty, C. D., and Westmore, J. B. (1997). Quantifying C-10-C-13 polychloroalkanes in environmental samples by high-resolution gas chromatography electron capture negative ion high resolution mass spectrometry. *Analytical Chemistry* **69**, 2762-2771.
- U.S. EPA (2011). Estimation Programs Interface Suite(TM) for Microsoft Windows, v 4.1., Vol. 2013.
- UNECE (2010). "The 1998 Protocol on Persistent Organic Pollutants, including the Amendments Adopted by the Parties on 18 December 2009."
- UNECE ad hoc expert group on POPs (2003). "Short chain chlorinated paraffins (SCCPs) Substance Dossier. Final Draft II."
- UNEP (2009). "Stockholm Convention on Persistent Organic Pollutants (POPs) as amended in 2009. Text and annexes."
- UNEP (2011). "Adoption of an amendment to Annex A," Geneva.
- UNEP (2012). "Report of the Persistent Organic Pollutants Review Committee on the work of its eighth meeting ". Stockholm Convention on Persistent Organic Pollutants.
- van der Gon, H. D., van het Bolscher, M., Visschedijk, A., and Zandveld, P. (2007). Emissions of persistent organic pollutants and eight candidate POPs from UNECE-Europe in 2000, 2010 and 2020 and the emission reduction resulting from the implementation of the UNECE POP protocol. *Atmospheric Environment* **41**, 9245-9261.
- Walse, S. S., Scott, G. I., and Ferry, J. L. (2003). Stereoselective degradation of aqueous endosulfan in modular estuarine mesocosms: formation of endosulfan gamma-hydroxycarboxylate. *Journal of Environmental Monitoring* **5**, 373-379.
- Wang, X. T., Zhang, Y., Miao, Y., Ma, L. L., Li, Y. C., Chang, Y. Y., and Wu, M. H. (2013). Short-chain chlorinated paraffins (SCCPs) in surface soil from a background area in China: occurrence, distribution, and congener profiles. *Environmental Science and Pollution Research* **20**, 4742-4749.
- Wania, F., and Dugani, C. B. (2003). Assessing the long-range transport potential of polybrominated diphenyl ethers: A comparison of four multimedia models. *Environmental Toxicology and Chemistry* **22**, 1252-1261.
- Wania, F., and McLachlan, M. S. (2001). Estimating the influence of forests on the overall fate of semivolatile organic compounds using a multimedia fate model. *Environmental Science & Technology* **35**, 582-590.
- Weber, J., Halsall, C. J., Muir, D., Teixeira, C., Small, J., Solomon, K., Hermanson, M., Hung, H., and Bidleman, T. (2010). Endosulfan, a global pesticide: A review of its fate in the environment and occurrence in the Arctic. *Science of the Total Environment* **408**, 2966-2984.
- Wong, F., Robson, M., Diamond, M. L., Harrad, S., and Truong, J. (2009). Concentrations and chiral signatures of POPs in soils and sediments: A comparative urban versus rural study in Canada and UK. *Chemosphere* **74**, 404-411.

- 560 Wong, F., and Wania, F. (2011). Visualising the equilibrium distribution and mobility of organic
561 contaminants in soil using the chemical partitioning space. *Journal of Environmental*
562 *Monitoring* **13**, 1569-1578.
- 563 Zhao, Z., Zeng, H., Wu, J., and Zhang, L. (2013). Organochlorine pesticide (OCP) residues in mountain
564 soils from Tajikistan. *Environmental Science-Processes & Impacts* **15**, 608-616.

565

566 Figure captions in the order of appearance

567 Figure 1: Chemical partitioning space maps for selected POPs, a) equilibrium phase distribution, b)
568 mobility potential in soils (modified after Wong and Wania (2011)). Data for the compound groups is
569 referred to in section 2.4.

570
571 Figure 2 (a-i): Latitudinal distribution for Σ Endosulfans, PeCB and SCCPs on ng/g SOM (a, b, c) and dry
572 weight basis (d, e, f). Also included is the log concentration ($\text{ng g}^{-1} \text{ dw}$) versus SOM (g, h, i). Woodland
573 (WL, ▲) and grassland (GL, ○) soil samples are plotted separately. One outlier for each compound was
574 omitted (2.8.1).

Table 1: Average soil concentrations \pm standard deviation and ranges, for Σ endosulfans and its constituents, PeCB and SCCPs for all soils combined (ng/g SOM). Samples which failed to meet the specified QA/QC criteria were excluded (see 3.1). The table also includes Σ_{31} PCBs, Σ_5 PBDEs and HCB (Schuster et al., 2011).

Arithmetic average \pm standard deviation											
Range (min-max)											
	>MDL	Σ endosulfans	endosulfan sulfate	α -endosulfan	β -endosulfan	PeCB	SCCPs		Σ_{31} PCBs ³⁾	Σ_5 PBDEs ³⁾	HCB ³⁾
All 2008	All 2008	3 \pm 3	3 \pm 3	0.04 \pm 0.03	0.04 \pm 0.08	1 \pm 1	35 \pm 100	All 2008	6 \pm 5	0.6 \pm 0.8	1 \pm 1
n = 57/53/58 ¹⁾	n = 56/52/23 ¹⁾	<0.02 ²⁾ -20	<0.005 ²⁾ -19	<0.003 ²⁾ -0.2	<0.002 ²⁾ -0.6	<0.08 ²⁾ -6	<0.6 ²⁾ -570	n = 70	0.2-27	0.01-4	0.04-7
Norway	Norway	3 \pm 4	3 \pm 4	0.03 \pm 0.03	0.06 \pm 0.1	0.8 \pm 0.7	22 \pm 87	Norway	8 \pm 6	0.3 \pm 0.4	1 \pm 1
n= 32/32/32 ¹⁾	n= 32/31/9 ¹⁾	0.2-19	0.1-19	<0.004 ²⁾ -0.1 ²⁾	<0.002 ²⁾ -0.6	<0.08 ²⁾ -4	<0.6 ²⁾ -490	n= 40	0.2-27	0.01-2	0.2-5
UK	UK	2 \pm 2	1 \pm 2	0.04 \pm 0.04	0.02 \pm 0.02	2 \pm 1	50 \pm 115	UK	5 \pm 3	1 \pm 1	0.8 \pm 1
n= 25/21/26 ¹⁾	n= 24/21/14 ¹⁾	<0.02 ²⁾ -8	<0.005 ²⁾ -7	<0.003 ²⁾ -0.2	<0.002 ²⁾ -0.1	0.2-6	<0.8 ²⁾ -570	n= 30	0.5-10	0.1-4	0.04-7
GL	GL	1 \pm 1	1 \pm 1	0.05 \pm 0.04	0.03 \pm 0.02	1 \pm 1	59 \pm 147	GL	5 \pm 5	0.5 \pm 0.8	1 \pm 1
n= 23/20/24 ¹⁾	n= 22/19/9 ¹⁾	<0.02 ²⁾ -5	<0.005 ²⁾ -5	<0.005 ²⁾ -0.2	<0.002 ²⁾ -0.08	<0.08 ²⁾ -6	<0.8 ²⁾ -570	n= 30	0.2-23	0.02-4	0.06-7
WL	WL	4 \pm 4	3 \pm 4	0.03 \pm 0.02	0.05 \pm 0.1	1 \pm 1	17 \pm 39	WL	8 \pm 6	0.7 \pm 0.7	1 \pm 1
n= 34/33/34 ¹⁾	n= 34/33/14 ¹⁾	0.1-20	0.1-19	<0.003 ²⁾ -0.1	<0.002 ²⁾ -0.6	0.2-4	<0.6 ²⁾ -175	n= 40	0.6-27	0.01-3	0.04-5

¹⁾ Number (n) of sites for which Σ endosulfans, PeCB and SCCPs were determined, respectively.

²⁾ One or more samples were below MDL ($\frac{1}{2}$ MDL used for statistical summaries).

³⁾ Data from (Schuster et al., 2011)

Table 2: Results from correlation analysis with statistical significance for latitude, land use and individual compounds for all soil in 2008. Samples which either (i) failed to meet the QA/QC criteria (low recovery etc.), or (ii) were below MDL, or (iii) qualified as outliers were not considered (see text for details).

Variables	Latitude	BD (g/cm ³)	BC	SOM	Σendo sulfans	Endosulfan sulfate	α-endosulfan	β-endosulfan	PeCB	SCCPs	HCB	Σ ₅ PBDE	Σ ₃₁ PCB
Latitude	1												
BD (g/cm ³)	-0.16	1											
BC	0,01	-0.56***	1										
SOM	0,18	-0.83***	0.63***	1									
Σendosulfans	0,24	-0.75***	0.46***	0.80***	1								
Endosulfan sulfate	0,26	-0.75***	0.45***	0.80***	0.99***	1							
α-endosulfan	0,24	-0.37	0,20	0.70**	0.49	0,42	1						
β-endosulfan	-0.11	-0.29	0,16	0.58*	0.91***	0.91***	0.86***	1					
PeCB	-0.13	-0.58***	0.57***	0.70***	0.58***	0.55***	0,230	0,12	1				
SCCPs	-0.19	-0.14	0.13	0.10	0.17	0.18	-0.35	0.14	0.19	1			
HCB	0.31*	-0.84***	0.49***	0.80***	0.82***	0.81***	0.74***	0.72***	0.63***	-0.01	1		
Σ ₅ PBDEs	-0.50***	-0.42**	0.28*	0.39**	0.38**	0.37**	0.44***	0.41**	0.49***	0.27*	0.44***	1	
Σ ₃₁ PCBs	0.08	-0.77***	0.49***	0.70***	0.73***	0.73***	0.70***	0.76***	0.62***	0.06	0.86***	0.54***	1

*:p<0.05, **: p<0.01, ***: p<0.001

n=59, except from: Σendosulfans and endosulfan sulfate (n=55), α-endosulfan (n=13), β-endosulfan (n=16), PeCB (n=51), SCCPs (n=22), HCB (n=48), Σ₅PBDES and Σ₃₁PCB (n=56).

