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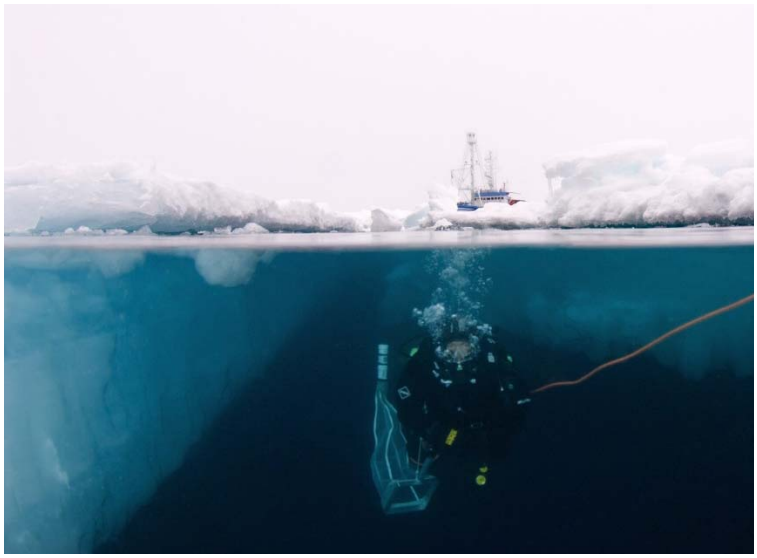
Selective processes for bioaccumulative up-take of persistent organic pollutants (POPs) in Arctic food webs



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Selective processes for bioaccumulative up-take of persistent organic pollutants (POPs) in Arctic food webs

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"The more clearly we can focus our attention on the wonders and realities of the universe about us, the less taste we shall have for destruction" Rachel Carson, 27 May 1907 – 14 April 1964.

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Front page, cover picture paper II: Peter Leopold

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Preface

Jimmy Cliff once sang “You can get it if you really want, but you must try, try and try”. I wonder if he thought about doing a PhD while he wrote the song…

Four years ago, I really looked forward to do this PhD, within the ArcRisk (EU FP7, Grant Agreement no 226534) project. I am very grateful for the funding from ArcRisk and for all the good and fruitful discussions with the involved colleagues. Especially Janet Pawlak, Lars-Otto Reiersen and Simon Wilson from AMAP have been very supporting during these four years. Thank you all!

This thesis would not have been doable without the continuous support from my main supervisors Roland Kallenborn (UMB/UNIS) and Dorte Herzke (NILU). Roland (Store Vennlige Kjempe; SVK) has been a great support whenever there has been a storm during this PhD. He is an endless source of optimism and always manages to make writing and labwork look quick and easy to do!

Dorte have had an almost infinite patience when it comes to explaining the mysteries of analytical chemistry. She is more or less always right about things as well, whether it is chemistry or what I should focus my time and writing on… Thanks to her and the lab at NILU/Tromsø, this thesis was realised in its present form. If it would not have been for NILU, and especially Dorte, Eldbjørg Heimstad, Nick Warner and Mikael Harju, I would not have been able to do any analyses. I always felt very welcome at NILU and have appreciated to be in a working environment where I had very nice chemistry colleagues and -discussions!

The work with chiral pesticides would not have been doable without the never-ending support from Nick. What he cannot explain about chirality and analytical chemistry is probably not worth knowing. I would also like to thank Einar Jensen, my supervisor at University of Tromsø for support, good discussions and ideas.

There are not only supervisors or people at NILU who deserves to be appreciated and mentioned here. Gerard Cornelissen (NGI) made paper I with the passive POM samplers come true. Thank you for your enthusiasm and all the emails!

I stayed at Greenland Institute of Natural Resources in Nuuk for some of my fieldwork. It was really nice with all the cool people there, you made my visits memorable. I have had a couple of expeditions with R/V Lance for sampling and teaching. It was always a pleasure to be onboard!

Ingeborg Hallanger (UiT) is a living dictionary when it comes to zooplankton and statistics. It all makes sense when you explain it!

I would also like to thank Geir Wing Gabrielsen (Norwegian Polar Institute) for your support during those years and the COPOL project, where I got the zooplankton samples from. Thanks to the ARCTOS network, I got to know several interesting people with different backgrounds. Svalbard Environmental Fund supported the “POPjakt i skolen”-project, which was closely related to my PhD work.

I spent quite some time in Tromsø to do this thesis. Without all the super-nice people with sofas, extra rooms and nice houses there (especially Yngve, Elena, Anna, Mikko, Sanja, Philipp, Ingrid and Magnus), I would not have been able to spend as much time at NILU as I did. I make sure I always have a spare room/sofa for you, wherever in the world I’ll be!

During my years at UNIS in Longyearbyen, fellow already-PhDs, PhDs-to-become, colleges and students made life in the office easier and nicer. Thank you Lorna, Malu, Monika x2, Daniel, Eike x2, Karoline, Rico, Archana, Anatoly, Miriam, David, Renat, Kine, Ingjerd, Laura, Silje, Aleksey, Louis, Teena, Emma, Tatyana, Øyunn, Ida Helene, Peter, Kristin, our fantastic librarian Berit and Courtney for correcting the language and grammar. A big thank you to Lucie Strub-Klein. She was always ready with a cup of tea when life and PhD did not go as I wanted and planned. I appreciated my colleagues at Arctic Technology and other nice people at UNIS as well for help, support and coffee/cake-breaks. I would also like to thank two-legged and four-legged friends in Team Qanik and Team Pelstryner for all nice trips! Longyearbyen is a nice place to live, especially if you like skiing, dog-sledging, hiking, diving and being outdoors. Thanks to all trip-partners during the years, fresh air and exercise kept me sane while doing this PhD!

And to my parents and Markus in Sweden, thanks for understanding why I choose to move North! You have always been very supportive, no matter what ideas I have had (almost…). Tack!

For those of you who are in the middle of your PhD:
You can get it if you really want
But you must try, try and try
Try and try, you'll succeed at last
Well, it seems like Jimmy Cliff did sing about the road towards a PhD degree!

Pernilla Carlsson,
Rijpfjorden, Svalbard, August 2013

List of abbreviations and scientific names

AMAP	Arctic Monitoring and Assessment Program
Apherusa glacialis	Arctic amphipod species
ArcRisk	Arctic Health Risks: Impacts on health in the Arctic and Europe owing to climate-induced changes in contaminant cycling
BFR	Brominated flame retardants
CC	*cis*-chlordane
COPOL	Contaminants in Polar Areas
DCPP	2-(2,4-dichlorophenoxy)propionic acid; Dichlorprop
DDD	Dichlorodiphenyldichloroethane
o,p'-DDD	1,1-dichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane
p,p'-DDD	1,1-dichloro-2,2-bis-(4-chlorophenyl)ethane
DDE	Dichlorodiphenyldichloroethylene
o,p'-DDE	1,1-dichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethene
p,p'-DDE	1,1-dichloro-2,2-bis-(4-chlorophenyl)ethene
DDT	Dichlorodiphenyltrichloroethane
o,p'-DDT	1,1,1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane
p,p'-DDT	1,1,1-trichloro-2,2-bis-(4-chlorophenyl)ethane
ECD	Electron capture detector
ECNI	Electron chemical negative ionisation
EF	Enantiomeric fractions
EI	Electron ionisation
EMEP	European Monitoring and Evaluation Programme
ESI	Electrospray ionisation mode
Gadus morhua	Atlantic cod
Gammarus wilkitzkii	Arctic amphipod species
GC	Gas chromatography
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
IS	Internal standard
K_{aw}	Partitioning coefficient air - water
K_{ow}	Partitioning coefficient octanol - water
K_{POM}	Equilibrium partitioning coefficient POM - water [L_{water}/kg_{POM}]
LOD	Limit of detection
LOQ	Limit of quantification
Melanogrammus aeglefinus	Haddock

MRM	Multiple reaction monitoring
MS	Mass spectrometry
OXY	*Oxy*chlordane
Pagophila eburnea	Ivory gull
PAH	Polycyclic aromatic hydrocarbons
PBDE	Polybrominated diphenyl ethers
PBT	Persistence, bioaccumulation and toxicity
PCB	Polychlorinated biphenyls
PCDD/F	Polychlorinated dibenzo-*p*-dioxins and -furans
PFAS	Perfluorinated alkylated substances
PFOS	Perfluorooctane sulfonic acid
PFOS-F	Perfluorooctane sulfonyl fluoride
POM	Polyoxymethylene
POP	Persistent organic pollutants
POPRC	Persistent Organic Pollutants Review Committee
PUF	Polyurethane foam
RSTD	Recovery standard
SRM	Standard reference material
SWIPA	Snow, water, ice and permafrost in the Arctic
TDI	Tolerable daily intake
TC	*trans*-chlordane
TF HTAP	Task Force on Hemispheric Transport of Air Pollution
Themisto libellula	Pelagic amphipod
Thysanoessa inermis	Krill species
UHPLC	Ultra high performance liquid chromatography

List of papers

The present thesis is based upon the following papers, which are referred to by their roman numerals in the text.

I. Carlsson P., Cornelissen G., Bøggild C.E., Rysgaard S., Mortensen J., Kallenborn R. 2012. Hydrology-linked spatial distribution of pesticides in a fjord system in Greenland. J. *Environ. Monit.* 14; 1437-1443. DOI: 10.1039/c2em30068k
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II. Carlsson, P., Warner, N.A., Hallanger, I.G., Herzke, D., Kallenborn, R. 2013. Spatial and temporal investigation of enantiomeric fractions for pesticides in *Calanus* spp. in three Arctic fjords. Submitted.

III. Carlsson, P., Herzke, D., Kallenborn, R. 2013. Enantiomer selective and quantitative trace analysis of selected persistent organic pollutants (POP) in traditional food from western Greenland. Submitted.

IV. Carlsson, P., Herzke, D., Kallenborn, R. 2013. Polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and perfluorinated alkylated substances (PFASs) in traditional sea-food items from western Greenland. Accepted in Environmental Science and Pollution Research.

Summary

The overall aim of the present study was to elucidate selective environmental up-take processes in Arctic food webs that lead to the enrichment of persistent organic pollutants (POP) in food items consumed by Arctic indigenous people. In addition, this study aimed to increase the scientific understanding of the principles behind climate change related influences on transport processes of contaminants. POPs bioaccumulate in the food web to animals at high trophic levels in the Arctic, as well as into humans. Processes concerning contaminant transfer in abiota and at low trophic levels as well as in Arctic local food are therefore of high importance.

This thesis is based on a series of field campaigns and the thereby generated, empirical data. Legacy pesticides were analysed in water samples from a Greenlandic fjord **(paper I)**. Four chiral contaminants were chosen for enantiomer selective analyses; α-hexachlorocyclohexane (α-HCH), *trans*-, *cis*- and *oxy*chlordane in zooplankton from Svalbard and Greenlandic traditional food items **(paper II, III)**. In addition, polychlorinated biphenyls (PCB), polybrominated diphenyl ethers (PBDE) and perfluorinated alkylated substances (PFAS) were also analysed in the food items **(paper IV)**. Svalbard and Nuuk, Greenland were chosen as study areas since these regions are representative for Arctic conditions, such as glaciers, changing periods with sunlight, low temperatures, different marine water masses, known long-range transport of POPs and few local sources for POP contamination. In addition, Greenland has a large population of indigenous people consuming traditional food on a daily basis, enabling the assessment of human exposure in further studies.

The pesticide distribution in meltwater in a Greenlandic fjord (Godthåbsfjord, Nuuk), indicated that glaciers and snow caps within the catchment area of the fjord are secondary sources of contaminants for the coastal marine environment. Chlordanes were identified as potential indicator compounds for meltwater runoff. The more volatile α-HCH and hexachlorobenzene (HCB) were associated with oceanic influence and therefore considered as less potential indicators of secondary sources **(paper I)**. Enantiomer selective analyses of chiral pesticides (α-HCH), *trans*- and *cis*-chlordane) and one metabolite (*oxy*chlordane) were performed to elucidate contaminant exposure for zooplankton from different Svalbard fjords, characterised by different water masses. Among the compounds, *trans*- and *oxy*chlordane were found to be most impacted by biodegradation. The enantiomeric fraction (EF) pattern of α-HCH was associated to ice cover/break-up. *Cis*-chlordane was found to be less degraded compared to *trans*-chlordane, and changes of EF of *cis*-chlordane were reflected in the deviation from racemic EF among *oxy*chlordane. Chiral pesticides and enantiomer selective analyses are recommended for further studies regarding its potential as marker for changes of the physical environment **(paper II)**.

Enantiomer selective analyses of chiral contaminants in Greenlandic traditional food items showed non-racemic EFs for almost all samples and compounds. The fish samples (salmon and halibut) showed a preferred degradation of (+)-α-HCH, while the marine mammals (seal and whale beef and narwhal mattak; blubber and skin) showed a preferred degradation of (-)-α-HCH. *Cis*-chlordane was racemic, and *oxy*chlordane close to racemic in seal meat, while both whale beef and the local delicacy narwhal mattak showed non-racemic EFs for these compounds. Hence, species specific distribution exists, and can be an important factor in future dietary advices, if/when more knowledge about the toxic effects of each enantiomer is present. The food items analysed were below tolerable daily intake (TDI) threshold levels for all compounds analysed, including PCB, PBDE and PFAS **(paper III, IV)**. There are few studies available regarding levels of PBDEs and PFAS in Greenlandic traditional food. The levels in the present study were generally slightly lower or comparable with other (when available) studies from Greenland. Only few congeners of PBDE were detected, and BDE-47 was the dominating, and sometimes the only detected congener. PFAS was detected in the marine mammals, but not in the fish samples. All fishes have been processed by the fish industry (i.e. washed, smoked, packed), which could be the reason for PFAS below limits of detection **(paper IV).**

Introduction

Persistent organic pollutants

Persistent organic pollutants (POP) are substances with physical-chemical properties that make them toxic, persistent enough to undergo long-range transport and bioaccumulate in lipid rich tissues in organisms (Stockholm Convention, 2013). Substances which fulfil the criteria of persistence, bioaccumulation and toxicity (the PBT criteria) are cause for concern and undergo risk assessment to determine whether they are harmful or not (Council of the European Union, 2006; Stockholm Convention, 2013). The definitions (in brief) of these terms, according to the Stockholm Convention, are as follows:

- Persistence: the substance should have a half-life in water >2 months or >6 months in marine sediment.
- Potential for long-range transport: Data from air, water or migratory species in remote areas showing long-range transport, or physical-chemical properties of the substance/results from models that indicate a potential for long-range transport.
- Bioaccumulation: The bioconcentration or bioaccumulation factor should be >5000, i.e. the log of the partitioning coefficient octanol-water (K_{ow}) >5, or if monitoring of species should indicate bioaccumulation.
- Toxicity (adverse effects): Toxicity data or evidence for (potential) impact on human and/or environmental health.