References

Schuster, J. K., Gioia, R., Moeckel, C., Agarwal, T., Bucheli, T. D., Breivik, K., Steinnes, E., and Jones, K. C. (2011). Has the Burden and Distribution of PCBs and PBDEs Changed in European Background Soils between 1998 and 2008? Implications for Sources and Processes. *Environmental Science & Technology* **45**, 7291-7297.

Figure 1 a), b)

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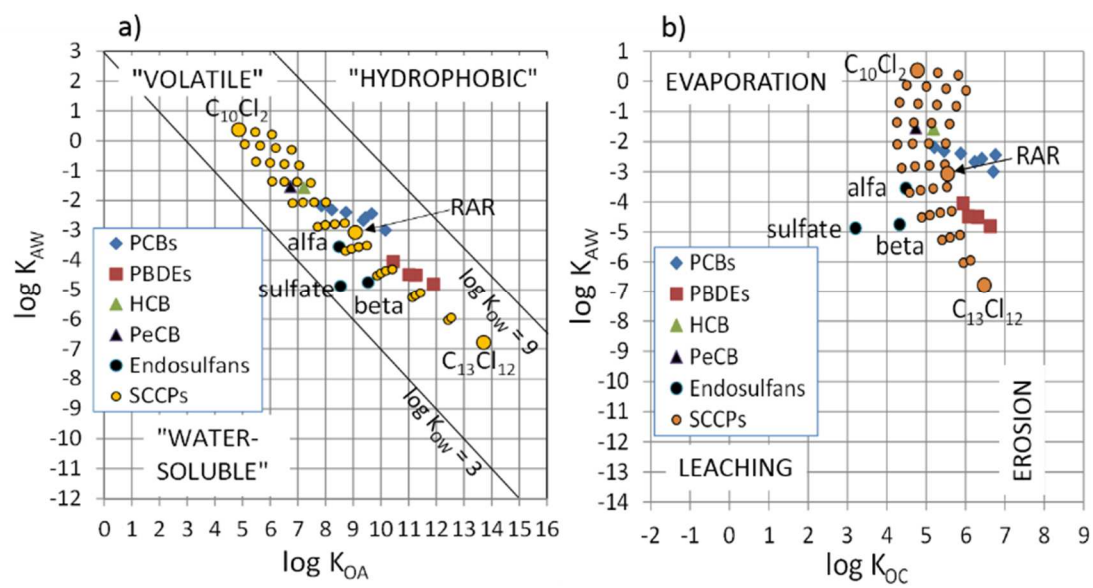
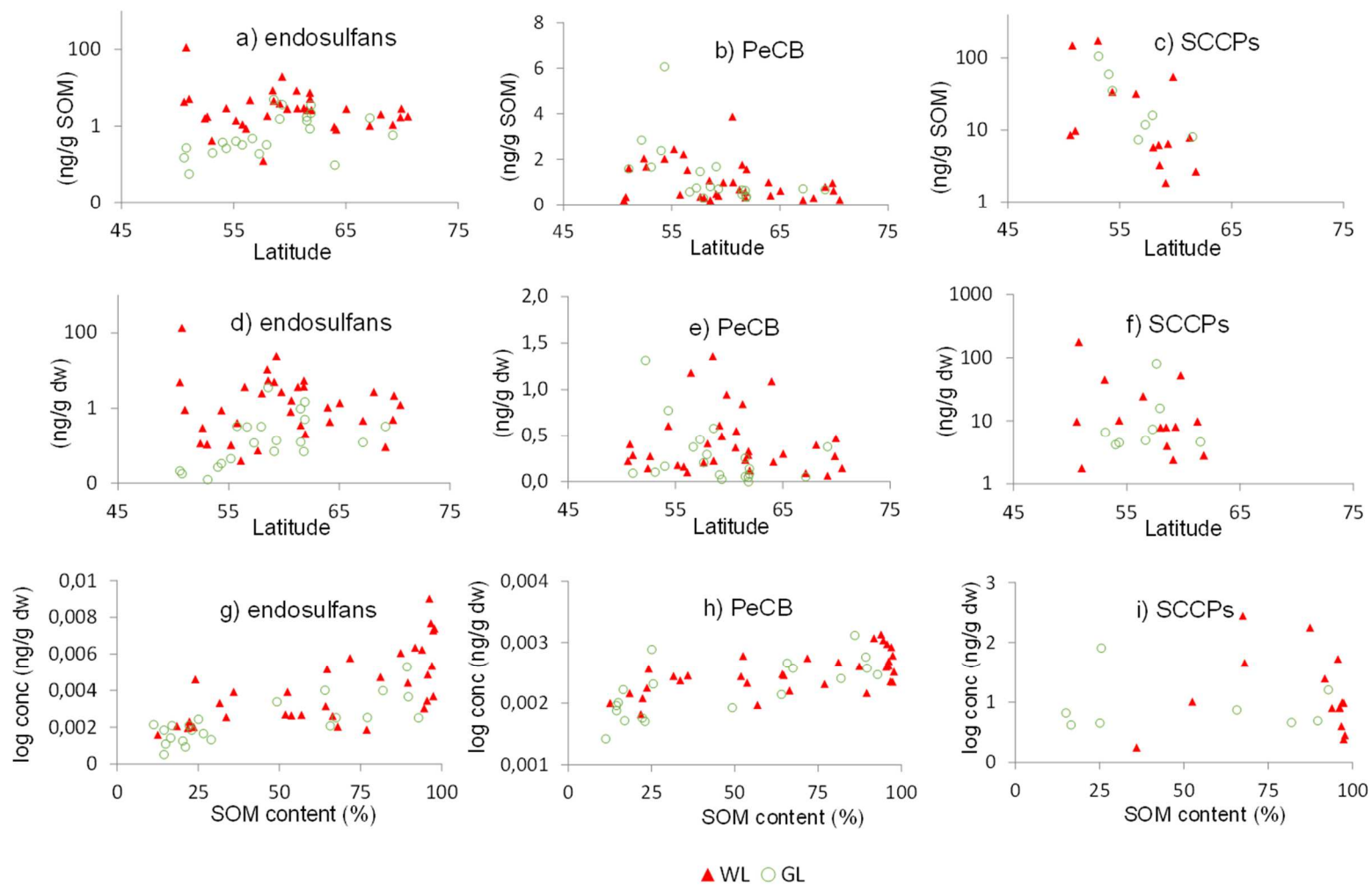


Figure 2 (a-i)



Supplementary material

**Endosulfan, pentachlorobenzene and short-chain chlorinated
paraffins in background soils from Western Europe**

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1. Tables

Table A1: Information related to sample site, sample characteristics, geographical coordinates and sample amount (dry weight and amount of soil organic matter (SOM)).

Country	Site	Land use	Latitude [°]	Longitude [°]	Sample amount g dw	SOM g SOM
United Kingdom	Bodwin	WL	50.58	-4.52	0.85	0.97
United Kingdom	Bodwin	GL	50.58	-4.52	2.04	0.29
United Kingdom	Okehamptons	WL	50.76	-4.00	0.73	0.87
United Kingdom	Okehamptons	GL	50.78	-3.91	3.04	0.20
United Kingdom	Tiverton	GL	51.03	-3.52	2.47	0.14
United Kingdom	Tiverton	WL	51.03	-3.51	2.01	0.36
United Kingdom	Aberystwyth	GL	52.20	-3.79	1.86	0.86
United Kingdom	Aberystwyth	WL	52.43	-4.03	2.56	0.18
United Kingdom	Corris	WL	52.64	-3.84	1.89	0.32
United Kingdom	Betsw-y-coed	WL	53.05	-3.80	2.61	¹⁾ 0.68
United Kingdom	Betsw-y-coed	GL	53.11	-3.78	2.41	¹⁾ 0.15
United Kingdom	Hazelrigg	GL	54.01	-2.78	2.35	0.17
United Kingdom	Hawkshead	WL	54.33	-3.00	1.74	0.52
United Kingdom	Hawkshead	GL	54.33	-3.00	1.97	0.25
United Kingdom	Ae, Dumfries	GL	55.20	-3.60	2.39	0.27
United Kingdom	Ae, Dumfries	WL	55.20	-3.61	3.20	0.24
United Kingdom	Clachan	GL	55.76	-5.54	0.75	0.77
United Kingdom	Clachan	WL	55.77	-5.53	1.80	0.66
United Kingdom	Colonsay	GL	56.08	-6.20	1.34	0.48
United Kingdom	Colonsay	WL	56.10	-6.18	2.75	0.13
United Kingdom	Tyndrum	WL	56.45	-4.71	1.18	0.92
United Kingdom	Glencoe	GL	56.66	-5.07	1.34	0.90
United Kingdom	Broadford	GL	57.28	-6.01	1.06	0.66
United Kingdom	Little Garv	GL	57.63	-4.70	1.79	0.26
United Kingdom	Little Garv	WL	57.63	-4.69	1.28	0.77
United Kingdom	Ullapool	GL	57.93	-5.19	0.93	0.93
United Kingdom	Ullapool	WL	57.99	-5.11	0.70	0.96
Norway	Birkenes	WL	58.48	8.29	0.74	0.94