POPs can be transported over long distances from their original sources and have therefore been of concern for both humans and Arctic wildlife due to the impact of POPs on hormone systems and carcinogenic features. The contaminants reach the Arctic after cycles of deposition and revolatilisation from southern latitudes, also known as global fractionation when some semivolatile organic contaminants undergo repeated steps of revolatilisation and condensation before they finally reach the Arctic (grasshopper effect). Contaminants detected in the Arctic are known to undergo long-range transport. The Arctic has therefore been of high interest regarding environmental pollution research and monitoring (Wania and Mackay, 1993; AMAP, 2003; Macdonald et al., 2005; Semeena and Lammel, 2005; AMAP, 2009b, a; Guglielmo et al., 2009; Hung et al., 2010; Stockholm Convention, 2013).

To reduce the environmental impact of POPs, the usage of the legacy POPs such as polychlorinated biphenyls (PCB), chlordanes, hexachlorocyclohexanes (HCH) and hexachlorobenzene (HCB) are prohibited, although some of them are allowed with restricted usage, within the Stockholm Convention. By-products, such as HCB are also regulated within this convention. The usage of

dichlorodiphenyltrichloroethane (*p,p´-/o,p´*-DDT) is prohibited, but allowed in some areas and also indoor to fight insects that cause diseases such as malaria (WHO, 2009). However, DDT and its metabolites are toxic to wildlife, and the most well-known effect is egg shell thinning among birds. It has recently become of concern again regarding the egg shell thickness among birds, e.g. ivory gulls (*Pagophila eburnea*) (Miljeteig et al., 2012).

Newly identified, POPs of emerging concern are constantly being reviewed and monitored by the Stockholm Convention, and tetra-hepta-brominated diphenyl ethers (BDE), perfluorooctane sulfonic acid (PFOS; international regulations with exemptions), α-, β-, and γ-HCH were added to the convention in 2009, while endosulfan (with exemptions) was added in 2011 (Stockholm Convention, 2013). Recommended candidate chemicals are constantly reviewed by the Persistent Organic Pollutants Review Committee (POPRC) to assess whether the substances fulfil the PBT criteria. The process consist of several steps; proposal by some of the Stockholm Convention parties, screening regarding evidence for fulfilment of PBT criteria, risk profile, risk management evaluation and, finally, decision of listing substance into the Stockholm Convention, including possible exemptions.

Structures of the contaminants analysed in this thesis are presented in figure 1a. Compound groups are presented with one of the common congeners/substances as example. The chiral compounds and their structures are showed in figure 1b.

Polychlorinated biphenyls

The first report of PCBs in wildlife was made in 1966 when samples were analysed for DDT and its metabolites (Jensen, 1972). The development of the electron capture detector (ECD) for quantitative gas chromatographic analysis during the late 1950's facilitated the detection of low levels of halogenated/chlorinated compounds, i.e. pesticides and PCBs. PCBs have been used extensively in electrical equipment, in house paint and as heat exchange fluids. The phasing out of PCBs began during the 1970's, when production was banned in some countries, but the usage of PCB was still allowed. Local sources of PCB in Svalbard (e.g. old capacitors, transformers and other electrical equipment) have been removed recently to prevent leakage of PCB into the Arctic environment (Pedersen et al., 2011). PCBs can affect immune and hormone systems, reproduction, behaviour, foetal development and are carcinogenic (AMAP, 2009a, b).

Hexachlorocyclohexanes

The production and usage of γ-HCH (>99% purity =Lindane®) have been phased out, and have been listed in the Stockholm Convention together with the by-products α- and β-HCH since 2009 (Stockholm Convention, 2013). Technical HCH was used extensively during the 1970-80's and

consist mainly of α-HCH (60-70%), γ-HCH (10-15%) and β-HCH (5-12%), but other isomers of HCH are also present (Iwata et al., 1993; Goss et al., 2008). α-HCH is the only chiral isomer of HCH. The levels in the atmosphere have decreased and are today mainly controlled by secondary sources, such as soil and oceans (Wöhrnschimmel et al., 2012a; Wöhrnschimmel et al., 2012b). β-HCH is more persistent and lipophilic than α-HCH and atmospheric levels decrease more slowly, even though α-HCH often evaporates from ocean to the air in the Arctic. All chlorine atoms in β-HCH are equatorial bound to the cyclohexane skeleton. Hence, this chemical expresses high persistency and lipophilic properties in environmental systems. Since α-HCH is more volatile than β-HCH, it is more easily transported to remote areas, e.g. the Arctic (Jantunen and Bidleman, 1996; Wöhrnschimmel et al., 2012a; Wöhrnschimmel et al., 2012b). γ-HCH is considered to be immunotoxic and to cause effects related to reproduction and development. α- and β-HCH are potentially cancerogenic (Stockholm Convention, 2013).

Hexachlorobenzene

HCB has previously been used as a fungicide. Today, HCB is released primarily as a by-product of the (pesticide and chemical) industry. It is a volatile substance and undergoes long-range transport to the Arctic (AMAP, 2003). During the early-mid 2000s, atmospheric levels of HCB seem to decrease in the Arctic, but not at the Zeppelin Mountain station (78^{o}55’ N, 11^{o}56’ E; Ny-Ålesund, Svalbard). This is probably caused by the evaporation of HCB from ice free waters to the atmosphere (Hung et al., 2010; Ma et al., 2011). HCB can affect reproduction in both human and other animals (Stockholm Convention, 2013). HCB may additionally possess dioxin-like properties (e.g. binds to the aryl-hydrocarbon receptor), but there are not sufficient studies where the HCB used was not contaminated with polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/F) and/or dioxin-like PCBs (Pohl et al., 2001; Van den Berg et al., 2006).

Chlordanes

The technical chlordane mixture consists mainly of *trans*- (TC) and *cis*-chlordane (CC), followed by *trans*-nonachlor and heptachlor. Several other chlordane and related compounds are also present (Dearth and Hites, 1991). Chlordane has been used as crop pesticide and as termiticide in houses and foundations, and indoor air has therefore been an important exposure route for humans (Stockholm Convention, 2013). Chlordanes are transported to remote areas and bioaccumulate in the food web, and hence, food is the major exposure route for people outside areas where chlordane have been used indoors (Deutch et al., 2004; AMAP, 2009a). Chlordanes affect the reproduction and immune systems (AMAP, 2009b). *Trans*-, *cis*- and *oxy*chlordane (OXY) and some of the minor components of technical chlordane are chiral.

Polybrominated biphenyl ethers

Polybrominated diphenyl ethers (PBDE) have been used as flame retardants in various materials, such as electric equipment, textiles and plastics. The technical mixtures penta- and octaBDE have been banned since 2004 in the EU and Norway, and the production in USA was voluntarily ceased in 2005. In 2001, the worldwide market of penta- and octaBDE was 7500 and 3790 metric tonnes, respectively (ACAP/AMAP, 2007). The bioaccumulation potential for decaBDE is still under debate, but it has been banned within EU since 2008 (BSEF, 2013). PBDE congeners have lower long-range transport potential than PCB congeners with similar molar mass, most likely due to a higher reactivity with hydroxyl radicals in the atmosphere, which shortens the lifetime of PBDEs in the atmosphere (Wania and Dugani, 2003; BSEF, 2013). PBDEs, and especially hydroxylated PBDEs have been reported to interfere with oestrogen and thyroid receptors (Darnerud et al., 2001; Meerts, 2001; de Wit, 2002).

Perfluorinated alkylated substances

Perfluorinated alkylated substances (PFAS) are a group of surface active compounds, where different perfluorinated sulfonates and carboxylic acids and fluorotelomer alcohols are the most common constituents. Due to their surface active properties, they have been used in e.g. GoreTex®, Teflon®, fire fighting foam and as emulsifiers. The production of PFOS (3500 metric tonnes in 2000) decreased when the major producer (3M) voluntarily ceased their production in 2002. In 2003, 3M produced 175 metric tonnes PFOS, although worldwide production of PFOA increased (Lau et al., 2007). Norway and EU have regulated the amount of PFOS allowed in different materials, such as firefighting foams and textiles (European Union, 2010). PFAS can affect intracellular organelles, the liver, immune and hormone systems (Lau et al., 2007; White et al., 2011). They bind / sorb to large surfaces (i.e. to proteins), while the legacy POPs accumulate and dissolve in lipid rich tissues (Lau et al., 2007; AMAP, 2009b). Among the PFAS, only PFOS, its salts and perfluorooctane sulfonyl fluoride (PFOS-F) are listed within the Stockholm Convention, but exemptions allow usage and production for several purposes (Stockholm Convention, 2013).

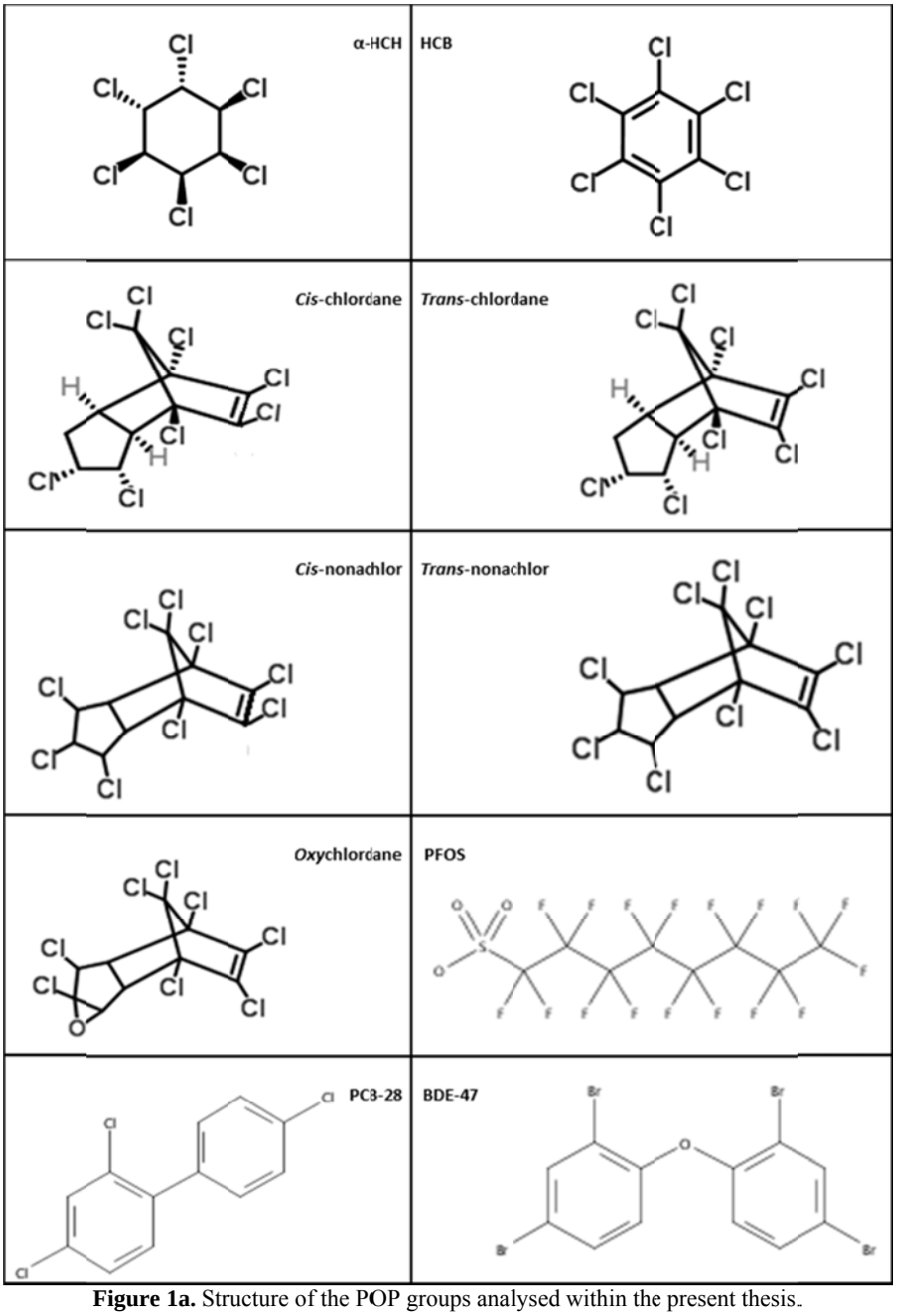

Figure 1a. Structure of the POP groups analysed within the present thesis. Molecule skeletons from www.chemspider.com.

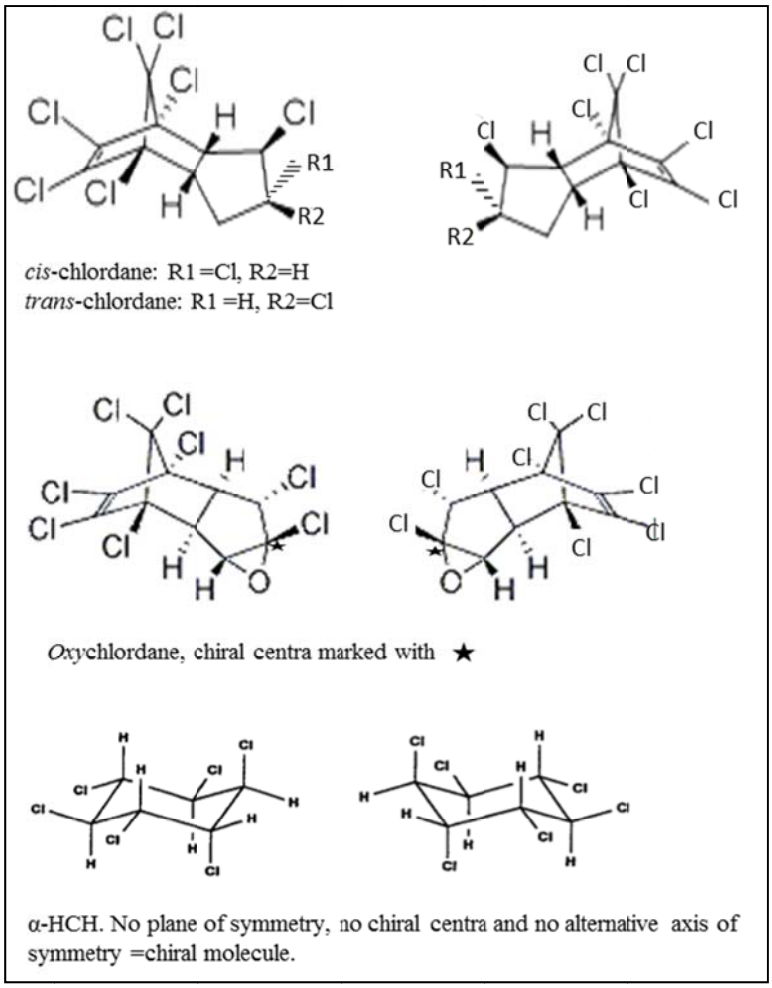

Figure 1b. Stereosymmetry of the chiral pesticides analysed in the present thesis. Molecule skeletons from www.waterresearch.nl.