Country	Site	Land use	Latitude [°]	Longitude [°]	Sample amount g dw	SOM g SOM
Norway	Ualand	WL	58.56	6.46	0.79	0.97
Norway	Ualand	GL	58.56	6.46	1.23	0.89
Norway	Treungen	GL	59.10	8.63	3.20	0.15
Norway	Treungen	WL	59.10	8.63	0.75	0.97
Norway	Onsøy	GL	59.31	11.00	2.96	0.11
Norway	Onsøy	WL	59.31	11.00	0.77	0.96
Norway	Utbjoa	WL	59.76	5.80	0.99	0.96
Norway	Nordmoen	WL	60.30	11.18	2.51	0.24
Norway	Ulvik	WL	60.67	6.94	1.27	0.72
Norway	Osen	WL	61.25	11.75	0.77	0.97
Norway	Fureneset	peat/GL	61.29	5.04	1.44	0.82
Norway	Hovlandsdal	GL	61.51	5.51	2.46	0.22
Norway	Hovlandsdal	WL	61.51	5.51	2.49	0.34
Norway	Sollia/Enden	WL	61.79	10.30	1.26	0.65
Norway	Sollia/Enden	GL	61.79	10.30	2.83	0.23
Norway	Utvikfjellet	WL	61.80	6.50	0.92	0.98
Norway	Venabu	GL (heath)	61.88	10.35	2.10	0.49
Norway	Venabu	GL	61.88	10.35	1.51	0.64
Norway	Lom	WL	61.91	8.70	2.86	0.22
Norway	Gaulstad	WL	63.95	12.13	0.86	0.95
Norway	Gaulstad	GL	64.01	12.10	2.35	0.21
Norway	Momyra	WL	64.10	10.50	1.00	0.54
Norway	Namsvatn	WL	65.04	13.64	1.29	0.64
Norway	Balvatnet	GL	67.13	16.02	2.26	0.17
Norway	Balvatnet	WL	67.13	16.02	1.23	0.57
Norway	Innhavet	WL	68.11	15.99	0.70	0.96
Norway	Tamokdalen	WL	69.17	19.81	2.56	0.22
Norway	Tamokdalen	GL	69.17	19.81	1.18	0.67
Norway	Grøt fjord	WL	69.85	18.73	1.78	0.52
Norway	Skoganvarre	WL	69.95	25.20	1.06	0.81
Norway	Vestertana	WL	70.47	27.95	1.29	0.90

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Table A2: Instrumental parameters for analysis of the compounds

Compound	Type of instrument	Type of column	Column size	Carrier gas	Temperature interval	Target ion
Endosulfan	GC/HRMS in ECNI mode, (Agilent 6890N GC coupled to VG Autospec)	Fused silica capillary column from J&W Scientific	Ultra 2, 25 m length, 0.2 mm I.D, 0.11 µm film thickness	Helium	Start°C: 70 (2 min.) Interval 1: 170°C/min by 20°C/min (3min.) Interval 2: 230°C/min by 5°C/min (3 min.) Injector temp. (°C): 260	[M] ⁻
PeCB	GC/HRMS in EI mode, (Agilent 6890N GC coupled to Autospec-Ultima)	Fused silica capillary column from J&W Scientific	Ultra 2, 25 m length, 0.11 mm I.D, 0.11 µm film thickness	Helium	Start°C: 45 (2 min.) Interval 1: 200°C/min by 15°C/min (3min.) Interval 2: 300°C/min by 15°C/min (5 min.) Injector temp. (°C): 260	[M] ⁺
SCCPs	GC/HRMS in ECNI mode,(Agilent 6890N GC coupled to VG Autospec)	Fused silica capillary column from Restek	Rxi®-5ms, 15 m length, 0.25 mm I.D, 0.25 µm film thickness	Helium	Start°C: 90 (2 min.) Interval 1: 245°C/min by 20°C/min Interval 2: 300°C/min by 20°C/min (5 min.) Injector temp. (°C): 260	[M-Cl] ⁻

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Table A3: Results for the recovery, i.e. range, average and standard deviation (SD) for soil and blanks samples, respectively (in %).

Internal standard	Soil samples		Blanks	
	Range	Average ±SD	Range	Average ±SD
¹³ C α-endosulfan	10-109	60±25	18-70	52±20
¹³ C β-endosulfan	11-96	53±15	11-65	39±28
¹³ C-endosulfan sulfate	6-73	30±15	13-35	22±8
¹³ C-PeCB	11-107	34±14	9-48	34±15
¹³ C- <i>cis</i> -chlordane (SCCPs)	37-68	53±13	n.a.	n.a.

Table A4: Average \pm standard deviation and ranges for the concentration of Σ endosulfans, pentachlorobenzene (PeCB) and short chain chlorinated paraffins (SCCPs), in addition to blank values. All results are expressed as ng/g dry weight (dw).

Average \pm standard deviation (SD)						
Range (min-max)						
	Σ endosulfans	endosulfan sulfate	α -endosulfan	β -endosulfan	PeCB	SCCPs
All 2008	2 \pm 4	2 \pm 4	0.01 \pm 0.01	0.03 \pm 0.1	0.4 \pm 0.3	14 \pm 45
n = 57/53/58 ¹⁾	<0.01-25	<0.002-24	<0.005-0.06	<0.002-0.7	<0.007-1	<0.8-281
Norway	3 \pm 5	3 \pm 5	0.01 \pm 0.02	0.05 \pm 0.1	0.3 \pm 0.3	12 \pm 50
n= 32/32/32 ¹⁾	0.02-25	0.01-24	<0.005-0.06	<0.002-0.7	<0.007-1	<0.8-281
UK	1 \pm 2	1 \pm 2	0.007 \pm 0.005	0.009 \pm 0.03	0.4 \pm 0.3	16 \pm 38
n= 25/21/26 ¹⁾	<0.01-9	<0.002-9	<0.005-0.02	<0.002-0.1	0.09-1	<0.8-179
GL	0.4 \pm 0.8	0.4 \pm 0.8	0.006 \pm 0.004	0.005 \pm 0.01	0.3 \pm 0.3	18 \pm 58
n= 23/20/24 ¹⁾	<0.01-4	<0.002-4	<0.005-0.02	<0.002-0.06	<0.007-1	<0.8-281
WL	3 \pm 5	3 \pm 5	0.01 \pm 0.02	0.05 \pm 0.1	0.4 \pm 0.3	11 \pm 32
n= 34/33/34 ¹⁾	0.05-25	0.04-24	<0.005-0.06	<0.002-0.7	0.07-1	<0.8-179
Blanks (ng/g d.w)		0.002 \pm 0.0004	0.002 \pm 0.002	0.001 \pm 0.001	0.004 \pm 0.003	0.4 \pm 0.4
n=5		<0.002 ²⁾	<0.005 ²⁾	<0.002 ²⁾	0.007 ²⁾ -0.008	0.8 ²⁾ -1
MDL		0.003	0.01	0.005	0.01	1.6
Canada and UK ³⁾	0.08-0.97	-	-	-	-	-
Tajikistan ⁴⁾	-	0.29-22.88	**nd-1.58	**nd-18.12	-	-
Antarctic ⁵⁾	-	-	-	-	0.38-1.3	-
Estiona ⁶⁾	-	-	-	-	<LOQ*-0.1	-
China ⁷⁾	-	-	-	-	-	0.42-210

¹⁾ Number (n) of sites for which Σ endosulfans, PeCB and SCCPs were analysed, respectively.

²⁾ One or more samples were below MDL ($\frac{1}{2}$ MDL used for statistical treatment) value used for statistical treatment.

* Limit of quantification, ** not detected

³⁾ Wong et al., (2009)

⁴⁾ Zhao et al., (2013)

⁵⁾ Borghini et al., (2005)

⁶⁾ Roots et al., (2010)

⁷⁾ Wang et al., (2013)

Table A5: Individual concentrations for each UK and Norwegian sites, expressed as ng/g dry weight (dw) and ng/g soil organic matter (SOM).

Country	Site	Landuse	Σendosulfans		endosulfan sulfate		α-endosulfan		β-endosulfan		PeCB		SCCPs	
			ng/g dw	ng/g SOM	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM
United Kingdom	Bodwin	WL	4.978	4.345	4.971	4.338	<0.005	<0.004	<0.002	<0.002	0.225	0.196	9.800	8.600
United Kingdom	Bodwin	GL	0.028	0.200	0.021	0.149	<0.005	<0.034	<0.002	<0.017	N.D.*	N.D.*	<0.800	<5.600
United Kingdom	Okehamptons	WL	9.071	7.543	8.938	7.433	<0.005	<0.004	0.128	0.106	0.408	0.340	180.000	150.000
United Kingdom	Okehamptons	GL	0.025	0.377	0.018	0.268	<0.005	<0.072	<0.002	<0.037	N.D.**	N.D.**	N.D.**	N.D.**
United Kingdom	Tiverton	GL	0.010	0.179	0.003	0.056	<0.005	<0.081	<0.002	<0.042	0.092	1.570	<0.800	<14.000
United Kingdom	Tiverton	WL	0.922	5.158	0.908	5.080	<0.005	<0.027	0.009	0.051	0.288	1.610	1.800	9.900
United Kingdom	Abergwesyn	GL	N.D.**	N.D.**	N.D.**	N.D.**	N.D.**	N.D.**	N.D.**	N.D.**	1.313	2.836	<0.800	<1.700
United Kingdom	Abergwesyn	WL	0.123	1.702	0.115	1.602	<0.005	<0.066	<0.002	<0.034	0.147	2.040	<0.800	<11.000
United Kingdom	Corris	WL	0.305	1.820	0.295	1.764	0.007	0.042	<0.002	<0.015	0.280	1.672	<0.800	<4.700
United Kingdom	Betsw-y-coed	WL	0.116	0.443	0.108	0.416	<0.005	<0.018	<0.002	<0.009	N.D.*	N.D.*	46.000	175.000
United Kingdom	Betsw-y-coed	GL	0.020	0.315	0.012	0.199	<0.005	<0.076	<0.002	<0.039	0.103	1.654	6.600	106.000
United Kingdom	Hewelrigg	GL	0.034	0.478	0.026	0.376	<0.005	<0.068	<0.002	<0.035	0.168	2.382	4.200	60.000
United Kingdom	Hawkshead	WL	0.892	2.961	0.880	2.922	0.009	0.031	<0.002	<0.008	0.608	2.019	10.300	34.000
United Kingdom	Hawkshead	GL	0.036	0.281	0.014	0.108	0.019	0.153	<0.002	<0.019	0.772	6.064	4.500	35.000
United Kingdom	Ae, Dumfries	GL	0.052	0.468	0.045	0.403	<0.005	<0.043	<0.002	<0.022	N.D.*	N.D.*	<0.800	<7.000
United Kingdom	Ae, Dumfries	WL	0.111	1.504	0.104	1.406	<0.005	<0.065	<0.002	<0.033	0.180	2.440	<0.800	<10.700
United Kingdom	Clachan	GL	0.339	0.332	0.332	0.325	<0.005	<0.005	<0.002	<0.002	N.D.*	N.D.*	<0.800	<0.770
United Kingdom	Clachan	WL	0.411	1.115	0.409	1.108	N.D.**	N.D.**!	<0.002	<0.007	0.163	0.441	<0.800	<2.100
United Kingdom	Colonsay	GL	<0.009	<0.025	<0.002	<0.005	<0.005	<0.013	<0.002	<0.007	N.D.*	N.D.*	<0.800	<2.200
United Kingdom	Colonsay	WL	0.046	1.014	0.039	0.856	<0.005	<0.104	<0.002	<0.053	0.101	2.216	<0.800	<17.000
United Kingdom	Tyndrum	WL	3.749	4.833	3.699	4.769	0.024	0.031	0.026	0.033	1.182	1.524	25.000	32.000
United Kingdom	Glencoe	GL	0.322	0.482	0.304	0.456	0.015	0.022	<0.002	<0.004	0.377	0.564	4.900	7.300
United Kingdom	Broadford	GL	0.125	0.201	0.118	0.190	<0.005	<0.008	<0.002	<0.004	0.457	0.736	7.400	12.000
United Kingdom	Little Garv	GL	N.D.**	N.D.**	N.D.**	N.D.**	N.D.**	N.D.**	N.D.**	N.D.**	0.207	1.455	81.000	570.000
United Kingdom	Little Garv	WL	0.082	0.136	0.075	0.124	<0.005	<0.008	<0.002	<0.004	0.208	0.346	<0.800	<1.300
United Kingdom	Ullapool	GL	0.332	0.333	0.325	0.326	<0.005	<0.005	<0.002	<0.002	0.295	0.297	16.000	16.000
United Kingdom	Ullapool	WL	2.525	1.847	2.505	1.832	<0.005	<0.003	0.016	0.011	0.415	0.303	7.900	5.800
Norway	Birkenes	WL	10.922	8.567	10.755	8.436	<0.005	<0.004	0.162	0.127	1.359	1.066	8.000	6.200
Norway	Ualand	WL	5.584	4.581	5.346	4.385	0.047	0.039	0.191	0.157	0.229	0.188	4.000	3.300
Norway	Ualand	GL	3.579	4.942	3.518	4.858	<0.005	<0.007	0.056	0.077	0.579	0.800	<0.800	<1.100

Country	Site	Landuse	Σendosulfans		endosulfan sulfate		α-endosulfan		β-endosulfan		PeCB		SCCPs	
			ng/g dw	ng/g SOM	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM
Norway	Treungen	GL	0.077	1.699	0.070	1.540	<0.005	<0.105	<0.002	<0.054	0.076	1.670	<0.800	<17.000
Norway	Treungen	WL	5.065	3.883	4.909	3.763	0.033	0.025	0.123	0.094	0.613	0.470	2.400	1.900
Norway	Onsøy	GL	0.145	3.811	0.138	3.622	<0.005	<0.125	<0.002	<0.064	0.027	0.695	<0.800	<20.600
Norway	Onsøy	WL	24.671	19.661	23.902	19.049	0.063	0.050	0.706	0.562	0.495	0.394	8.000	6.500
Norway	Utbjoa	WL	2.746	2.840	2.713	2.807	<0.005	<0.005	0.028	0.029	0.945	0.978	53.000	55.000
Norway	Nordmoen	WL	0.815	8.480	0.799	8.319	0.005	0.050	0.011	0.111	0.372	3.876	<0.800	<8.200
Norway	Ulvik	WL	1.645	2.920	1.606	2.849	0.015	0.027	0.024	0.043	0.554	0.983	<0.800	<1.400
Norway	Osen	WL	3.723	2.956	3.656	2.903	<0.005	<0.004	0.062	0.049	0.844	0.670	9.900	7.900
Norway	Furunes	peat/GL	0.986	1.737	0.971	1.711	<0.005	<0.008	0.010	0.018	0.256	0.451	4.600	8.000
Norway	Hovelandsdal	GL	0.132	1.463	0.125	1.383	<0.005	<0.053	<0.002	<0.027	0.058	0.641	<0.800	<8.700
Norway	Hovelandsdal	WL	0.363	2.693	0.356	2.640	<0.005	<0.035	<0.002	<0.018	0.238	1.762	<0.800	<5.800
Norway	Sollia/Enden	WL	3.857	7.491	3.813	7.406	<0.005	<0.009	0.039	0.076	0.289	0.562	<0.800	<1.500
Norway	Sollia/Enden	GL	0.076	0.938	0.069	0.850	<0.005	<0.059	<0.002	<0.030	0.051	0.626	<0.800	<9.700
Norway	Utvikfjellet	WL	5.514	5.208	5.376	5.078	0.061	0.058	0.076	0.072	0.332	0.313	2.800	2.700
Norway	Venabu	GL (heat)	0.513	2.183	0.506	2.153	<0.005	<0.020	<0.002	<0.010	0.085	0.361	<0.800	<3.400
Norway	Venabu	GL	1.490	3.513	1.481	3.492	0.007	0.016	<0.002	<0.006	0.140	0.330	<0.800	<1.900
Norway	Lom	WL	0.212	2.725	0.205	2.633	<0.005	<0.061	<0.002	<0.031	0.121	1.557	<0.800	<10.000
Norway	Gaulstad	WL	1.064	0.964	1.057	0.957	<0.005	<0.004	<0.002	<0.002	1.092	0.989	<0.800	<0.700
Norway	Gaulstad	GL	0.016	0.176	0.009	0.096	<0.005	<0.053	<0.002	<0.027	<0.007	<0.079	<0.800	<8.800
Norway	Momyr	WL	0.449	0.836	0.442	0.822	<0.005	<0.009	<0.002	<0.005	0.217	0.403	<0.800	<1.500
Norway	Namsvatn	WL	1.409	2.827	1.402	2.813	<0.005	<0.010	<0.002	<0.005	0.304	0.609	<0.800	<1.600
Norway	Balvatnet	GL	0.128	1.714	0.121	1.618	<0.005	<0.064	<0.002	<0.032	0.052	0.696	<0.800	<10.500
Norway	Balvatnet	WL	0.482	1.043	0.475	1.028	<0.005	<0.010	<0.002	<0.005	0.095	0.205	<0.800	<1.700
Norway	Innhavet	WL	2.758	2.031	2.751	2.026	<0.005	<0.004	<0.002	<0.002	0.399	0.294	<0.800	<0.580
Norway	Tamokdalen	WL	0.099	1.167	0.092	1.083	<0.005	<0.056	<0.002	<0.029	0.067	0.788	<0.800	<9.300
Norway	Tamokdalen	GL	0.335	0.588	0.328	0.576	<0.005	<0.008	<0.002	<0.004	0.378	0.663	280.000	490.000
Norway	Grøt fjord	WL	0.506	1.732	0.498	1.707	<0.005	<0.016	<0.002	<0.008	0.279	0.955	<0.800	<2.700
Norway	Skoganvarre	WL	2.207	2.893	2.180	2.857	0.025	0.032	<0.002	<0.003	0.472	0.619	<0.800	<1.000
Norway	Vestertana	WL	1.254	1.802	1.228	1.764	<0.005	<0.007	0.022	0.031	0.149	0.213	<0.800	<1.100

75 <: refers to ½ MDL (method detection limit) used for statistical summaries. N.D.: not detected (Σendosulfans (n=2), and SCCPs (n=1) due to matrix effects **, PeCB (n=6):5 samples due to low
76 % recovery * and 1 sample due to matrix effects**

Table A6: Results from correlation analysis with statistical significance for latitude, land use parameters and individual compounds for UK soils in 2008. Samples which either (i) failed to meet the QA/QC criteria (low recovery etc.), (ii) were below method detection limit (MDL), or (iii) qualified as outliers were not considered (see text for details)