Chirality

Louis Pasteur was the first to isolate two types of sodium ammonium tartrate crystals (enantiomeric separation) and described in his report that the separate solutions rotated linearly polarised light to the right or to the left (Pasteur, 1848). Some years later, Lord Kelvin named this phenomenon "chirality", which comes from cheir=hand in Greek (Lord Kelvin., 1894; Bentley, 2010).

Chirality is an important tool within chemistry, physics, biology, pharmacy and medicine, where it plays a crucial role in e.g. diagnosis and treatment of diseases. However, while one enantiomer of a substance can have beneficial effects, another enantiomer might cause severe diseases. This was the case for the thalidomide incident during the early 1960's, when children were born with defective and/ or missing limbs due to the teratogenic effect of the S-enantiomer. The S-form was teratogenic, while the R-form exhibited the desired medical sedative effect (Stephens, 2009). However, the R-enantiomer can be converted into the S-enantiomer under the favourable storage conditions (Testa et al., 1993;

Caldwell, 1995). Some pesticides (e.g. mecoprop and dichlorprop) have been manufactured and sold as single enantiomer products, when only one of the enantiomers is active as pesticide. In this case, the costs for agricultural production can be lowered and, thus, less amount of the pesticide is applied compared to racemic mixtures. However, this is only possible if a (cost effective) chiral synthesis or separation form the racemate exists (Williams, 1996).

The enantiomers of a chiral compound differ in their three-dimensional (stereochemical) structures. However, they are characterised by the same physical-chemical properties such as K_{ow}, boiling point, solubility and electronic affinity. A major and simple chiral feature is one or more asymmetric centres in a molecule. However, there are several other types of chirality described in the literature. The asymmetric centre is usually described as a tetraedal carbon atom, which binds to four different atoms or substituents. However, a free electron pair can replace an atom/substituent at a stereogenic centre, e.g. when sulphur is the asymmetric centre. Another form of chirality is axial chirality (atropisomers), where free rotation around a bond is hindered due to their specific substitution patterns on the basic molecular structure (steric hindrance). This is the case for atropisomeric PCBs that lack a plane of symmetry. PCBs with chlorine substituents in minimum two of the *ortho* positions and one in a *meta* position have a steric hindrance for rotation. Hence, these atropisomers are chiral because they are non-planar and lack both an axis of symmetry and a centre of inversion. There are 78 of the 209 PCB congeners that fulfil these requirements, but only 19 of them that are stable atropisomers at room temperature, depending on their rotational energy barriers (Harju and Haglund, 1999). Even if a compound lacks a plane of symmetry, it might have a centre of symmetry and hence, be considered chiral. This is the case for α-truxillic acid. α-HCH is chiral because it does not contain a plane, centre or an alternating axis and hence, fulfils the requirement of absence of an improper axis (Kallenborn and Hühnerfuss, 2001). Enantiomers can have (+)- or (-)- prefix, which indicates which way they rotate plane polarised light. A (+)-enantiomer rotates the plane polarised light to the right (dextrorotatory), while a (-)-enantiomer rotates it to the left (levorotatory). Some chiral compounds are assigned R- and S- for their enantiomers. The R- and S- prefixes indicate the 3D-configuration of the substituents around the chiral centre. When the order of atom numbers at the substituents decreases clockwise, the substance is designated with "R-" as prefix. The "S-" prefix indicates that the decrease is counter clockwise. This rule is part of the Kahn-Ingold-Prelog rules for naming of stereoisomers (Cahn et al., 1966; Prelog and Helmchen, 1982; IUPAC, 1997).

Almost all biological processes and especially processes regarding hormones, amino acids, peptides, protein and lipids are enantiomer selective (McMurry, 2007). As a consequence of this, chirality and enantioselectivity are important features during target specific development of e.g. insecticides and pharmaceutical drugs. Appropriate knowledge regarding differences in toxicity and metabolism of the

enantiomers of a molecule has helped to optimise the manufacturing of chemicals and reduce the environmental impact in modern chemical production processes. One example is 2-(2,4-dichlorophenoxy)propionic acid (dichlorprop; DCPP), where (R)-DCPP is the active herbicide of the DCPP-enantiomers. A selective microbial degradation of the (R)-enantiomer has been reported, which means that the (S)-enantiomer is released and enriched in the nature as a "by-product" (Ludwig et al., 1992a).

Transport of contaminants to the Arctic

POPs reach the marine Arctic environment mainly via long-range atmospheric transport and volatilisation from the ocean (AMAP, 2003; Macdonald et al., 2005; Hung et al., 2010). Other sources can be secondary sources, or local sources, such as previous usage of PCBs and incineration (Pedersen et al., 2011). The impact on the environment of the local sources is, of course, strongly dependant on the location, amount and distance. Secondary sources of POPs in the Arctic can be previous sinks of POPs, e.g. soils, snow and ice caps and sediments, which can become bioavailable again due to climate changes. Regarding PCBs, the transport of PCBs into the Arctic might be more efficient than earlier estimations, and for some PCBs, large sinks can be found in remote areas due to atmospheric transport, biotic transport (e.g. guano from birds (Evenset, 2006; Evenset et al., 2007)), and deposition, followed by storage in soil (Moeckel et al., 2008). The secondary sources have highest impact on levels of penta-hexa-chlorinated PCBs. Those congeners have higher vapour pressure compared to the high-chlorinated PCBs, and longer residence time in air than the low-chlorinated PCBs (Kallenborn et al., 2012a; Lammel and Stemmler, 2012; Stemmler and Lammel, 2012).

The study presented here was an integrated part of the project "*Arctic Health Risks: Impacts on health in the Arctic and Europe owing to climate-induced changes in contaminant cycling*" (ArcRisk). Increased precipitation, reduced ice cover and affected weather systems are effects of a changing climate, causing the transport pathways of contaminants to vary more strongly and contribute to the release of contaminants from old sinks (Macdonald et al., 2005; AMAP, 2011a, b; Kallenborn et al., 2012a; Grannas et al., 2013). There are several river outflows into the Arctic, and the catchment area has been estimated to cover almost entire Russia and large parts of Canada (AMAP, 2003). Increased meltwater runoff, soil erosion and precipitation in these areas could increase the fluvial transport of both legacy and emerging POPs into the Arctic (Kallenborn et al., 2012a). Monitoring of POPs in Arctic air has proven to be a versatile tool to discover changes in concentrations of legacy POPs over time and to discover emerging contaminants and investigate their long-range transport potential. The contaminants that undergo long-range transport in air/water to the Arctic can thereafter be incorporated into the Arctic (marine) food web (AMAP, 2003; Hung et al., 2010; Kallenborn et al., 2012b; Krogseth et al., 2013).

Biotic transport and uptake and of contaminants in the Arctic

Dissolved POPs in the free water masses of the oceans might eventually accumulate in the marine food webs. The first biotic step in this food chain is plankton, which are the link between the delivery of POPs into the water via abiotic (transport) processes (e.g. meltwater, precipitation and soil drainage) and bioaccumulation further up in the pelagic food chain (Borgå et al., 2001; AMAP, 2003, 2009b, 2011a; Hallanger et al., 2011a; Stockholm Convention, 2013). Sinking particles in the oceans can carry contaminants to the bottom sediments, but these contaminants can become bioavailable for scavenging and filtrating organisms, *inter alia* annelids, molluscs, benthic fishes and crustaceans after remediation and disturbance of the sediment in shallow seas (Ilyina et al., 2006; Ilyina et al., 2008; O'Driscoll et al., 2013).

A rising sea temperature will facilitate the migration of fishes from temperate areas into the Arctic. The migration of such species (e.g. Atlantic cod; *Gadus morhua* and haddock; *Melanogrammus aeglefinus*) is considered as a potential transport route for contaminants into the Arctic food web and hence, affect the contaminant levels in local Arctic food (AMAP, 2011b; Kallenborn et al., 2012a; Renaud et al., 2012). Whether species originating from non-Arctic water masses carry more contaminants than Arctic species or have a similar level is not clearly understood yet, neither is the total impact of changes in the food web upon the contaminant exposure for Arctic species (Borgå et al., 2010; Hallanger, 2010; Kallenborn et al., 2012a). A change of zooplankton species (i.e. from Arctic to Atlantic species) might not lead to a different contaminant load within the zooplankton themselves. Nevertheless, the Atlantic species *Calanus finmarchicus* contain less energy compared to its Arctic relative; the *Calanus glacialis*. In order to gain the similar energy resources, the predators would have to rely more on *C. finmarchicus* than *C. glacialis* as food source (Scott et al., 2000).

The effects of remobilisation and remediation of soils and sediments due to a changing climate in the Arctic regarding the POP distribution and bioavailability is not well-known. Especially the knowledge of low trophic levels as the link between abiotic environmental processes and biotic uptake with regards to changing environment and climate is scarce (Kallenborn et al., 2012a). However, there are several studies regarding bioaccumulation of POPs in zooplankton (Borgå et al., 2001; Hallanger, 2010; Hallanger et al., 2011a; Hallanger et al., 2011b; Hallanger et al., 2011c)

Ice caps and contaminants as tracers of physical processes

Two of the key findings within the recently published "Snow, water, ice and permafrost in the Arctic" (SWIPA) report were: 1). "There is evidence that two components of the Arctic cryosphere – snow and sea ice –are interacting with the climate system to accelerate warming", and 2). "The past six

years (2005–2010) have been the warmest period ever recorded in the Arctic. Higher surface air temperatures are driving changes in the cryosphere" (AMAP, 2011b). The anticipated increase of melting ice and snow caps in the Arctic can release pollutants that have, until now, been stored in the snowpack. These contaminants will then be bioavailable again, which could cause a temporarily increase of the old legacy POPs, even though some of them have been banned since the 1970s (Blais et al., 2001a; Blais et al., 2001b; Bogdal et al., 2009a; AMAP, 2011b; Bogdal et al., 2011; Kallenborn et al., 2012a).

There are indications for melting Alpine glaciers as secondary sources of pollutants. However, there are only a few studies and they have often used only one replicate of sediment cores from lakes receiving glacial meltwater (Bogdal et al., 2009a; Bogdal et al., 2009b; Bogdal et al., 2011; Schmid et al., 2011). In addition to the low sample numbers, the reported recovery rates varied too much for drawing extensive conclusions from these available data. Based upon the available data, it is therefore questionable whether this theory could be applied for the Greenlandic ice cap. There are measurements of pesticides in ice caps at Svalbard, but these studies were also based on only one sample per location and far away from the coast (Hermanson et al., 2005; Ruggirello et al., 2010). Therefore, the current scientific information does not allow satisfactory conclusions regarding the impact of POP contamination in the ice caps as secondary sources of POPs to the receiving Arctic Ocean.

A large ice cap, such as the Greenlandic ice cap is considered as an important reservoir of POPs. Therefore the following criteria must be fulfilled:

- ¤ Significant accumulation of snow since the usage of POPs began (i.e. during the 20th century).
- ¤ The ice calving into the oceans has to be a sink of POPs, e.g. received and accumulated POPs via precipitation or from meltwater that contains POPs.

POPs reach Arctic ice caps via long-range atmospheric transport and precipitation (AMAP, 2003; Macdonald et al., 2005; Hung et al., 2010). Even if the snow melts during the summer, the POPs could accumulate in the ice cap, or they could be flushed out in the annual meltwater. There are very few studies regarding POPs and melting ice caps, although there are a few studies reporting PCBs, pesticides, polycyclic aromatic hydrocarbons (PAHs), PBDEs and other brominated flame retardants (BFR) in ice caps from Svalbard (Hermanson et al., 2005; Ruggirello et al., 2010) and northeast Canada (Gregor et al., 1995; Peters et al., 1995). Regarding the second criteria, the calving ice from a large ice cap is the oldest ice and is mostly of preindustrial origin; hence it should not contain POPs. Nevertheless, an increase in meltwater from glaciers could imply an increase in POP delivery to the receiving Arctic ocean if the POPs delivered by long-range transport during the 20th century have precipitated and accumulated on the glacier surface and have thereafter been stored in the old ice, which is now subject for melting. Surface melt of the glacier can penetrate deeper layers of the snow

and firn. The meltwater in the Greenlandic ice cap moves horizontally at altitudes lower than ~1350 m above sea level. Snow present at this altitude and lower is subject for run-off, while the snow melt in the zone between 1500-2000 m is retained within the firn column (Humphrey et al., 2012).

With an increase in meltwater runoff, more contaminants could become bioavailable if the snow and meltwater originates from the industrial period. The Greenlandic ice cap was chosen as a study object in the present project to assess possible routes of transportation and cycling of contaminants in the Arctic. This is the second largest ice cap in the world, is relatively easy accessible compared to other Arctic ice caps, and the remobilisation of contaminants from the Greenlandic ice cap and its surroundings would have an impact on the traditional food for the indigenous people of Greenland (AMAP, 2011b; Grannas et al., 2013).

Use of manmade contaminants as tracers of biological processes

Even though POPs per definition bioaccumulate (K_{ow} >5) and can undergo long-range transport, some are more volatile than others (e.g. α-HCH compared to β-HCH). Hence, substances with a high air-water partitioning coefficient (K_{aw}) will evaporate from the ocean more easily than substances with a low K_{aw}. In the water though, small and slightly lipophilic molecules among the POPs (e.g. HCHs), will partition to the water phase to a higher extent compared to larger and more hydrophobic molecules (Wania and Dugani, 2003). While ratios between different contaminants can be influenced by their different physical-chemical properties such as resistance to photodegradation, volatility, bioaccumulation and metabolism, enantiomeric fractions (EF) are not affected since the (+)- and (-)-enantiomer have the same physical-chemical properties. In other words, a non-racemic EF indicates that enantiomer selective uptake/transformation processes takes place and that those processes most likely are caused by biological factors, e.g. crossing of membranes in animals or other stereoselective (enzymatic) processes or microbial enantiomer selective degradation (Kallenborn et al., 1991; Ludwig et al., 1992b; Möller et al., 1994; Jantunen and Bidleman, 1996; Wöhrnschimmel et al., 2012a; Wöhrnschimmel et al., 2012b).