Variables	Latitude	BD(g/cm ³)	BC	SOM	Σendosulfans	endosulfan sulfate	α-endosulfan	β-endosulfan	PeCB	SCCPs	HCB	Σ ₅ PBDEs	Σ ₃₁ PCBs
BD (g/cm ³)	-0.12	1											
BC	-0.02	-0.56**	1										
SOM	0.13	-0.83***	0.64***	1									
Σendosulfans	0.21	-0.75***	0.47*	0.80***	1								
Endosulfan sulfate	0.23	-0.75***	0.46*	0.79***	1.00***	1							
α-endosulfan	0.24	-0.37	0.25	0.70	0.48	0.41	1						
β-endosulfan	-0.01	-0.28	0.16	0.60	0.92	0.92	0.86	1					
PeCB	-0.17	-0.59**	0.59**	0.71***	0.58**	0.55**	0.22	0.05	1				
SCCPs	-0.19	-0.14	0.13	0.10	0.17	0.18	-0.35	0.14	0.19	1			
HCB	0.22	-0.84***	0.50*	0.80***	0.81***	0.81***	0.75***	0.76***	0.65**	-0.01	1		
Σ ₅ PBDEs	-0.52**	-0.44*	0.30	0.41*	0.39*	0.38	0.46*	0.39*	0.49*	0.27	0.49*	1	
Σ ₃₁ PCBs	0.04	-0.76***	0.50**	0.70***	0.73***	0.73***	0.73***	0.76***	0.63***	0.06	0.87***	0.56**	1

*, p<0.05, **, p<0.01, ***, p<0.001

n=27, except from: Σendosulfans and endosulfan sulfate (n=24), α-endosulfan (n=5), β-endosulfan (n=4), PeCB (n=21), SCCPs (n=14), HCB (n=22), Σ₅PBDE and Σ₃₁PCB (n=26)

All data were log-transformed with exception of latitude and land use.

84 Table A7: Results from correlation analysis with statistical significance for latitude, land use and individual compounds for Norwegian soils in 2008.
85 Samples which either (i) failed to meet the QA/QC criteria (low recovery etc.), (ii) were below method detection limit (MDL), or (iii) qualified as
86 outliers were not considered (see text for details)

Variables	Latitude	BD (g/cm ³)	BC	SOM	Σendosulfans	Endosulfan sulfate	α-endosulfan	β-endosulfan	PeCB	SCCPs	HCB	Σ ₅ PBDEs	Σ ₃₁ PCBs
Latitude	1												
BD (g/cm ³)	0.13	1											
BC	0.08	-0.56***	1										
SOM	0,01	-0.78***	0.71***	1									
Σendosulfans	-0.23	-0.75***	0.55**	0.86***	1								
Endosulfan sulfate	-0.22	-0.75***	0.54**	0.85***	1.00***	1							
α-endosulfan	-0.10	-0.68	0.51	0.85**	0.95***	0.95***	1						
β-endosulfan	-0.41	-0.21	0.20	0.58*	0.94***	0.94***	0.90***	1					
PeCB	-0.09	-0.68***	0.60***	0.80***	0.77***	0.78***	0.31	0.14	1				
SCCPs	-0.09	-0.52	0.12	0.05	-0.17	-0.16	0.62	-0.34	0.65	1			
HCB	-0.08	-0.89***	0.60**	0.88***	0.89***	0.89***	0.78***	0.68***	0.75***	0.03	1		
Σ ₅ PBDEs	-0.55**	-0.60***	0.31	0.57**	0.74***	0.74***	0.80***	0.69***	0.52**	0.25	0.72***	1	
Σ ₃₁ PCBs	-0.26	-0.79***	0.57**	0.73***	0.74***	0.72***	0.89***	0.75***	0.66***	-0.08	0.88***	0.77***	1

87 *:p<0.05, **: p<0.01, ***: p<0.001

88 n=32, except from: Σendosulfans and endosulfan sulfate (n=31), α-endosulfan (n=8), β-endosulfan (n=12), PeCB (n=30), SCCPs (n=8), HCB (n=26), Σ₅PBDE and Σ₃₁PCB (n=30)

89 All data were log-transformed with exception of latitude and land use.

Table A8: Results from correlation analysis with statistical significance for latitude, land use and individual compounds for GL soils in 2008. Samples which either (i) failed to meet the QA/QC criteria (low recovery etc.), (ii) were below method detection limit (MDL), or (iii) qualified as outliers were not considered (see text for details)

Variables	Latitude	BD (g/cm ³)	BC	SOM	Σendosulfans	Endosulfan sulfate	α-endosulfan	β-endosulfan	PeCB	SCCPs	HCB	Σ ₅ PBDEs	Σ ₃₁ PCBs
Latitude	1												
BD (g/cm ³)	0.03	1											
BC	0.001	-0.64***	1										
SOM	0.13	-0.88***	0.79***	1									
Σendosulfans	0.47*	-0.71***	0.44*	0.77***	1								
endosulfan sulfate	0.50*	-0.69***	0.41	0.75***	0.99***	1							
α-endosulfan	-1.00*	0.35	-0.85	-0.50	-0.93	-0.90	1						
β-endosulfan	-	-	-	-	-	-	-	1					
PeCB	-0.31	-0.53*	0.66**	0.71***	0.30	0.23	0.98***	-	1				
SCCPs	0.23	-0.13	0.18	-0.05	0.21	0.25	-	-	-0.19	1			
HCB	0.14	-0.77***	0.52*	0.81***	0.81***	0.79***	-	-	0.67**	-0.24	1		
Σ ₅ PBDEs	-0.37	-0.45*	0.14	0.31	0.27	0.24	0.82***	-	0.52*	0.50*	0.51*	1	
Σ ₃₁ PCBs	-0.09	-0.64**	0.27	0.58**	0.55**	0.53*	-	-	0.65**	0.13	0.82***	0.68***	1

*: p<0.05, **: p<0.01, ***: p<0.001

n=24, except from: Σendosulfans and endosulfan sulfate (n=22), α-endosulfan (n=3), β-endosulfan (n=2), PeCB (n=19), SCCPs (n=8), HCB (n=20), Σ₅PBDE and Σ₃₁PCB (n=22)

All data were log-transformed with exception of latitude and land use).

Table A9: Results from correlation analysis with statistical significance for latitude, land use and individual compounds for WL soils in 2008. Samples which either (i) failed to meet the QA/QC criteria (low recovery etc.), (ii) were below method detection limit (MDL), or (iii) qualified as outliers were not considered (see text for details)

Variables	Latitude	BD (g/cm ³)	BC	SOM	Σendosulfans	endosulfan sulfate	α-endosulfan	β-endosulfan	PeCB	SCCPs	HCB	Σ ₅ PBDEs	Σ ₃₁ PCBs
Latitude	1												
BD (g/cm ³)	-0.15	1											
BC	-0.06	-0.41*	1										
SOM	0,13	-0.75***	0.42*	1									
Σendosulfans	0.04	-0.59***	0.35*	0.77***	1								
endosulfan sulfate	0.04	-0.60***	0.35*	0.77***	1.00***	1							
α-endosulfan	0.33	-0.69*	0.23	0.92***	0.92***	0.92***	1						
β-endosulfan	-0.07	-0.25	0.20	0.63*	0.90***	0.90***	0.86***	1					
PeCB	-0.11	-0.51**	0.41*	0.61***	0.65***	0.65***	0.001	0.01	1				
SCCPs	-0.32	-0.11	0.08	0.18	-0.10	-0.10	-0.48	0.07	0.40	1			
HCB	0.34	-0.80***	0.48*	0.83***	0,70	0.70***	0.72***	0.70***	0.49**	-0.04	1		
Σ ₅ PBDEs	-0.72***	-0.31	0.31	0.37*	0.70***	0.30	0.33	0.35*	0.43*	0.20	0.27	1	
Σ ₃₁ PCBs	-0.00009	-0.68***	0.60***	0.73***	0.64***	0.64***	0.67***	0.77***	0.43*	0.04	0.76***	0.40*	1

*, p<0.05, **, p<0.01, ***, p<0.001

n=34, except from: Σendosulfans and endosulfan sulfate (n=33), α-endosulfan (n=10), β-endosulfan (n=14), PeCB (n=32), SCCPs (n=14), HCB (n=27), Σ₅PBDE and Σ₃₁PCB (n=33)

All data were log-transformed with exception of latitude and land use

2. Text

2.1. Drying and sieving

Wet soil samples from (18-89 gram) (see Table A1), were placed on alumina foil (WrapFilm Systems Ltd, Telford, UK) and weighted prior to drying in an oven (Heraeus, UT 6120) WVR, Hanau (Offenbach, Germany) at approximately 27 °C. In order to obtain completely dry samples, the soil was regularly weighted until stable weight was reached, which were obtained within approximately two weeks. To further assure complete dryness, the soil samples were placed in a desiccator for minimum one hour, and the weighting was repeated. Moreover, for evaluation of possible contamination during the drying process, parallels of diatomaceous earth (DE) was “dried” with the soil samples, and analysed as method blanks. There were no indications of contamination, hence the blank values were low (Table A4 and A2.5). Completely dry soil samples were further sieved (mesh size 2 mm diameter, Retsch GmbH, Haan, Germany). The sieve was cleaned with acetone and *n*-hexane between each sample. Dried, sieved soil samples were stored in brown glass bottle covered with alumina foil and a PP-lid (VWR, Rommen, Norway) in order to protect potential light sensitive compounds, and stored in a fridge until further sample preparation.