Changes of contaminants ratios in the environment compared to technical mixtures

Changes of ratios between certain contaminants and/or their metabolites compared to a technical, "fresh" mixture have been used at several occasions to elucidate whether the contaminants come from a new source or if they are "old sins". E.g. the ratio between DDT and its metabolites dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD) and between *trans*- and *cis*-chlordane (TC:CC) found in the environment can be compared to the ratios in their respective technical mixtures. These ratios can provide information regarding the "age" and

weathering status of the mixture, where a decrease of the TC:CC and the DDT:DDE ratio can be used to indicate weathered and old sources of the respective insecticides (Bossi et al., 2008; Becker et al., 2012). *Trans*-chlordane degrades faster than *cis*-chlordane in the atmosphere and hence, TC:CC <1 indicates old sources, while ratios >1 is considered as fresh chlordane (Jantunen et al., 2000). However, the heptachlor mixture also contains *trans*-chlordane, which can add an uncertainty around the TC:CC ratio. Since both *trans*- and *cis*-chlordane are chiral, their EFs are a better indication of primary versus secondary sources. Air from areas where chlordanes have been used contains fresh, racemic (50:50 of each enantiomer) *trans*- and *cis*-chlordane, while air from remote areas often contains non-racemic chlordanes (Jantunen et al., 2000; Bidleman et al., 2012). Non-racemic *trans*- and *cis*-chlordanes in air is often the result of microbial enantiomer selective degradation in soil, which can be considered as a secondary source of chlordanes (Bidleman et al., 2013). An increase of erosion due to less permafrost in Arctic areas could lead to an increased air-soil exchange of contaminants, where a deviation from the racemic EF for chiral pesticides would indicate that they come from a secondary source (Bidleman et al., 2012; Kallenborn et al., 2012a).

An increase of the ratio *o,p'*-DDT : *p,p'*-DDT can indicate that dicofol has replaced technical DDT as primary source, since *o,p'*-DDT is, in general, a larger impurity in dicofol than *p,p'*-DDT (Becker et al., 2012). *p,p'*-DDT is the main DDT compound in technical DDT mixtures, followed by *o,p'*-DDT. The exact composition of the technical mixture varies from manufacturer to manufacturer (WHO, 2009). This, especially in combination with the usage of dicofol and differences in volatility between the DDT compounds can make it difficult to use the DDT:DDE ratio to assess if it is an old or new source (Kurt-Karakus et al., 2006). DDT is degraded in the environment to DDE, although compounds in the dicofol mixture can also degrade to DDE. Hence, the usage of DDT:DDE ratio has its limitations (Becker et al., 2012).

PCBs have been produced in several mixtures and countries, e.g. Arochlor (USA), Canechlor (Japan), Clophen (Germany), Sovol (Russia) and Chlorofen (Poland). Each mixture has its own fingerprint of congeners, but there are several mixtures and variations of these with different degrees of chlorination (Ivanov and Sandell, 1992; Kannan et al., 2005; Takasuga et al., 2006). These fingerprints can be used relatively close to a primary source to assess the source, but since volatility and the potential for biodegradation availability differ between the congeners, the further away from the source (both regarding distance and time of release), the less information regarding the source can be gained from the congener profiles. However, although PCB production is prohibited, PCB in paint (PCB-11) and unintentional production during combustion have recently been reported (Hu et al., 2008; Hu and Hornbuckle, 2009; Rodenburg et al., 2009; Pedersen et al., 2011).

Technical HCH is a mixture of several isomers in different proportions, where α-, β- and γ-HCH are the most common. Changes of these proportions in nature could be a useful indication of new/old sources. Since the HCH in use today is only lindane (γ-HCH), relatively high levels of γ-HCH compared to α-HCH would indicate a fresh source. Due to changes in the formulation of the commercial product, there are some uncertainties in this method to assess new/old sources.

Changes of chiral EF ratios in the environment compared to technical mixtures

Chiral pesticides are, with a few exceptions, produced and applied as racemic mixtures, and the enantiomers have the same physical-chemical properties. However, enantioselective degradation in the environment can change their EF, and enantioselective analyses of e.g.α-HCH, *trans-, cis-* and *oxy*chlordane can be a versatile tool to differentiate between old and new sources of these contaminants. As an additional tool to assess new/weathered sources of DDT, enantiomer selective analyses of the chiral *o,p'*-DDT and *o,p'*-DDD can be performed, although analyses of DDT was outside the scope of this thesis.

Evaporating α-HCH from the sea when the ice cover melts shows a non-racemic ratio and hence, had been subject for biological processes. Meanwhile, α-HCH in air above ice covered ocean shows nearly racemic EF (Jantunen, 2009; Pućko et al., 2010; Wong et al., 2011). EFs for chiral pesticides have recently been used as tracers for the origin of air masses and as a tool to elucidate exchange processes between water and air masses (Genualdi et al., 2009; Jantunen, 2009). They can also be used to differentiate between primary, fresh sources and old and weathered secondary sources (Bidleman et al., 1998; Bidleman and Falconer, 1999). Several factors such as K_{ow}, and exchange rates between air and water could influence ratios between different contaminants, since they have slightly different physical-chemical properties and are compared with each other. Hence, EFs of a chiral contaminant can be more useful compared to ratios between different contaminants to assess different sources (Bidleman and Falconer, 1999).

There are also studies indicating that enantiomeric selective uptake is tissue specific, at least for some species, and that high levels of the chiral pollutants can induce metabolic enantiomer selective processes, which changes the EF (Kallenborn et al., 1991; Hühnerfuss et al., 1993; Möller et al., 1994; Kallenborn and Hühnerfuss, 2001; Hoekstra et al., 2003; Warner and Wong, 2006; Warner et al., 2009; Wong et al., 2011). This needs to be taken into account when EFs are used to differentiate between sources. Organisms at low trophic levels are less susceptible to such processes, and thus, reflect the signature of the surrounding physical environment.

Dietary uptake of persistent organic pollutants for Arctic indigenous people as tracers for physiological processes

The projected temperature increase in the Arctic (due to currently observed climate change) will have effects on ice cover and levels of meltwater runoff. It will also affect POPs and their related transport and biotransformation processes, raising concerns about the possible impact on human health in the Arctic.

There are several recent studies and reviews addressing contaminants in blood, plasma and serum among people living in the Arctic and exposure from Arctic food items for PCBs, pesticides and PFAS (Deutch et al., 2004; Johansen et al., 2004; Deutch et al., 2006; Deutch et al., 2007a; Deutch et al., 2007b; Del Gobbo et al., 2008; AMAP, 2009a; Dallaire et al., 2009; Chateau-Degat et al., 2010; Donaldson et al., 2010; Polder, 2010; Rylander et al., 2010; Sturm and Ahrens, 2010; Donaldson et al., 2012; Lindh et al., 2012; Long et al., 2012; Rylander et al., 2012; Specht et al., 2012; Hanssen et al., 2013), but little information is available regarding PBDEs (Dallaire et al., 2009). Information about PBDE exposure from Arctic food items is scarce. Most articles discussing PBDE levels in biota have focused on liver or blubber tissues and not muscles, which, in general, is the most common food item (Christensen et al., 2002; Vorkamp et al., 2008; Vorkamp et al., 2011). Nevertheless, some papers present information about PBDE levels in fish muscle (filet) as well (Vives et al., 2004; Kelly et al., 2008). None of the studies mentioned here have considered enantiomer selective processes for the assessment of selective uptake and exposure of target pollutants.

There is a lack of data regarding contaminants of emerging concern. Some data regarding PFAS in Inuits from Greenland have been published (Long et al., 2012). However, that study is based on data from several different years and areas, which could affect comparisons among different settlements. The exposure to contaminants from local food depends on the intake of the food items. There are few studies about this, especially studies over several years and recent food habits. To compare the contaminant exposure for all indigenous people in the Arctic is beyond the scope of this thesis. I have chosen to use Western Greenland as a study area due to the representativeness of the region as well as population structure and density. Greenland is the only Arctic region with one large ice cap as well as indigenous people living along the coastline. Danish authorities have good knowledge about the consumption of traditional and modern food items, enabling uptake assessments for human exposure via the food (Johansen et al., 2004; Deutch et al., 2007a). With regards to Arctic climate change, which affects melting processes and travelling routes such as ice covered fjords, the processes happening in Greenland are of major scientific interest for the estimation of potential impacts on human societies. The people of Greenland also have a relatively close connection and input from Denmark regarding western food items, and especially in the larger settlements (Nuuk), where western

food items are available in the local shops. The choice of diet has changed over the years in Greenland towards a more western diet, and traditional food items are today contributing 25-30% of the total daily energy intake (Deutch et al., 2004; Deutch et al., 2006; Deutch et al., 2007a).

Objectives

The research work described in this thesis has been conducted as a part of the European Union FP7 project ArcRisk (Arctic Health Risks: Impacts on health in the Arctic and Europe owing to climate-induced changes in contaminant cycling), where one of the aims was: "Explore the transfer of pollutants from the abiotic Arctic environment, introduced into the Arctic food webs and transferred to higher trophic level organisms (e.g., fish, marine mammals, reindeer)". The ultimate consumption by indigenous arctic people and the possible role of climate variability and global climate change on these processes has also been considered within the project. This includes bioaccumulation and biomagnification factors of selected 'emerging' contaminant groups in specific food webs and organisms relevant to human diet. The here presented research work was also linked thematically into the International Polar Year project Contaminants in Polar Areas (COPOL, Norway).

The presented study evaluates the altered distribution and bioaccumulation pathways of contaminants in the Arctic. This includes assessments of the exposure risk for Arctic indigenous people in a changing environment. Water and organisms representing low trophic levels (e.g. zooplankton) were chosen to illustrate the transfer from abiotic into biotic environments. Marine mammals and predating fish (Skjoldal, 2004), belonging to the traditional diet of indigenous people where selected as representatives for higher trophic levels. Empiric data from quantitative analyses of selected POP were produced in order to assess processes for uptake of POPs within the marine Arctic food web. For the elucidation of biochemical transformation and selective bioaccumulation, enantiomer selective analytical methods have been applied. Thus, in addition to the quantification of legacy POPs and POPs of emerging concern, four chiral contaminants were chosen for enantiomer selective analyses (α-HCH, *trans-*, *cis-* and *oxy*chlordane). Samples were collected in Svalbard and Greenland.

The primary processes investigated within this PhD work were:

¤ Secondary mobilisation: Glacier and meltwater runoff and transport of POPs into the ocean

¤ Changing oceanographic conditions: Reflections of contaminants in different water masses and associated zooplankton

¤ Enantiomeric selective uptake of pesticides residues in local arctic food: Fate of chiral pesticides in local Arctic human food

¤ Accumulation processes for POPs of emerging concern into human food: Insight in levels and patterns of emerging contaminants in local Arctic food

As working hypothesis, the following questions were initially asked:

¤ Can pesticide distribution patterns be used as an oceanographic tool for characterisation of local hydrology in coastal Arctic water systems?

(paper I)

¤Can Arctic zooplankton be used as indicators for the contaminant signature of the water mass they are representing?

(paper I, II)

¤ Can enantiomer distribution of chiral pesticides in Arctic zooplankton communities be used as a tool to discriminate populations in different water masses?

(paper II)

¤ Can pesticides levels in water and zooplankton be used as sentinels for regional climate changes effects?

(paper I, II)

¤ Can enantiomeric signatures of chiral pesticides in Arctic zooplankton, fishes and mammals be used as tracers for selective uptake and/or transformation processes?

(paper II, III)

¤ Are the current POP levels in Greenlandic traditional food of health related concern via dietary exposure**?**

(paper III, IV)

Methods

Fieldwork and study area

Water samples were collected in Godthåbsfjord, Nuuk, Greenland (figure 2a, 2b) during summer 2010 using passive polyoxymethylene (POM) samplers **(paper I)**. The food items (fresh and smoked salmon, smoked halibut, seal and whale beef and narwhal mattak) were bought at the local market in Nuuk during the same field campaign **(paper III)**. Sympagic amphipods (*Apherusa glacialis, Gammarus wilkitzkii*) were collected by divers during an expedition (Norwegian Polar Institute, Tromsø, Norway) north of Svalbard in 2010. Pelagic zooplankton (mainly *Calanus* spp.) were collected during several expeditions (2007-2011) in fjords around Svalbard **(paper II,** table 1, figure 2a and 3). All Greenland samples were kept frozen (-20°) in Nuuk, Greenland and the Svalbard samples onboard the research vessel and finally shipped to Longyearbyen, Svalbard for further analysis. Examples of sample matrices (water, zooplankton and seal) are shown in figure 4.

Table 1. Overview of zooplankton sample locations and years. All sampling campaigns were in July except for one ice sampling campaign in May 2011. Some concentration levels in the zooplankton have been published earlier, see references in the table.

Sample area	2007	2008	2009	2010	2011
Kongsfjorden	(Hallanger et al., 2011a)	(Hallanger et al., 2011b)	Paper II		Paper II
Liefdefjorden		(Hallanger et al., 2011b)	Paper II		
Rijpfjorden			Paper II		Paper II
Pack ice				Paper II	Paper II

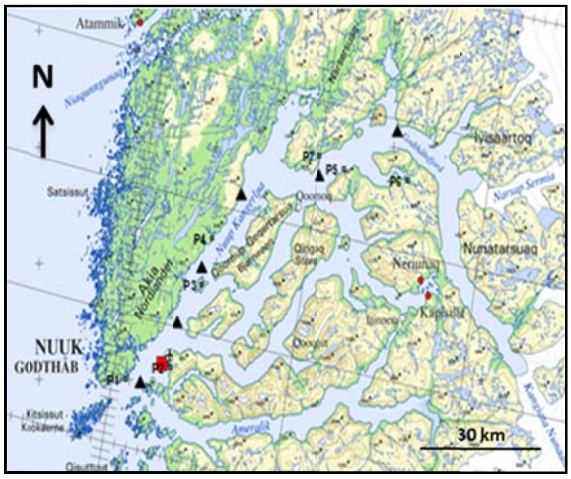

Figure 2a. (left picture): Map with the sample areas (Nuuk, Greenland and Svalbard). Map from Arctic Monitoring and Assessment Program (AMAP).
Figure 2b. (right picture)**:** Map over Godthåbsfjord and POM stations (P). The triangles represent oceanographic stations. Nuuk is situated at 64°11' N, 51°43' W. The distance between Nuuk and P7 is 60 km. Map from Greenland Institute of Natural Resources.

Figure 3. Map from the Norwegian Polar Institute over Svalbard and the fjords where the zooplankton were sampled. The sympagic fauna in 2010 was sampled below the sea ice, northeast of Nordaustlandet at 81°N, 30°E. The ice station from 2011 was situated west of Svalbard, at 80°9'N, 4°19'E and North of Svalbard (80°35'N 13°42'E and 81°3'N, 15°50'E). Map from the Norwegian Polar Institute.

Figure 4. Examples of samples analysed. Seawater, water close to glaciers, zooplankton and seal.