2.2. Sample preparation

Solvents used for extraction and clean-up (acetone, *n*-hexane, and *iso*-octane) were of Suprapur grade from SupraSolv, Merck (Darmstadt, Germany). Diethyl ether (glass distilled grade), was obtained from Rathburn (Walkerburn, Scotland). Sulphuric acid and adsorbents used for clean-up and extraction, i.e. Florisil PR (0.15-0.25 mm (60/100 mesh), silica gel (0.063-0.20 mm) and anhydrous sodium sulfate was also obtained from Merck (Darmstadt, Germany). DE was purchased from Dionex, ASE® Prep DE (SunnyVale, CA, USA).

2.2.1. Accelerated solvent extraction (ASE)

Extraction of the soil samples were performed by use of a Dionex Accelerated Solvent Extractor unit (California, USA). The soil samples were placed in a 33 mL cells, and the cells were packed as shown in Figure A2. By use of florisil, the ASE procedure provides clean-up in addition to extraction of the samples. In order to achieve a porous sample for enhancement of the extraction, the soil samples should contain ≥ 25 % of DE, which were mixed with the individual soil samples, generating a soil/25% DE mixture. Furthermore, internal standards (A2.3) were added on top of the soil/25% DE mixture in the cell, before filling the cell with only

DE (Figure A2). The samples were extracted by use of acetone/*n*-hexane: 1/1 (w/w) as a solvent. The samples were extracted with four cycles, 80 % flush volume and with pressure (N_2 gas) and temperature, 1500 Psi and 100 °C, respectively.

2.2.2. Clean-up

The samples were analysed for Σ endosulfans (α -endosulfan, β -endosulfan and endosulfan sulfate), pentachlorobenzene (PeCB) and short-chain chlorinated paraffins (SCCPs), and a comprehensive clean-up procedure were needed. As illustrated in Figure A3, the ASE extracts were divided into two equal aliquots, with solely silica fractionation for compounds degraded by concentrated sulphuric acid (Σ endosulfans), and acid treatment together with silica fractionation for the acid stable fraction (PeCB and SCCPs). For endosulfan analysis (see Figure A3) one aliquot was reduced to 0.5 mL followed by clean-up by fractionation with a silica column. For more information concerning the silica method, see Halse et al., (2011). It was required to have two separate fractions to collect the various Σ endosulfans. The first fraction was eluted with 30 ml *n*-hexane/10 % diethyl ether and was analysed for α -endosulfan, while the second fraction was eluted with additionally 20 mL *n*-hexane/10 % diethyl ether and was analysed for both β -endosulfan and endosulfan sulfate (see A2.4).

For analysis of PeCB and SCCPs, the respective aliquot (Fig. A3) was reduced to 0.5 mL by evaporation. Hereafter, the extract was transferred to a centrifuge tube, adjusted to 2 mL, and treated with 2 mL concentrated sulphuric acid (Halse et al., 2011). After final sulphuric acid treatment, the extracts were reduced to 0.5 mL for further clean-up by fractionation with a silica column (Halse et al., 2011). All final fractions were reduced to approximately 0.5 mL and solvent exchange to *iso*-octane and transferred to a small vial with a screw-cap.

Before analyses, the extracts were reduced to approximately 50 μ L by nitrogen (5.0 Ultra, Yarapraxair, Haugenstua, Norway) and recovery standard (A2.3). Some extracts of the second fraction were exposed to precipitation, hence it was necessary to centrifuge (Jouan CR3, DJB Labcare Ltd, Buckinghamshire, UK) these samples at 1900 revolutions per minute (rpm) for 10 minutes prior to transferring the sample to a new vial.

2.3. Analysis

For quantification and also for monitoring the recovery rates for the sample treatment, all the samples were added a mixture containing 50 μ L of different internal standard prior to

extraction and clean-up. The internal standards consist of ^{13}C - α -endosulfan, ^{13}C - β -endosulfan, ^{13}C -endosulfan sulfate, ^{13}C -pentachlorobenzene and ^{13}C -*cis*-chlordane, to monitor the endosulfans, PeCB and SCCP, respectively. Several ^{13}C -labeled standards were added for parallel analysis of other compounds. However since the method blanks prove that the ^{13}C -labeled compounds did not interfere with the measurements, the completed list is not given here. All standards were purchased from LGC, formerly Promochem AB (Borås, Sweden). In order to quantify the recovery of the internal standards, the extracts were added recovery standards. All extracts were added 20 μL of TCN (1,2,3,4-tetrachloronaphtalene), as recovery standard.

Analysis of the Σ endosulfans was carried out by a high resolution gas chromatography on an Agilent 6890N gas chromatograph coupled to an Autospec operating at accelerated voltage of 6000 Volt in electron capture negative ion (ECNI) mode (80eV) (GC/HRMS(ECNI)). The endosulfan isomers were separated using an Ultra 2 (25 m \times 0.2 mm inner diameter, 0,11 μm film thickness (J&W Scientific)) fused silica capillary column (see Table A2). With helium as a carrier gas (flow rate 0,9 mL/min), the GC operated in splitless mode (Halse et al., 2011). See Table A2 for more detailed information concerning the temperature program. The endosulfan isomers were monitored at mass/charge ratio (m/z) of the molecular ions $[\text{M}]^-$. The m/z ratio for the selected ions were 405.8139/407.8110 (^{12}C α , β -endosulfan), and 385.8322/387.8292 (^{12}C endosulfan sulfate) and 414.8441/416.8412 (^{13}C α , β -endosulfan) and 394.8624/396.8594 for ^{13}C labelled endosulfan sulfate. The sum of the area of the two monitored ions was used in the quantification and the ratio between the two ions was used for verification. The ion ratio between the isotope signals should be within 20 % of the theoretical value.

The PeCB was analysed with an Agilent 6890N gas chromatograph coupled to a high resolution mass spectrometer operating with accelerating voltage of 8000 Volt (Autospec-Ultima) in electron impact (EI) mode (37eV) (GC/HRMS(EI)). The column used was an Ultra 2 (25 m \times 0.11 mm inner diameter, 0,11 μm film thickness (J&W Scientific)) fused silica capillary column. Along with the endosulfans, PeCB was injected to the GC operating in a splitless mode with helium as the carrier gas (1ml/min). See Halse et al., (2011) for more details concerning the operating parameters. The temperature program is given in Table A2. The PeCB component was monitored at m/z of the molecule ion $[\text{M}]^+$. m/z of the selected ions were 249.8491/251.8462 and 255.8693/257.8663 for the ^{12}C PeCB and ^{13}C labelled PeCB,

respectively. As for the endosulfans, the sum of the area of the two monitored ions was used in the quantification and the ratio between the two ions was used for verification.

SCCPs were analysed with an Agilent 6890 gas chromatograph coupled to a VG AutoSpec, high resolution mass spectrometer, operating at 6000 V in ECNI mode (GC/HRMS-ECNI). To achieve necessary separation a Restek Rxi®-5ms (15 m×0.25 mm inner diameter, 0,25 µm film thickness), fused silica capillary column was used with a constant helium flow of 1 mL/min. The injector temperature was 260°C, see Table A2 for more detailed information concerning the operating parameters. The MS operated in ECNI mode (80-120 eV) using methane at a pressure of 2×10^{-5} mbar as moderating gas. The SCCPs were identified by use of the following m/z values (monitoring the $[M-Cl]^-$ ions), 277.0084 ($C_{10}Cl_5$), 291.0241 ($C_{11}Cl_5$), 314.9636 ($C_{10}Cl_6$), 360.9432 ($C_{11}Cl_7$), 374.9588 ($C_{12}Cl_7$), 380.8886 ($C_{10}Cl_8$), 394.9042 ($C_{11}Cl_8$), 408.9199 ($C_{12}Cl_8$), 422.9355 ($C_{13}Cl_8$), 430.8623 ($C_{11}Cl_9$) and 444.8779 ($C_{12}Cl_9$), with 273.9403 (^{13}C -*cis*-chlordane) as the internal standard. The quantification of the SCCPs was performed according to a method described by Tomy and co-workers (1997).

2.4. Method validation of the ASE extraction procedure

In order to evaluate the efficiency of the ASE extraction, e.g. the number of cycles, adequate flush volume by monitoring the recovery rates, four ASE cells were filled with dried background soil (W.L soil, Harestua, Norway) and spiked with internal standard (see section A2.3). The ASE was furthermore programmed to run each individual sample twice, in order to generate two ASE extracts of each sample (E1 and E2). All extracts were cleaned and prepared according to the same procedure as the collected soil samples (section A2.2.2). Furthermore, to evaluate the extraction pattern of the various endosulfans, three clean-up sub fractions of E1 and E2 were executed by adding increasing amount of solvent volume (*n*-hexane/10 % diethyl ether to the column. Hence, the first fraction contained 30 mL of eluent, the second fraction contained 20 mL of eluent, while the last fraction was added a final volume of 20 mL eluent (see Fig. A3). Clean-up of the PeCB and the SCCPs extracts was carried out in accordance to section A2.2.2.

The average percentage recovery and standard deviation (SD) for sum of the individual extracts for the endosulfans of the first ASE extracts (E1) were $46 \pm 5\%$, $70 \pm 8\%$, $80 \pm 7\%$ and for the second extract (E2) $1.5 \pm 0.7\%$, $1.1 \pm 0.6\%$ and $1 \pm 0.4\%$ (E2), for α -, β -endosulfan and endosulfan sulfate, respectively. Results from the recovery test for the individual endosulfans

revealed that the recovery for β -endosulfan and endosulfan sulfate was improved by adding more eluent. Unfortunately, increasing the amount of eluent will also increase the possibility to wash out matrix compounds, and hence require separation of more interfering matrix compounds. It was therefore decided to limit the number of fractions for which the recovery was within an optimum range i.e. 38-52%, 49-70%, 23-38% for α -endosulfan, β -endosulfan and endosulfan sulfate, respectively. Consequently two clean-up fractions (30 mL and 20 mL) was the final solution for the endosulfans.

The average percentage recovery and SD for E1 and E2 for PeCB was $25 \pm 3\%$ and $0.5 \pm 0.3\%$. Samples which were recognized with recovery $< 10\%$, was removed from the data set. A low recovery is attributed to the higher volatility of this compound.

As ^{13}C -labeled 1,5,5,6,6,10-hexachlorodecane was not available when these soil samples were prepared, the recovery for the SCCPs was monitored by use of *cis*-chlordane as an internal standard (Tomy et al., 1997). It should be kept in mind that SCCPs is a complex mixture of chlorinated paraffins and is eluting over a wide range along the capillary column. The uncertainty are caused by several factors e.g. i) impossible to achieve complete peak separation and ii) the internal standard (i.e. *cis*-chlordane) used may not be adequate due to lack of knowledge regarding the individual response factors. The uncertainty in the measurement for the SCCPs may accumulate to $\pm 50\%$ (Sverko et al., 2012). The average percentage of recovery and SD for E1 of ^{13}C *cis*-chlordane was $46 \pm 15\%$, while the average recovery and SD for E2 was $0.6 \pm 0.1\%$.

Results for all soil samples revealed that some results had to be discarded due to matrix related disturbances, i.e. the ion ratio was not satisfying. Hence, results for endosulfan sulfate ($n=2$), α -endosulfan ($n=3$), β -endosulfan ($n=2$) within the Σ endosulfans in addition to PeCBs ($n=1$) and SCCPs ($n=1$) was removed.

Recoveries for all samples, including soil samples (not the method development samples) and blanks are presented in Table A3. For the various endosulfans, the range in the percentage of recovery varied between soil and blank samples. The sometimes low recovery for endosulfan sulfate for some soil sites ($\sim 6\%$), may be caused by reduced amount of eluent added together with matrix related effects disturbing the fractionation potential in the column. However, all three individual ^{12}C endosulfans have been monitored by ^{13}C labelled internal standards.

Consequently, the low recovery does not influence the measured concentrations, but may increase the uncertainty in the measurements. Concerning PeCB, the range of percentage recovery for the soil samples (11-107%) which was somewhat wider compared to the recovery found for the blanks (9-48 %) (Table A3). For PeCB, a few soil samples with recovery <10% (n=5) were removed from the data-set. Recovery for the SCCPs was monitored by use of *cis*-chlordane, and it was assumed that loss of SCCPs reflects loss of *cis*-chlordane. Selected soil samples were quantified for *cis*-chlordane and the average percentage recovery varied between 37-68% (see Table A3).

2.5. Blanks and method detection limit (MDL)

Method blanks (n=5) consisting of DE were “dried”, cleaned-up and analysed following the same preparation and quantification method as used for the soil samples (section A2.1-A2.3). Table A4 provides information regarding the levels found in the blank samples. The concentrations found in the DE samples were all at the same level. The method detection limit (MDL) was calculated as the average concentration found in the blank samples plus three times the SD. When the target compounds were not detected in the blank samples, an instrumental detection limit (IDL) was used (Halse et al., 2011). Furthermore, when the target compounds were not detected in soil samples or fell below the calculated MDL, ½ of the MDL value normalized on the site specific SOM values was used for statistical summaries. See table A5 for the individual sites with concentrations below MDL.

2.6. Determination of soil parameters

The content of soil organic matter (SOM) was determined by loss on ignition (LOI) at 550 °C. 1-10 gram of the individual soil samples were weighed out and placed in a muffle furnace for 4 hours. Further, after being cooled properly, the soil samples were placed in a desiccator and re-weighed after 30 minutes. Percentage LOI was determined using the ratio between the loss and the initial weight of the sample. Other parameters of the soil samples have been characterized in a former study, and information concerning the bulk density and black carbon (BC), together with temperature values was obtained from Schuster and co-authors (2011).

2.7. Partitioning and fate in soil

Following Wong and Wania (2011), we have mapped the equilibrium distribution and mobility potential in soils of selected POPs. Figure 1a) shows the equilibrium phase distribution plot of log K_{OA} vs log K_{AW} (note: as $\log K_{OW} = \log K_{OA} + \log K_{AW}$, log K_{OW} appears as diagonal bands).

Data on physical-chemical properties for selected POPs (PCBs, PBDEs, HCB, individual endosulfans, PeCB and SCCPs) used to create these plots were taken from the literature (European Commission Joint Research centre, 1999; Li et al., 2003; Shen et al., 2005; US EPA, 2011; Wania and Dugani, 2003). Concerning the phase distribution of the SCCPs, two sets of data was used. One was the EU risk assessment approach (EU-RAR) (European Commission Joint Research centre, 1999), which contains of an average set of SCCP properties, shown as RAR in Figure 1., and the other approach includes a wide range of physical-chemical properties going from the $C_{10}Cl_2$ to $C_{13}Cl_{12}$, using data from Gawor et al. (2013). If found in soils, organic contaminants which are located in the upper left region in Figure 1a) will favor the air-filled pores, while substances located in the lower left region will have a preference to be solved in the water phase while chemicals located in the upper right region will have a strong affinity for sorption to organic solids. Figure 1b, presents the mobility potential of selected POPs in soils. In Figure 1b, we have instead plotted $\log K_{OC}$ vs $\log K_{AW}$, (assuming $K_{OC}=0.35 \cdot K_{OW}$ (Seth et al., 1999)). In this plot, components located in the upper left are more prone to vaporization, whereas components located in the lower left region are more prone to leaching, while components in the lower right are most prone to erosion. As demonstrated by Wong and Wania (2011) it is possible to use the equilibrium phase distribution plot to estimate the percentages of chemical which resides in the air- and water-filled pore space as well as the percentage sorbed to organic solids for a given soil with certain characteristics (e.g. SOM content) at a specific temperature and water content (Wong and Wania, 2011). This can also be done for the mobility plot (Fig. 1b), yet requires various mass transfer coefficients to be specified. However, as our study deals with multiple sites and soil conditions, such calculations have not been attempted as we are only interested in how these POPs are positioned relative to each other in order to compare how different POPs are expected to distribute and behave in soils. For a more detailed discussion, we refer to Wong and Wania (2011).

2.8. Statistical analysis

In order to evaluate any linear relationship between two variables, Persons correlation (r) was estimated in Excel. Along with this, an significance value (p) for each correlation was also calculated, based in Student's t-distribution. Various sample groups were tested in order to evaluate if the correlation was significant or not, by testing the null hypothesis. The null hypothesis states that the difference in the mean of the datasets tested, was zero. A two tailed t-test was implemented due to the datasets tested was both higher and lower compared to

each other. If the p-value was lower than 0.05 ($p < 0.05$), the datasets tested was significantly different from each other, and the null-hypothesis could be rejected. Similar, if the p-value was above 0.05 ($p > 0.05$), the dataset tested was not significantly different from each other and the null hypothesis could not be rejected.

2.8.1. Outliers

The z-score was calculated for individual compounds as the ratio between the observed value and the average value, divided by the standard deviation. Four sites were identified with outliers for one or more compounds or compound groups. For Okehampton (WL, UK), the concentration of Σ_5 PBDEs was 1.817 ng/g dw ($z=3.2$). The concentration for PeCB at Birkenes (WL, Norway) was 1.359 ng/g dw ($z=3.02$), and the concentration of SCCPs at Tamokdalen (GL, Norway) was 280 ng/g dw ($z=3.7$). Onsøy (WL, Norway) was identified with outliers for several compounds, i.e. Σ endosulfans, endosulfan sulfate, β -endosulfan, and Σ_{31} PCB was 24.671 ng/g dw ($z=5.9$), 23.902 ($z=5.9$) ng/g dw, 0.706 ng/g dw ($z=3.6$) and 25.130 ng/g dw ($z=4.8$), respectively. Consequently these observations were excluded from the correlation analysis and the figures.