Chemicals and materials

All solvents used were of pesticide grade (Merck, Darmstadt, Germany) except for the methanol used for PFAS analyses (Lichrosolv, Merck, Darmstadt, Germany). All equipment was pre-cleaned with either methanol (POMs) or acetone and *n*-hexane (stainless steel and glass utensils used in field) before sampling. Acetone and/or methanol were used to rinse equipment in field to avoid cross contamination between samples. All glassware exposed to samples was burned at 450 ^{o}C for 6h. The ^{13}C labelled internal standards (IS) used were purchased from Cambridge Isotope Laboratory (CIL), Andover, USA (pesticides and PBDEs), Wellington laboratories, Ontario, Canada (PCB and PFAS). Octachloronaphtalene (OCN; Supelco, Bellefonte, USA) was used as recovery standard (RSTD) for the pesticides, PCB and PBDEs. The 3,7-dimethyl-branched perfluorodecanoic acid (bPFDcA; 97% purity, ABCR Karlsruhe, Germany) was used as RSTD for the PFAS. The (+)-enantiomer of the analysed enantiomeric compounds (α-HCH, *trans-, cis-* and oxychlordane) were purchased from Dr Ehrenstorfer GmbH (Augsburg, Germany). Silica (Merck, Darmstadt, Germany), sodium sulphate (Merck, Darmstadt, Germany) and Florisil (Sigma-Aldrich Steinheim, Germany) were heated at 450 ^{o}C for 8 h prior to usage to avoid contamination. 5 vol-% deionised water (Millipore Billerica, MA, USA) was added for deactivation of the silica. All silica used had the mesh size 70-230. ENVI-Carb for the PFAS analyses was purchased from Sigma-Aldrich (Taufkirchen, Germany). The nitrogen (5.5 quality) used for evaporation came from AGA, Oslo, Norway, the helium (6.0 quality) and methane (5.5) from Hydrogas, Porsgrunn, Norway. Pesticides, PCB and PBDE analyses were conducted with a 30 m DB5-MS column (0.25 mm id and 0.10 µm film thickness; J&W, Folsom, USA). For enantiomer selective analyses, a 15m BGB-172 (chiral separator: 20% *tert*-butyldimethylsilyl-β -cyclodextrin dissolved in 15% phenyl-, 85% methylpolysiloxane) from BGB Analytik AG, Böckten, Switzerland was used. The columns used for separation of PFAS was a Waters Acquity UPLC HSS 3T column (2.1 × 100 mm, 1,8 µm) equipped with a Waters Van guard HSS T3 guard column (2.1 × 5mm, 1.8 µm). A Waters XBridge C_{18} column (2.1 x 50mm, 5 µm) was installed as a precolumn after the pump and before the injector. Quantification standards of the analysed compounds were obtained from Ultra Scientific, Kingstown, USA (PCBs and pesticides), Wellington laboratories, Ontario, Canada (PFAS) and CIL, Andover, USA (PBDEs). Standard reference material (SRM) was obtained for the biological samples (NIST 1945; whale blubber was used for POPs and PFAS ILS 2011, fish tissue A, from the Perfood project, KBBE; grant agreement no. 227525 was used for PFAS).

Analyses of pesticides in water

A passive sampling method was used for water samples in **paper I.** Stripes of polyoxymethylene (POM; -CH_2-O-CH_2-) samplers (55 µm thick) were moored in the tidal zone (0-5 m) at eight different locations in the Godthåbsfjord area during the melting season 2010 (figure 5). They were deployed during four months (June-September) to allow enough time to reach equilibrium with the water. The equilibrium partitioning coefficient POM-water (K_{POM}; L_{water}/kg_{POM}) does not change with temperature (tested for 8-20 ^oC) and have been used for calculations of contaminants in the Baltic Sea at 6-10 ^oC, which are the expected summer temperatures in the surface water of Godthåbsfjord (Cornelissen et al., 2008b). Due to the long exposure time, the POMs were assumed to reach equilibrium in the Godthåbsfjord. Temperature and salinity data for each station was recorded during oceanographic studies and with moored instruments throughout the season.

Figure 5. POM together with floating and marking devices, ready to be deployed for three months in the inner parts of Godthåbsfjord.

Concentration-independent compound-specific equilibrium partitioning constants (K_{POM}) for 55 and 17 µm thick POM, K_{POM-55} and K_{POM-17}, respectively, were established in **paper I** for the following compounds: HCB, *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor and *oxy*chlordane. K_{POM} for the other pesticides of interest were available in the literature (Endo et al., 2011). The POMs were allowed to reach equilibrium (30 days of shaking with saline water containing the pesticides). Thereafter, the POMs were extracted with the same method as the POMs from the field (Cornelissen

and Gustafsson, 2004; Cornelissen et al., 2008a). In brief, IS was added to the samples that were cold-extracted with *n*-hexane and thereafter cleaned-up on silica columns (5% deactivated) with *n*-hexane:dichloromethane (3:1, v/v) as eluent. The volume was reduced to 100 µL under a gentle N_2 stream before analysis.

Analyses of polychlorinated biphenyls, polybrominated diphenyl ethers and pesticides in biota

Local food items were collected at the local market in Nuuk, Greenland. Fresh salmon, smoked salmon and halibut, seal and whale beef and narwhal mattak (skin and blubber) were analysed for pesticides, PCB, PBDE and PFAS **(paper III, IV)**. Pelagic zooplankton (*Calanus* spp. (*C. hyperboreus, C. glacialis, C. finmarchicus*), *Themisto libellula,* and krill (Euphasiids, mostly *Thysanoessa inermis*) samples were analysed for a suite of legacy POPs within the COPOL project. Pesticide levels in zooplankton from 2007 and -08 have been published earlier (Hallanger, 2010; Hallanger et al., 2011a; Hallanger et al., 2011b). All zooplankton samples and food items were analysed for EFs of α-HCH, *trans-*, *cis-*, and *oxy*chlordane **(paper II III).** The sympagic fauna was collected during this project and analysed for levels of PCBs and pesticides using the same method as in Hallanger (2010), before the enantiomeric analyses were conducted. Only the extraction part in the methods differed for zooplankton and other biota (fish and mammals). While the zooplankton were homogenised and extracted with cyclohexane/acetone (3:1 v/v) using ultrasonic and centrifugation, the fish and mammals were homogenised and dried with sodium sulphate (1:20 w/w). The samples were thereafter cold-extracted with cyclohexane/acetone (50:50 v/v). Internal standards were added before the extraction step. After extraction, both zooplankton and fish/mammals were cleaned-up with a gel permeation chromatography (GPC) system and Florisil^{TM} columns. Before analyses, OCN was added to all samples as RSTD. The results were not corrected for recovery. The clean-up procedure for fish and mammals has been described in Herzke et al. (2005). The amount of extractable organic material was determined gravimetrically.

Analyses of perfluoroalkylated substances in biota

The food items in **paper IV** were analysed for PFAS with the following method: One gram of the tissue was spiked with ^{13}C labelled IS and samples were extracted with methanol in ultrasonic bath and concentrated to 1 mL. Thereafter, ENVI-Carb and acetic acid were added to the extract. After additional centrifugation, 0.5 mL of each sample was transferred to vials. Prior to quantification, bPFDcA was added as recovery standard. An aliquot of 100 µL of each sample were transferred to LC-vials and 100 µL of a 2 mM aqueous ammonium acetate solution was added to all samples (Herzke et al., 2009).

Chromatographic separation and quantification

All analyses were performed at the same laboratory (NILU/Tromsø). α-, β-, γ-HCH; *trans*- and *cis*-chlordane, *trans*- and *cis*-nonachlor, *oxy*chlordane and HCB were analysed in **paper I, II and III**. In addition, 26 PCB congeners, 14 PBDE congeners and 16 PFAS compounds were analysed in the Greenlandic food items **(paper IV).** The specific compounds are listed in the appendix (table A1).

Chlorinated and brominated compounds

The temperature program used for PCB, PBDEs and pesticides are shown in table 2. Further details are described in an earlier study (Bustnes et al., 2008). PCBs and PBDEs were analysed by injecting 1 µL with a split/splitless injector, operated in splitless mode at 250 °C (Agilent Technologies, 7683B) into an Agilent 7890A gas chromatograph (GC), that was equipped with a 30 m DB5-MS column (flow rate of the carrier gas helium was 1 mL/min). The GC was connected to a Quattro microTM mass spectrometer (MS) from Micromass MS technologies; Manchester, UK), which was equipped with an electron ionisation (EI) ion source (ionisation energy: 70 eV) and operated in multiple reaction monitoring (MRM) mode. The transfer line temperature was held at 280 °C and the source temperature was set to 220 °C. Pesticides and HCB were analysed by injecting 1 µL with a split/splitless injector at 250 °C (Agilent Technologies) into the GC (Agilent 7890), which was connected to an MS (Agilent 5973 single quadrupole) operated in single ion monitoring (SIM) and electron chemical negative ionisation (ECNI) mode with methane as reagent gas. The transfer line temperature was held at 280 °C and the source temperature was set to 220 °C.

Table 2. GC temperature programs.

Ramp °C/min	T (°C)	isothermal (min)	Ramp °C/min	T (°C)	isothermal (min)
PCB			**Pesticides**		
	70	3		70	3
15	180		15	180	
5	280	6	5	280	5
PBDE			**Enantiomeric analyses**		
	70	3		90	1
25	180		20	160	
6	280	6	1	280	16
5	320	10	20	240	13

Fluorinated compounds

PFASs were analysed by ultrahigh performance liquid chromatography tandem mass-spectrometry (UHPLC-MS/MS). Analysis was performed on a Thermo Scientific quaternary Accela 1250 pump with a PAL Sample Manager coupled to a Thermo Scientific Vantage MS/MS (Vantage TSQ). An injection volume of 10 µL was used for sample separation on the column system mentioned in the section "chemicals and materials". Separation was achieved using 2 mM ammonium acetate (NH_4OAc) in 90:10 methanol/water (A) and 2 mM methanolic NH_4OAc (B) as the mobile phases. The instrument was operated in negative electrospray ionisation mode (ESI-). Details regarding analytical LC and MS conditions, collision energies and S-lens settings are provided in Hanssen et al. (2013). Parent ions and monitored transitions are presented in appendix (table A2).

Enantiomeric analyses of pesticides in biota

Enantiomeric analyses were conducted with the same GC-MS setup as for the pesticide analyses, but with an enantiomer selective column (BGB-172). The temperature program is presented in table 2. All samples were analysed for the enantiomers of α-HCH, *trans*-, *cis*- and *oxy*chlordane and the EF was calculated using the areas of the enantiomers in the chromatograms (equation 1). The average EF $\pm$ 2 standard deviations as confidence interval was considered racemic and was calculated from the quantification standards. The elution order was confirmed by literature (Genualdi et al., 2009) and enantiomeric pure standards. The elution order was: (-)-α-HCH < (+)-α-HCH < (+)-OXY <(-)-OXY < (+)-TC <(+)-CC <(-)-CC < (-)-TC and the separation of the enantiomers are showed in figure 6. The average of the EFs $\pm$2 standard deviations in the standard chromatograms was set as the range for racemic values; α-HCH (0.51 $\pm$0.02), *trans*-chlordane (0.49-0.50 $\pm$0.02), *cis*-chlordane (0.50-0.51 $\pm$0.04) and *oxy*chlordane (0.51 $\pm$0.06). The variation of the average of *trans*- and *cis*-chlordane is due to a slight difference in the average between the zooplankton analyses and the food item analyses. However, the variation is low and within the standard deviation.

$$\mathrm{EF} = \frac{[(+)]}{[(+) + (-)]} \quad \text{Eq. 1.}$$

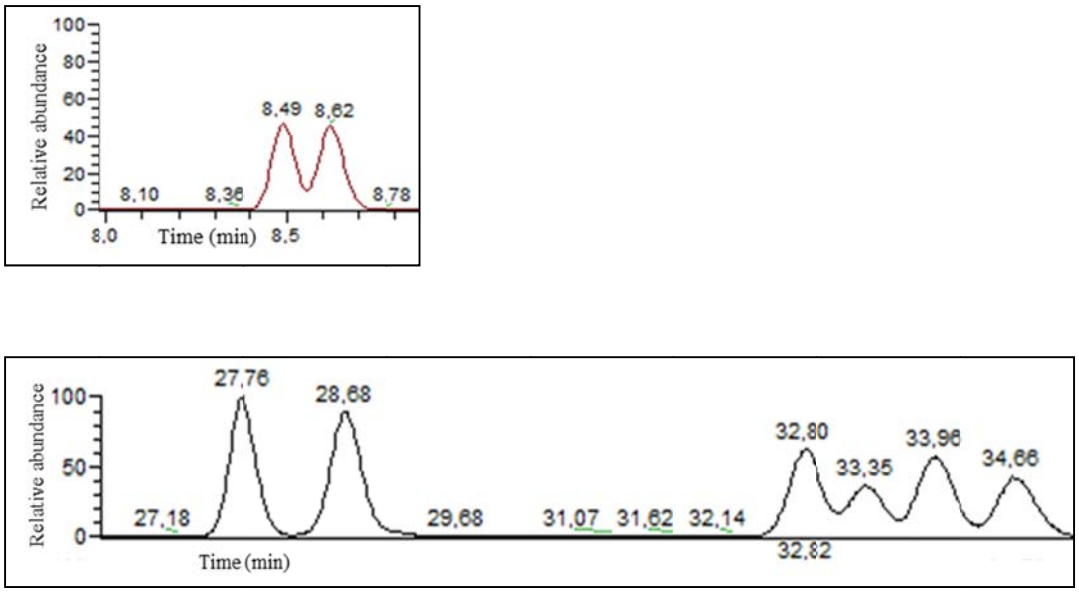

Figure 6. Enantiomeric separation of α-HCH (upper chromatogram). (+)-α-HCH elutes at 8.49 minutes before (-)-α-HCH (8.62 minutes). Lower chromatogram: Enantiomeric separation of (+)-*oxy*chlordane (27.76 min), (-)-*oxy*chlordane (28.08 min), (+)-*trans*-chlordane (32.82 min), (+)-*cis*-chlordane (33.39 min), (-)-*cis*-chlordane (34.01 min) and (-)-*trans*-chlordane (34.72 min). Figure from **paper III.**

Quality control

Blanks and SRMs was analysed for every 10th **(paper II-IV)**. No SRMs were available for the water samples **(paper I).** A field blank (POM material) was analysed within **paper I** to assess any contamination issues in field and during transportation. The limit of detection (LOD) was calculated as 3 times the signal-to-noise ratio for each compound and the limit of quantification (LOQ) was set to 10 times signal-to-noise or 10 times the laboratory blank in case a substance was detected in the blanks.

The enantiomer selective analyses were performed at NILU/Tromsø. MassLynx (version 4.0, Waters, Milford, USA) was used for quantification of PCBs, pesticides, PBDEs and enantiomeric fractions in **paper II-IV,** Xcalibur (version 2.0.7, Thermo Fisher Scientific Inc., Stockholm, Sweden) was used for the quantification of pesticides in **paper I** and LCQuan (version 2.5.6, Thermo Fisher Scientific Inc., Stockholm, Sweden) was used for the quantification of PFAS in **paper III.** One quantification and one qualifier mass were acquired for each POP substance. The ion ratio was set to ±20%.

LODs and recovery information can be found in the respective publications.