3. Figures

Figure A1 Map showing sampling sites in UK and Norway.(Schuster et al., 2011)

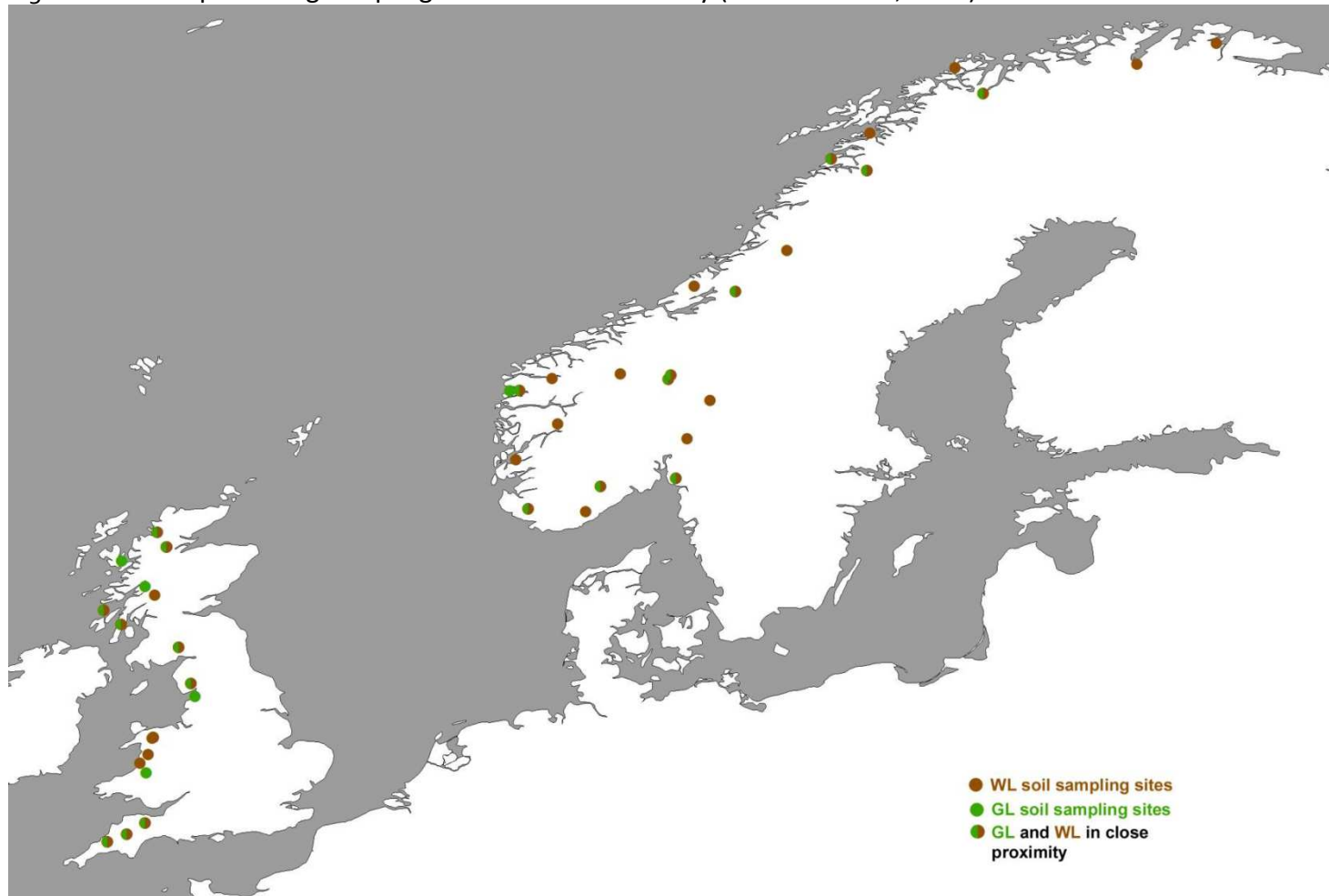


Figure A2 ASE cell with sample and packing material (DE and florisil)

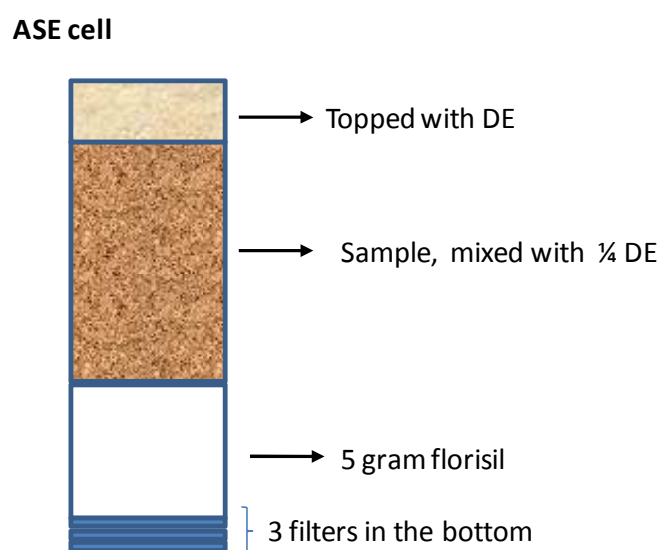
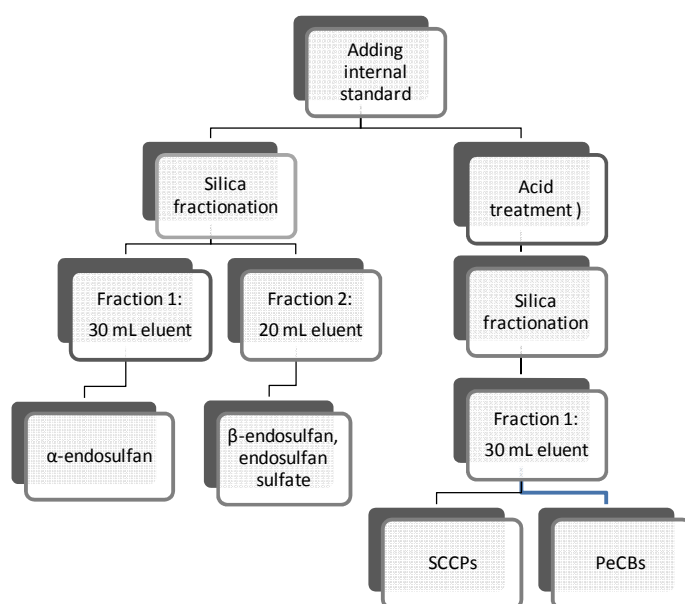


Figure A3 Flowchart for the clean-up and quantification.



4. References

- Borghini, F., Grimalt, J. O., Sanchez-Hernandez, J. C., and Bargagli, R. (2005). Organochlorine pollutants in soils and mosses from Victoria Land (Antarctica). *Chemosphere* **58**, 271-278.
- European Commission Joint Research Centre (1999). "European Union Risk Assessment Report."
- Gawor, A., and Wania, F. (2013). Using quantitative structural property relationships, chemical fate models, and the chemical partitioning space to investigate the potential for long range transport and bioaccumulation of complex halogenated chemical mixtures. *Environmental Science-Processes & Impacts* **15**, 1671-1684.
- Halse, A. K., Schlabach, M., Eckhardt, S., Sweetman, A., Jones, K. C., and Breivik, K. (2011). Spatial variability of POPs in European background air. *Atmospheric Chemistry and Physics* **11**, 1549-1564.
- Li, N. Q., Wania, F., Lei, Y. D., and Daly, G. L. (2003). A comprehensive and critical compilation, evaluation, and selection of physical-chemical property data for selected polychlorinated biphenyls. *Journal of Physical and Chemical Reference Data* **32**, 1545-1590.
- Roots, O., Roose, A., Kull, A., Holoubek, I., Cupr, P., and Klanova, J. (2010). Distribution pattern of PCBs, HCB and PeCB using passive air and soil sampling in Estonia. *Environmental Science and Pollution Research* **17**, 740-749.
- Schuster, J. K., Gioia, R., Moeckel, C., Agarwal, T., Bucheli, T. D., Breivik, K., Steinnes, E., and Jones, K. C. (2011). Has the Burden and Distribution of PCBs and PBDEs Changed in European Background Soils between 1998 and 2008? Implications for Sources and Processes. *Environmental Science & Technology* **45**, 7291-7297.
- Seth, R., Mackay, D., and Muncke, J. (1999). Estimating the organic carbon partition coefficient and its variability for hydrophobic chemicals. *Environmental Science & Technology* **33**, 2390-2394.
- Shen, L., Wania, F., Lei, Y. D., Teixeira, C., Muir, D. C. G., and Bidleman, T. F. (2005). Atmospheric distribution and long-range transport behavior of organochlorine pesticides in north America. *Environmental Science & Technology* **39**, 409-420.
- Sverko, E., Tomy, G. T., Marvin, C. H., and Muir, D. C. G. (2012). Improving the Quality of Environmental Measurements on Short Chain Chlorinated Paraffins to Support Global Regulatory Efforts. *Environmental Science & Technology* **46**, 4697-4698.
- Tomy, G. T., Stern, G. A., Muir, D. C. G., Fisk, A. T., Cymbalisty, C. D., and Westmore, J. B. (1997). Quantifying C-10-C-13 polychloroalkanes in environmental samples by high-resolution gas chromatography electron capture negative ion high resolution mass spectrometry. *Analytical Chemistry* **69**, 2762-2771.
- US EPA (2011). Estimation Programs Interface Suite(TM) for Microsoft Windows, v 4.1.
- Wang, X. T., Zhang, Y., Miao, Y., Ma, L. L., Li, Y. C., Chang, Y. Y., and Wu, M. H. (2013). Short-chain chlorinated paraffins (SCCPs) in surface soil from a background area in China: occurrence, distribution, and congener profiles. *Environmental Science and Pollution Research* **20**, 4742-4749.
- Wania, F., and Dugani, C. B. (2003). Assessing the long-range transport potential of polybrominated diphenyl ethers: A comparison of four multimedia models. *Environmental Toxicology and Chemistry* **22**, 1252-1261.
- Wong, F., Robson, M., Diamond, M. L., Harrad, S., and Truong, J. (2009). Concentrations and chiral signatures of POPs in soils and sediments: A comparative urban versus rural study in Canada and UK. *Chemosphere* **74**, 404-411.
- Wong, F., and Wania, F. (2011). Visualising the equilibrium distribution and mobility of organic contaminants in soil using the chemical partitioning space. *Journal of Environmental Monitoring* **13**, 1569-1578.
- Zhao, Z., Zeng, H., Wu, J., and Zhang, L. (2013). Organochlorine pesticide (OCP) residues in mountain soils from Tajikistan. *Environmental Science-Processes & Impacts* **15**, 608-616.