Main results

Paper I

The paper summarises a pilot study where passive water samplers made of polyoxymethylene (POM) were applied to sample pesticide residues in a sub-Arctic fjord system (Godthåbsfjord, western Greenland). The major goal was to evaluate pesticides residues as potential tracers for the contribution of different (fresh-) water masses to the fjords hydrology.

The levels of pesticides were low compared to studies from the Canadian Arctic, but comparable with studies from Svalbard. These findings are supported by the ocean current system, which transports ocean water from Svalbard towards the southern tip of Greenland and up along the western coast. α-HCH and HCB dominated the samples and the average concentrations were 11 pg/L and 50 pg/L, respectively. The levels, patterns and concentrations indicate that they were not suitable as markers for fresh water masses since they represent atmospheric long-range transport. On the other hand, the chlordanes analysed in this study (*trans-*, *cis-* and *oxy*chlordane and *trans*-nonachlor) are potential candidates as tracers for different freshwater sources since they were present at localities in the inner parts of the fjord, closer to the freshwater sources. Air samplers were also deployed to assess the atmospheric contribution and long-range transport versus local sources. No local sources were identified.

The present study shows the potential scientific value of linking levels and distribution patterns of selected pesticide with freshwater masses and oceanic water. It was the first study to assess pesticide distribution pattern in a Greenlandic fjord.

Paper II

Paper II describes a study which utilised one of the most comprehensive data sets available today for chiral pesticides in zooplankton samples collected over several years (2007-2011) in Arctic fjords around Svalbard. The fjords investigated were: the Atlantic water influenced Kongsfjorden, the Atlantic and Arctic influenced Liefdefjorden and the Arctic water fjord Rijpfjorden. The winter ice cover varied from almost none (Kongsfjorden) to the ice covered Liefdefjorden (ice break-up in June-July) and Rijpfjorden (ice break-up in late July). Additional sampling was conducted in the pack ice (ice station). The zooplankton samples (*Calanus* spp.*, Themisto libellula, Thysanoessa inermis* (krill), *Apherusa glacialis* and *Gammarus wilkitzkii* were analysed for EFs for α-HCH, *trans*-, *cis*- and *oxy*chlordane. EFs can be used as a tool to investigate whether zooplankton POP contamination patterns reflects biological and/or physical processes in the water masses.

EF varied annually and between locations and species. No degradation trends for certain enantiomers were observed, except for an enrichment of (+)-*oxy*chlordane at all stations (median EF 0.53-0.86). Median EFs for α-HCH varied between 0.38-0.59, *trans*-chlordane varied between 0.29-0.55 and c*is*-chlordane was close to racemic (0.46-0.55). The average EF ± 2 times standard deviations in the standards were: α-HCH: 0.51 $\pm$0.02, *trans*-chlordane: 0.50 $\pm$0.02, *cis*-chlordane: 0.51 $\pm$0.04 and *oxy*chlordane: 0.51 $\pm$0.06. The deviations from racemic EF in the samples were most likely caused by enantiomer selective microbial degradation in the water masses and the variation in ice cover and ice breakup between the fjords. Ice cover hinders evaporation and also affects the start date of the spring phytoplankton bloom. Most of the enantiomer selective degradation of chiral pesticides is likely to happen during the spring phytoplankton bloom when microbial activity has its peak. This is also reflected by the EF pattern in the zooplankton. Due to the time lag between these fjords, the zooplankton were sampled in July, but during different seasons in the respective fjords (i.e. after spring bloom, just after ice breakup and in the middle of the ice breakup). Very little data regarding chiral pesticides in Arctic zooplankton exists. **Paper II** contributes to the knowledge about the EF signals in zooplankton in the marine Arctic food web, as a consequence of changes in their physical environment. Even though the data set is very large, the many factors present (i.e. years, species, locations, contaminants, ice cover, water masses) would have required an even larger data set in order to provide a sufficient statistical basis for a full elucidation of all processes.

Paper III

In this study, we used EFs as a tool to elucidate selective uptake processes of chiral pesticides in traditional human marine food items from Greenland. The food items chosen were raw and smoked fish (salmon and halibut), whale and seal meat and narwhal mattak. The EFs were non-racemic (≠0.5) for all samples except for α-HCH in narwhal, *trans*-chlordane in whale meat and smoked salmon and *cis*- and *oxy*chlordane in seal meat. The EFs for α-HCH were <0.5 for all fish samples, but >0.5 for the mammalian samples. The differences indicate that even among different fish species, the uptake/degradation mechanisms can vary. Some of the differences in EFs could be explained by uptake/degradation at lower trophic levels, but the selective uptake is more likely to happen at higher trophic levels, due to higher amount of complex, chiral molecules and enantioselective processes present in those animals. However, most pesticides were racemic in the seal meat, but that does not exclude selective biotransformation in seals, since the EFs are known to vary between organs.

Three of the target pesticides (*cis-, trans*- and *oxy*chlordane) belong to the chlordane group (cyclodiene pesticides), while the fourth target pesticide was α-HCH. However, there were no similar trends for the chlordanes, which imply that the specific stereochemical structure is an important criterion for the metabolism of the chiral compounds in biota.

Based on earlier food basket studies, we estimated the daily exposure from the present food sources. For the chiral pesticides, this was done for each enantiomer, something that can be important in the future if there will be more information available regarding the relative toxicity of each enantiomer. The levels of pesticides in the samples analysed did not exceed the tolerable daily intake (TDI). Earlier reported intake of these food items were used for calculations of intake levels. However, seal and whale blubber and liver were not analysed. There are more literature data present on contaminant levels in blubber and liver tissue compared to muscle (filet/beef). Literature has shown that even if little amount of those items are consumed, they represent a quite high pollutant load.

We conclude that enantiomeric analyses can provide additional information regarding uptake/degradation processes that cannot be explained by achiral analyses. The combination of chiral analyses and more knowledge regarding the toxicity of each enantiomer could be an important tool for providing more nuanced food advices regarding traditional food.

Paper IV

PCBs, PBDEs, PFAS and achiral pesticides were analysed in the same food items as in **paper III** to present an overview of the contaminant levels and distribution in these food items. The daily intake of the investigated pollutants was below the recommended TDI for human consumption in all cases. ∑PCBs varied from 41 ng/g lw in halibut to 1147 ng/g lw in narwhal mattak. Among the analysed PBDE congeners, BDE-47 was the only congener detected in almost all food items, ranging from <LOD in smoked halibut up to 21 ng/g lw in whale beef.

PFAS were present in the analysed marine mammal samples, but not in the analysed fish items. Mostly long-chained PFAS were detected, and at low levels. PFOS were the dominating PFAS compound, with median concentrations between 1.2-8.0 ng/g ww in the marine mammals. The total PFAS concentration ranged between 2.9 ng/g ww in whale beef to 13.5 ng/g ww in seal beef. On a wet weight basis comparison, ∑PCB contributed to 23% of the total amount of PCB and PFAS in seal beef, compared to 63% in whale beef and 94% in narwhal mattak.

This study showed that the exclusion of blubber and organs, such as liver from the diet have a strong positive effect on the intake of POPs. These food items contribute only to a small part of the total diet. Hence, exclusion/lowered intake of them do not contribute to a large reduction of traditional food in the diet. There are only few recent studies regarding emerging contaminants in Greenlandic human food items and it is therefore difficult and not in the scope of this work to make diet recommendations.

Discussion

Pesticides as tracers for water masses in a sub-Arctic fjord system

The results of **paper I** indicated a trend regarding pesticide distribution pattern within the Godthåbsfjord, with fewer pesticides closer to the mouth compared to the inner parts of the fjord. Two air samplers were deployed to assess the atmospheric contribution and whether it differed between the inner (station P6) and the outer (station P2) part of the fjord (figure 2b). The pesticide composition in the air was rather similar between the stations. HCB was present at both stations while α-HCH was present at low levels in the outer part of the fjord. Hence, it was assumed that the atmospheric contribution and any ocean-air exchange processes of the analysed pesticides to the fjord would be rather similar for the whole fjord. Differences in the composition of pesticides in the water would then be caused by marine geochemical and biological processes representative for the respective water masses.

The Godthåbsfjord receives meltwater from the Greenlandic ice cap and from other, smaller snow caps. **Paper I** indicates that the number of legacy pesticides available in the water mass increases towards the meltwater origin. There are very few studies regarding the actual input of contaminants from ice caps to the ocean, even though there are studies available regarding contaminants stored in Arctic ice caps (Gregor et al., 1995; Peters et al., 1995; Masclet et al., 2000; Hermanson et al., 2005; Ruggirello et al., 2010; Meyer et al., 2011). The samples in those studies often originate from locations far from the location where the ice cap meets the ocean, which makes it difficult to assess the identity and amount of pesticides which are delivered to the ocean from the ice caps. The complexity of transport of POPs within a snowpack makes it difficult to assess how much of the deposited POPs reach the ocean. POPs migrates downwards from the snow surface, but some POPs will also evaporate back to the atmosphere. The transport and movements of POPs become even more complex when meltwater and –channels are taken into consideration (Herbert et al., 2005; Herbert et al., 2006). **Paper I** was among the first studies to investigate pesticides linked to meltwater runoff in a sub-Arctic fjord. The decrease of individual pesticides present in the water towards the mouth of the fjord could be due to biological, physical and geochemical processes, such as adsorption to sinking particles, bioaccumulation in marine biota, degradation and evaporation. The dilution effect of pesticides in a melting snow pack compared to pesticides transported with ocean currents should not be underestimated either. Melting ice caps in the Arctic could increase the amount of available legacy pesticides. Due to their size, large ice caps (e.g. Greenland ice cap) contain larger volumes of contaminants compared to small (e.g. Agassiz ice cap), where the stored amount of pesticides are relatively low (Macdonald et al., 2005). However, the melting snow is younger, and for small glaciers and ice caps, the meltwater runoff can originate from industrial time (Blais et al., 2001a; Schmid et al., 2010). The local impact of contaminants from meltwater runoff needs to be investigated further.

The POM samplers proved to be easy to handle in the field and provide the requested data. They were deployed during four months to allow enough time to reach equilibrium. The disadvantage compared to active water samplers is the time aspect; these passive samplers need to be retrieved four months after deployment and provide an average picture instead of the immediate (daily) situation. Active samplers can be collected after ~hours-day of sampling and they represent a daily situation at the location. Nevertheless, to assess contaminants in the meltwater, it was beneficial to use passive samplers in **paper I,** because they represent the situation in the fjord over time (i.e. covered most of the melting season). Breakthrough problems with HCB have been reported for active samplers equipped with double polyurethane foam (PUF) plugs. Hence, HCB concentrations could then be underestimated (Oehme et al., 1995; Jantunen et al., 2000; Hung et al., 2005; Bossi et al., 2008). Such problems have not been reported for passive POM samplers.

Zooplankton as tracers of contaminants in water masses

A non-racemic EF in a watermass can be caused by microbiological degradation or emissions from secondary sources to the air, followed by deposition into the ocean. Water and air samples from different regions can therefore show different EFs due to differences in the selective uptake/degradation processes at the source origin (Ludwig et al., 1992b; Jantunen and Bidleman, 1996; Bidleman et al., 1998; Covaci et al., 2010). In **paper II**, zooplankton species from different fjords around Svalbard were chosen to elucidate changes of the physical environment. According to earlier studies of enantiomer selective uptake of pesticides in zooplankton and other species at low trophic levels, zooplankton are assumed to reflect the EF of the pesticides in the water mass and not any enantiomeric selective uptake processes. Hence, a non-racemic EF in the zooplankton would indicate enantiomer selective processes in the water mass (e.g. microbial degradation), sediment or in the prey of zooplankton (Bidleman and Falconer, 1999; Moisey et al., 2001; Bidleman et al., 2003; Hoekstra et al., 2003; Borgå and Bidleman, 2005; Warner et al., 2005). There are fewer metabolic processes going on in zooplankton compared to animals occupying higher trophic levels, e.g. whales (Moisey et al., 2001; Hoekstra et al., 2003).

An EF >0.5 of *oxy*chlordane was observed for all zooplankton samples in **paper II**. This quality has earlier been suggested as enantiomeric selective bioformation of (+)-*oxy*chlordane in zooplankton and amphipod species, caused by enantiomer selective degradation of parent chlordane compounds, such as *trans*- and *cis*-chlordane (Hoekstra et al., 2003; Warner and Wong, 2006; Bidleman et al., 2013). Hence, it is difficult to distinguish whether non-racemic EFs of *oxy*chlordane are a result of biodegradation within the zooplankton themselves, or a reflection of enantioselective microbial degradation processes within the water mass. As seen in **paper II**, EFs for *trans*-chlordane vary to a

higher extent than *cis*-chlordane and are considered to biomagnify to a lesser extent compared to *cis*-chlordane (Hoekstra et al., 2003). Based on few samples and assumed non-normality distribution, the data needs to be treated carefully regarding the statistic evaluation. Results from **paper II** showed low EFs for *trans*-chlordane in *Calanus* spp. from the ice station and Kongsfjorden. Both stations were dominated by Atlantic water during the sampling campaign, but Kongsfjorden was ice free. On the other hand, (+)-*trans*-chlordane was degraded in Rijpfjorden during 2011 as well, but to a lesser extent. Rijpfjorden is dominated by Arctic water. Hence, the EF of *trans*-chlordane in zooplankton might not only reflect different water masses, but also, to some extent, biodegradation processes in the water mass and/or in the benthos **(paper II).** EFs of α-HCH is associated with ice cover, which is showed in **paper II** and recent studies that have reported changes of EF of α-HCH in the air above the sea as a result of ice break-up (Jantunen et al., 2008; Wong et al., 2011).

There are only a few active research groups working with enantiomeric pesticides in Arctic biota, and especially regarding processes at lower trophic levels. Hence, few studies of EF of chiral pesticides in zooplankton are available, also from other locations around the world. Even though the data set in **paper II** was the largest (temporally and spatially) dataset available for chiral pesticides in Arctic zooplankton, the complexity of the factors affecting EFs were high. Nevertheless, **paper II** contributes to increased knowledge about the behaviour of chiral pesticides in biota at low trophic levels.

Changes of EFs can be caused by e.g. microbial degradation (Kallenborn and Hühnerfuss, 2001). Microbial activity increases with temperature (Madigan and Martinko, 2006). With decreased permafrost and increased meltwater runoff from/via soil, enantiomer selective analyses will be a powerful tool to assess secondary sources. Potentially increased microbial degradation of pollutants can also be elucidated with enantiomer selective analyses.

Chiral pesticides and biological transformation processes in marine animals

Enantiomer selective analyses of α-HCH, *trans-, cis-* and *oxy*chlordane were performed on a wide range of sample types; zooplankton, fishes, whale and seal meat. As demonstrated in **paper III**, EFs can be used as tracers for enantiomer selective uptake/degradation processes in fish and mammals, while the non-racemic EFs in zooplankton **(paper II)** reflect the surrounding physical environment rather than selective uptake in the zooplankton.{Bidleman, 2012 #325}

As demonstrated in **paper II and III** together with recent research, selective uptake/degradation processes of chiral pesticides vary and there is not always degradation of only one of the enantiomers

(Bidleman et al., 2012). EFs in biota are influenced by diet, the local surrounding environment, metabolism capacity, selective uptake mechanisms such as membrane transports and microbial degradation in the ocean surface and sediments. Enantiomer selective degradation in animals can be facilitated by cytochrome P450 and similar enzymes, which has been demonstrated for chiral PCBs (Warner et al., 2009; Kania-Korwel et al., 2011) and the chiral metabolites of methoxychlor (Hu and Kupfer, 2002).

The high metabolism capacity observed in narwhal mattak **(paper III)** could be cause for concern regarding degradation of other xenobiotics, such as pharmaceuticals. Metabolites and degradation of xenobiotics can lead to more persistent, toxic or more bioavailable compounds. For example, PCBs can undergo hydroxylation in polar bears (Letcher et al., 2009), and BDE-209 can degrade to less brominated PBDEs in fish (Kierkegaard et al., 1999; Stapleton et al., 2004). There is information available about the degradation pathways of PFAS, although they are not yet fully understood (Buck et al., 2011). Pharmaceuticals and their metabolites reach the environment via waste water, where they can be further degraded by microorganisms (Pérez and Barceló, 2007). Biotransformation of chiral pesticides in combination with other examples of degradation in marine mammals show that known metabolites of xenobiotics should be monitored and new/unknown xenobiotics and their metabolites have to be screened in food items, especially in animals feeding at high trophic levels. New techniques, such as metabolomics and proteomics could provide insight into the processes responsible for selective uptake and degradation (Wong, 2006).

Contaminants in Greenlandic traditional Arctic food items and human exposure

The POP levels in the Arctic are currently decreasing, but high levels of POPs and heavy metals in local food, especially in intestines and blubber from animals that occupy high trophic levels in the marine food web still exist (AMAP, 2009a, 2011a). However, the daily intake of local food has decreased. As a positive side effect of this, contaminant exposure has decreased in some areas. An exclusion of the food items with highest levels of POPs, such as intestines and blubber, can reduce the intake of contaminants to tolerable levels, even though the total intake of local food can remain almost the same **(paper III, IV,** Johansen et al., 2004; Deutch et al., 2006). The social, cultural, economic and nutritional benefits of traditional Arctic diets have been emphasised in recent reports and studies during the last years (Van Oostdam et al., 2005; AMAP, 2009a). Nevertheless, marine food items, and especially marine mammals, have been identified as a circumpolar indicator for high levels of legacy POPs, such as pesticides and PCBs in human blood, milk and plasma, and hence, this is reflected in blood and plasma analyses of indigenous Arctic people (Deutch et al., 2004; Van Oostdam et al., 2005; Deutch et al., 2006; Deutch et al., 2007a; Gobas et al., 2009; Chateau-Degat et al., 2010). Environmental processes that are enhanced by warmer temperatures (e.g. increased melting of glaciers

and snow caps) can eventually increase the amount of POPs available in the marine systems and hence, levels in Arctic marine food **(paper I,** Kallenborn et al., 2012a). The size and impact of contaminants from glaciers are not well understood, especially not for the Greenlandic icecap. The amount of contaminants buried in Agassiz icecap has been estimated to be small, although the estimation was based on few data (Macdonald et al., 2005). However, primary production is believed to increase in a warmer Arctic, which can lead to a dilution effect of contaminants in the phytoplankton, and hence, less bioavailable POPs (ACIA, 2005; Borgå et al., 2010). Monitoring of EFs of pesticides in water and through the food chain can indicate whether a decrease of contaminants, caused by microbial degradation and phytoplankton "dilution" would be a more important process than the potential increase of contaminants, released from large snow/ice caps and soil **(paper I, II).** For human health, the decreased in intake of local foods is anticipated to be more significant than effects caused by climate change in humans (Undeman et al., 2010; Armitage et al., 2011; Quinn et al., 2012).

Levels of POPs in local food from Greenlandic compared to the Russian and Canadian Arctic

There are few, if any, studies regarding PBDEs, PFAS and chiral pesticides in food baskets and food items from Greenland. **Paper IV** showed low levels of PBDEs (BDE-47 and -99) and PFAS in traditional Greenlandic food, while **paper III** showed selective uptake/degradation processes of chiral pesticides in almost all food items analysed. Enantiomers can have different toxic effects on organisms, which have been showed for DDT (McBlain, 1987; Hoekstra et al., 2001). However, there is very little research about different toxic potential of the enantiomers among α-HCH, *trans-, cis-* and *oxy*chlordane. When and if such research will be available, **paper III** contributes with more understanding of exposure and fate of the different enantiomers in local Arctic food.

The overall temporal trends in Arctic air are decreasing levels of α- and γ-HCH, ΣDDTs, Σchlordanes and ΣPCBs (Hung et al., 2010; Riget et al., 2010). This is, to some extent reflected in time trends in Arctic biota. ΣPCB has decreased in e.g. seabirds and marine mammals from Canada and northern Norway/Svalbard and α- and γ-HCH has decreased in marine mammals from Canada and Greenland. Chlordanes and HCB have also decreased, but with a less pronounced trend (Riget et al., 2010). This is reflected in Greenlandic food items, where levels of PCBs had decreased in 2004 compared to food items collected in 1976, while levels of chlordanes were similar in samples from those years (Deutch et al., 2006). Levels of legacy POPs in **paper III and IV** were lower, or in line with recent studies from Greenland (Riget et al., 2004; Vorkamp et al., 2004). PBDE and PFAS in the Greenlandic food items were difficult to compare due to few analyses of muscle tissues and the same species from especially Greenland, but also scarce data from other parts of the Arctic. A time trend in seal blubber indicates decreasing levels of PBDEs (Vorkamp et al., 2011). The levels of PBDE in fish and

mammals in **paper IV** are in accordance with this trend, with few congeners detected and generally lower, or similar levels compared to other studies from nearby areas.

PFAS was not detected in the fish samples in **paper IV**, which is in accordance with fish from Faroe Islands (Eriksson et al., 2013) and Arctic char from Nunavut, Canada (Ostertag et al., 2009). Industrially processed (e.g. washing, packing) can be the cause for the non-detected PFAS in fish. The seal meat contained higher levels of PFOS as well as ∑PFAS compared to seal from Nunavut, Canada (PFOS: 0.2 ng/g ww, ∑PFAS: 1.1 ng/g ww; Ostertag et al., 2009). The whale beef and narwhal mattak in **paper IV** also showed levels comparable to Nunavut regarding PFOS (1.5 ng/g ww in beluga blubber), but lower compared to the beluga meat. **Paper IV** and Ostertag et al. (2009) showed similarities in the preferred accumulation of PFAS compounds in whale meat (i.e. PFOS, followed by long-chained PFAS; PFNA, PFUnA, PFDcA), which indicates comparable sources and exposure routes in western Greenland and northeast Canada.

Levels of contaminants in blood from human inhabitants of the Arctic depend to a large extent upon their dietary habits, and high dietary intake of marine mammals is associated with high levels in human blood (AMAP, 2009a; Quinn et al., 2012). In general, people from Scandinavia had lower levels of POPs in their blood compared to people in Arctic communities, where food items such as marine mammals were much more frequently consumed (AMAP, 2009a). This illustrates the importance of monitoring legacy and emerging contaminants in Arctic food items, including their pathways, remediation and degradation processes (**paper I- IV**, Kiviranta et al., 2004; AMAP, 2009a; Chateau-Degat et al., 2010; Rylander et al., 2011b; Törnkvist et al., 2011).

The contribution of traditional food to the energy intake has also decreased during the last decades and are today highest in northern Canada (10-36%), followed by southern Greenland (11-22%) and northwestern Alaska (Van Oostdam et al., 2004; AMAP, 2009a; Sheikh et al., 2012). Nevertheless, some populations are still exceeding the TDI for certain POPs, which is related to a relatively high intake of animal tissues (especially blubber and intestines) at high trophic levels from the marine food web, such as pilot whale in Faroe Islands and polar bears in East Greenland (AMAP, 2009a) . Local food items from the Russian Arctic were found to be contaminated during processing, storing and cooking from indoor sources, mainly by PCBs and DDTs (Dudarev, 2012). The levels of contaminants in the animals before processing were low compared to in other areas of the Arctic, but levels in human plasma and blood were comparable with indigenous people from Greenland and Canada (AMAP, 2009a). People consuming high amounts of marine mammals and fish had higher blood POP levels than inland people (AMAP, 2009a). This is the circumpolar trend, but a reduction of the intake of blubber and intestines from marine mammals can cause a major reduction of the exposure **(paper III, IV).** Recent studies regarding POP in Russian food items showed levels similar to other European

countries in most food items, except for higher levels of PCBs in eggs compared to Scandinavia (Polder, 2010). Fish, together with dairy products and eggs were the main sources of POPs in Russia (Polder, 2010; Polder et al., 2010). All POP levels were lower in the Russian fish samples (Polder et al., 2010), compared to the Greenlandic fish samples in **paper III and IV**.

Ecological and toxicological articles about the bioaccumulation of POPs in Arctic animals often report levels of contaminants in eggs, blubber and liver, but seldom in muscle tissue (Riget et al., 2010). However, contaminants in muscle tissues have been reported in food basket studies and biota surveys around the Arctic (Deutch et al., 2007a; Polder et al., 2010; Dudarev, 2012), but there are some differences in species composition, if species were reported at all. Muscle tissues, i.e. beef and fish filets were chosen in **paper III and IV** since they are more common food compared to blubber and intestines, especially from a circumpolar perspective.

A changed transport pattern of POPs into the Arctic can change sources of exposure for humans in the Arctic. In a warmer climate, POPs will evaporate from secondary sources such as soil, undergo long-range transport and eventually scavenge from the air via increased precipitation (Noyes et al., 2009; Kallenborn et al., 2012a; Grannas et al., 2013). The combination of weathered, long-range transported POPs and the already present secondary sources in the Arctic (e.g. glaciers, snow caps) can increase levels of banned contaminants in the Arctic **(paper I,** Blais et al., 2001a; Grannas et al., 2013). However, monitoring of chiral contaminants in the air and water will be a versatile tool to discover and differentiate between those secondary sources **(paper I, II,** Bidleman et al., 2012). Once the chiral pesticides accumulate in fish and mammals, the changes in EFs are affected by metabolism and internal transport processes to a higher extent compared to the situation at lower trophic levels **(paper II, III,** Hühnerfuss et al., 1992; Möller et al., 1994; Wiberg et al., 2000). Hence, enantiomer selective analyses are more powerful at low trophic levels (e.g. zooplankton; **paper II**) and in abiotic matrices for interpretation of sources origin and for indications of changed source exposure and transport patterns (Bidleman et al., 1998). However, the effect of the release of these sources will eventually affect local Arctic food and the related human health. Even though these contaminants are banned, levels in the Arctic food web and hence, human food items, could increase due to evaporation from secondary sources. This needs to be taken into account in health assessments, in addition to decreased intake of local food (Deutch et al., 2006; Undeman et al., 2010; Armitage et al., 2011; Quinn et al., 2012). POP is one of many factors that impact human health among indigenous people. Economic status, public health, education, social and cultural status also need to be taken into account (Rylander et al., 2011a).

New versus old sources of persistent organic pollutants

The Arctic Ocean has earlier been considered as a sink for α-HCH, but could today be referred to as a secondary source (Jantunen and Bidleman, 1995; Wöhrnschimmel et al., 2012b). Declining concentrations in the atmosphere will enhance degassing from the ocean due to an increase of the fugacity ratio (f_{water}/f_{air}). This will favour partitioning of α-HCH into air over partitioning into water (Ludwig et al., 1992b; Jantunen and Bidleman, 1996). The phenomena is illustrated by changes of EFs for α-HCH in surrounding air during sea ice melting, when non-racemic α-HCH evaporates from the ocean (Jantunen et al., 2008; Jantunen, 2009; Pućko et al., 2010). Ice cover hinders exchange processes. This is in accordance with larger deviation from racemic α-HCH in zooplankton collected from below the ice compared to zooplankton from Kongsfjorden, which is considered as almost ice free during the whole year and is dominated by Atlantic water masses **(paper II)**.

The contribution from local sources (e.g. previous usage of PCBs) can be discovered by comparison of e.g. PCB congener profiles in abiotic samples and stationary animals (Hop et al., 2001; Sagerup et al., 2009; Kristoffersen et al., 2012). This approach is difficult for non-stationary fishes and mammals, such as the analysed samples in **paper III.** The differences of degradation and metabolism rates for PCB congeners within a food chain can also add some uncertainty to such profile analyses. Enantiomer selective analyses of chiral contaminants are a more powerful tool than congener comparisons for assessments of primary versus secondary sources. EFs can be used to differentiate between water masses, to elucidate exchange processes between air and water and fate of secondary sources **(paper II,** Bidleman et al., 1998; Bidleman and Falconer, 1999; Jantunen, 2009; Wong et al., 2011; Bidleman et al., 2012). The large data set in **paper II** contributes to the understanding and elucidation of non-racemic EFs in zooplankton. Among the contaminants analysed, EFs of α-HCH was related to ice cover. EFs of *trans*- and *oxy*chlordane seemed to be most susceptible for biotransformation processes, and changes of EFs in *cis*-chlordane was reflected by deviations from racemic in *oxy*chlordane.

Impacts of climate change upon contaminant uptake and transfer processes

A less ice covered Arctic (both in mass and in time) facilitates the evaporation of contaminants stored in the ocean to the air (Macdonald et al., 2005; Jantunen et al., 2008; AMAP, 2011b; Ma et al., 2011). An increased delivery from melting ice and snow caps to the ocean could theoretically increase the amount of POPs reaching oceans and lakes (Blais et al., 2001a; Blais et al., 2001b; Bogdal et al., 2009a; Schmid et al., 2011). **Paper I** was a first step towards investigating this in large ice cap systems such as the Greenlandic ice cap. The observed difference between water samples strongly influenced by meltwater and water masses with a large contribution from the ocean supports the idea

of glaciers as secondary sources of contaminants. However, the environmental conditions differ between the Alpine/Canadian small glaciers and the Greenlandic ice cap. The melting ice in the Alps' glaciers was estimated to originate from 1950-70s, and hence contain POPs (Bogdal et al., 2009a; Schmid et al., 2011). The melting ice at the glacier fronts in Greenland is several thousands years old. Nevertheless, it contains large amounts of annual snow cover and can be influenced by complex processes such as meltwater/-channels, draining of POPs from snow into ice and thawing/refreezing (Humphrey et al., 2012; Grannas et al., 2013). Changed precipitation patterns can also affect transport and deposition of POPs in the Arctic. Eventually, these factors can lead to transport of POPs into the ocean and the receiving marine ecosystem via the melting and calving ice at the ice cap fronts **(paper I,** Herbert et al., 2005; Kallenborn et al., 2012a; Grannas et al., 2013). Non-racemic EFs of chiral contaminants in zooplankton can be an indication of secondary sources present in the environment **(paper II).**

Not only changes in temperature and the associated meltwater runoff can affect the transport and fate of POPs. Changes in microbial activity, ice cover and sea surface temperature caused by climate change can also affect degradation processes and the exchange of semivolatile organic compounds between ocean and air, which, in a longer perspective, can affect contaminant patterns in marine animals, especially at low trophic levels **(paper II),** (Bidleman et al., 2003; Bidleman et al., 2012).

Air levels of HCB have increased at Zeppelin (Ny-Ålesund, Svalbard), probably as a result of ice free fjords during the last years (Hung et al., 2010; Ma et al., 2011; Kallenborn et al., 2012a). The amount and fate is not yet well understood. Results from **paper I and II** contributes to an increased knowledge of the fate and behaviour of pesticides in the environment. Ice cover, in addition to phytoplankton bloom, water masses and biotransformation affect the contaminant load and -pattern at low trophic levels. Eventually, this will affect the contaminant load in food items. Since contaminant exposure via food depends on amount of intake as well as on type of food (i.e. vegetables, offal from marine mammals), it is a complex task to elucidate exposure risks for the future. More information regarding trends and levels of contaminants **(paper III, IV)** and dietary intake are needed to assess human exposure in the future. The combined effect of anticipated changed contaminant sources (primary versus secondary), changed food web structure and the decrease of local food intake needs to be investigated (Noyes et al., 2009; Armitage et al., 2011; Quinn et al., 2012). Less sea ice will facilitate boat travels to terrestrial areas available by boat as well as fishing. Hence, terrestrial animals might become more important food items compared to seal, since seal hunting depends on sea ice cover (ACIA, 2005; AMAP, 2011b). Fish can also become more important, and warmer water could facilitate migration of new species. Whether fish species such as Atlantic cod and haddock will survive and reproduce further north is currently under research (Varpe Ø. and Fiksen Ø., 2010;

Renaud et al., 2012). How and whether this will be reflected in the diet of indigenous people is difficult to say. In addition, the contribution of local food items in the diet has decreased among indigenous people during the last years in Greenland (Deutch et al., 2007a), Alaska (Ballew et al., 2006) and Canada (Receveur et al., 1997; Nakano et al., 2005), while there are indications for increased contribution of local food in the Chukotka peninsula (Kozlov, 2004).

Limitations and restrictions

Fieldwork in the Arctic is not only demanding and challenging, but also very costly. These factors limit the possibility to obtain large sample sets, replicates and samples from certain areas. Via several good contacts and collaborations, I have collected samples from both Greenland and Svalbard. However, it could be preferable to have samples from only one region, e.g. to assess selective uptake/degradation from water to zooplankton to fish at the same place. On the other hand, the hypothesis for the present thesis was that the processes themselves are similar in a circumpolar perspective, and hence, it was more appropriate to collect samples from different locations in the Arctic. Svalbard does not have indigenous people or a strong culture regarding the consumption of local food, and Greenland was therefore the most suitable location to collect food items. These samples represent common food items of the Western Arctic Regions. The collaboration with the COPOL project provided zooplankton material from several years and locations with different environmental conditions, which would not have been possible to access from other Arctic locations.

The aim of the ArcRisk project was, amongst others, to contribute to an understanding of the effects of a changing climate upon contaminant exposure for humans in the Arctic. The project targeted a large geographical area, where there are socio-economical differences between populations as well as different transportation routes for contaminants reaching the Arctic. However, the present thesis aims to contribute to the understanding of processes that happens on a circumpolar scale. The studied processes were chosen because they are important in a circumpolar perspective, little or only scarce information was available and they should be relevant for contaminant exposure for humans. Hence, processes related to transfer of contaminants from an ice cap to the ocean **(paper I)** are likely to be similar whether it is the Greenlandic ice cap or an ice cap at Svalbard, although the POPs present and their levels can differ.

Enantiomer selective biotransformation processes such as microbial degradation and enzyme facilitated degradation are circumpolar. However, there are variations between areas regarding which enantiomer that undergoes selective uptake/degradation. Biotransformation of a certain enantiomer should therefore not be extrapolated from one area to the whole Arctic, but the occurring degradation process as such can be expected to be valid for other areas and similar species as well **(paper II, III)**.

Further research regarding biodegradation processes should focus on the connection between transfer of contaminants from benthic to pelagic food webs.
Finally, indigenous food items vary with locations and seasons. It was beyond the scope of the present thesis and ArcRisk to assess contaminant levels in food baskets from the whole Arctic. In the perspective of trends towards more contribution from western type of food items, fish and meat from marine mammals were chosen because they are more similar to urban food than intestines and blubber from marine mammals **(paper III, IV)**.

Regarding pesticide analyses in water, biota and food items from Russia, and especially from the former Soviet Union, it can be difficult to access information. Many of the old analyses can be associated with large errors and lack of proper quality control (Zhulidov et al., 2000). Sample collection in remote parts of Russia has often been associated with greater logistical challenges compared to sampling in the central parts of Greenland (i.e. Nuuk).

Finger prints of e.g. PCB congeners can be useful in air and abiotic environments, but uptake and degradation of the congeners in biota differs, which can affect the finger print. However, the congener pattern or presence of specific congeners in biota could give an indication of the origin of the PCB mixture and whether local sources contributions of POPs can be detected in animals (Sagerup et al., 2009). Challenges such as different affinity for sampling medium can also affect the ratio between compounds. In such cases, EF would still be usable since the EF itself would not be affected by loss of the target compound. Analyses of chiral pesticides require additional chromatographic analyses compared to regular quantitative pesticide analyses. However, no extra clean-up procedures are needed, and the costs connected to enantiomer selective analyses are therefore not much higher than regular analyses. Enantiomer selective analyses is a useful tool and especially together with ratios for different compounds and finger prints for mixtures. Hence, enantiomeric distribution was chosen instead of congener profiles to elucidate processes in the present thesis. It would have been beneficial to analyse EFs in the water samples from Greenland and additional water samples from the Svalbard fjords. Due to low levels of the pesticides in water, and additional matrix problems during enantiomer selective analyses, this was not possible within this thesis. In general, low detection frequency for some compounds and limited number of sample replicates available is a challenge with regards to obtaining a good statistical power.

Future perspectives

The combination of monitoring and research has proven to be a valuable tool to assess trends and changes of behaviour pattern among POPs, such as increasing levels of HCB in air at Zeppelin station (Hung et al., 2010; Becker et al., 2012). There are several programs and organisations responsible for the long-term monitoring of contaminants globally (e.g. European Monitoring and Evaluation Programme; EMEP) as well as in the Arctic (Arctic Monitoring and Assessment Program; AMAP, Northern Contaminants Program (Canada), and Task Force on Hemispheric Transport of Air Pollution; TF HTAP). Implementation of the monitoring of chiral pesticides in water/animals at low trophic levels could provide valuable data regarding old/new sinks. Not only changes of levels can be determined, but processes other than solely atmospheric transport can be elucidated. **Paper I** showed how water samples can give an indication of local meltwater sources of pesticides. A combination of passive water samplers and analyses of POPs in animals from low trophic levels could give good indications for changes of the physical environment and uptake of contaminants from the water mass **(paper I, II).** Monitoring will contribute to more samples over time and hence, higher statistical power within the dataset. Appropriate analytical methods are important for inter-laboratory comparisons.

Paper II contributes to an increased understanding of pesticide fate with regards to a changing climate. The environmental processes, which are linked to climate changes and affect EF pattern and pesticide accumulation in zooplankton are circumpolar. Increased meltwater runoff will make secondary sources of contaminants, such as soil and snow caps available to the marine Arctic ecosystem, which has already been reported from glaciers in the Alps and in Canada (Blais et al., 2001a; Blais et al., 2001b; Bogdal et al., 2009a; Bogdal et al., 2009b; Bogdal et al., 2011; Schmid et al., 2011). Changes of the physical environment, such as warmer water temperatures and/or inflows of new water masses will have an impact on the ice cover in the Arctic (Cottier et al., 2007; Pavlov et al., 2013; Rudels et al., 2013) and the linked behaviour and environmental fate of contaminants in the Arctic (Wong et al., 2011; Kallenborn et al., 2012a; Grannas et al., 2013).

Meltwater runoff from secondary sources will deliver contaminants into the local marine food web. **Paper I** showed a linkage between meltwater runoff and pesticide patterns. The implications of this process need to be investigated further. Oceanographic conditions, such as currents, mixing rates, particle content and –scavenging can affect this process and should be taken into account. Once bioavailable in the marine food web, the POPs will bioaccumulate via the food web into edible fishes and mammals **(paper III, IV)**. According to models, the total concentration of PCBs are assumed to decrease in the Arctic due to the reduction of primary sources, However, an increased volatilisation, mobility and runoff from secondary sources due to a warmer climate will increase the levels in the

Arctic environment (Lamon et al., 2009). Abiotic media and animals at low trophic levels are suitable for monitoring of the contribution from secondary sources. Changes of levels and contaminant patterns at high trophic levels can indicate altered food web structures caused by climate changes (Kallenborn et al., 2012a). Diet is the most important exposure route of POPs. Therefore, fish and marine mammals were analysed in **paper III and IV**. Recent findings assess changes of diet as a more important factor compared to direct effects of climate changes regarding contaminant exposure for humans (Undeman et al., 2010; Armitage et al., 2011; Quinn et al., 2012). However, the effects in the Arctic marine food web related to climate changes and contaminants are more difficult to assess, although recent models suggest decreased bioaccumulation as a result of increased phytoplankton mass and hence, a dilution effect of contaminants (Borgå et al., 2010). Levels, uptake/degradation processes and the effects of legacy POPs as well as screening for new contaminants should therefore be monitored in the Arctic food web to verify models. The focus should be towards top predators, since they might be more susceptible to indirect climate changes (e.g. changed food web structure and habitat) compared to indigenous people, since the intake of traditional food is decreasing and hence, the dietary exposure reduced (Receveur et al., 1997; Macdonald et al., 2005; Van Oostdam et al., 2005; Deutch et al., 2006; Kallenborn et al., 2012a). Exposure to heavy metals was beyond the scope of the present thesis, but should be taken into account for a more holistic health perspective.

Empirical data of contaminants in water are needed to improve Arctic food web models, since the available data sets of POPs in the Arctic Ocean include very few measurements. Ocean monitoring stations with deployed passive samplers could provide time series of contaminants and oceanographic conditions, which could contribute to an estimation of the amount of contaminants stored in glaciers and snow caps. Food web models would benefit from such data to improve the predictions of the amount of contaminants that can reach the marine Arctic environment.

Main conclusions

The present thesis is a continuation of recent work on contaminants in Arctic food webs. It contributes to the understanding of enantiomer selective degradation in Arctic marine food webs and contains one of the first studies of EFs in zooplankton as a tool to elucidate changes in the physical environment. The zooplankton dataset covers not only different species, but also temporal and geographical variations. The first study of pesticides linked to meltwater in a Greenlandic fjord is also part of the present thesis.

Paper I indicated that more types of pesticides were present close to the ice cap (especially chlordanes), while ocean water influenced stations mainly contained α-HCH and HCB. To better understand the role of meltwater, glaciers and snow caps regarding their role as secondary sources of POPs, it is recommended to follow up these results with more extensive sampling of water, sediment, snow and ice samples as close as logistically possible to the glacier fronts. Enantiomer selective analyses of contaminants in glacier, water, sediment and zooplankton samples from the same area would give valuable knowledge and insight in transport and transformation of contaminants from secondary sources. Especially since **paper II** indicates the chlordanes as potential tracers for changes of the physical environment, and **paper I** indicates chlordanes as potential tracers for freshwater runoff (i.e. secondary sources).

The present thesis contributes to the understanding of levels of pesticides, including EFs when applicable, PCBs, PBDEs and PFASs in traditional Greenland food items, such as raw and smoked fish (salmon and halibut), whale and seal meat and narwhal mattak. ΣHCH and Σchlordanes were lowest in smoked salmon (5 and 38 ng/g lw, respectively) and highest in narwhal mattak (98 and 1027 ng/g lw, respectively). EFs were non-racemic in all samples, although with a few exceptions (α-HCH in narwhal, *trans*-chlordane in whale beef and *cis*- and *oxy*chlordane in the seal meat). There were indications for different biotransformation processes of α-HCH in fish, where (+)-α-HCH was preferentially degraded, compared to (-)-α-HCH in mammals. ΣPCBs ranged from 37 ng/g lw in smoked halibut to 1146 ng/g lw in narwhal mattak in the food items analysed, while BDE-47 ranged from <LOD in smoked halibut, to 21 ng/g lw in whale beef. ΣPFAS was detected in whale beef (2.9 ng/g ww), narwhal mattak (3.7 ng/g ww) and seal (13.5 ng/g ww).
Food is the main contaminants exposure route for humans, and the results from **paper III** and **IV** shows levels below the TDI threshold. This was mainly due to exclusion from the diet of local food items such as intestines and blubber, which will have a positive effect on the POP exposure. Nevertheless, such reduction will not impact the health benefits of traditional food considerably.

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Appendix

Table A1. IUPAC names and CAS numbers for the compounds analysed.

PCB			PBDE		
IUPAC Name	**Congener**	**CAS-number**	**IUPAC Name**	**Congener**	**CAS number**
2,2',5-Trichlorobiphenyl	18	37680-65-2	2,4,4'-Tribromodiphenyl ether	28	41318-75-6
2,4,4'-Trichlorobiphenyl	28	7012-37-5	2,2',4,4'-Tetrabromodiphenyl ether	47	5436-43-1
2,4',5-Trichlorobiphenyl	31	16606-02-3	2,2',4,5'-Tetrabromodiphenyl ether	49	243982-82-3
2,2',4,4'-Tetrachlorobiphenyl	47	2437-79-8	2,3',4,4'-Tetrabromodiphenyl ether	66	189084-61-5
2,2',4,5'-Tetrachlorobiphenyl	49	41464-40-8	2,3',4',6-Tetrabromodiphenyl ether	71	189084-62-6
2,2',5,5'-Tetrachlorobiphenyl	52	35693-99-3	2,2',3,4,4'-Tetrabromodiphenyl ether	77	93703-48-1
2,3',4,4'-Tetrachlorobiphenyl	66	32598-10-0	3,3',4,4'-Tetrabromodiphenyl ether	85	182346-21-0
2,4,4',5-Tetrachlorobiphenyl	74	32690-93-0	2,2',4,4',5-Pentabromodiphenyl ether	99	60348-60-9
2,2',4,4',5-Pentachlorobiphenyl	99	38380-01-7	2,2',4,4',6-Pentabromodiphenyl ether	100	189084-64-8
2,2',4,4',6-Pentachlorobiphenyl	100	39485-83-1	2,3',4,4',6-Pentabromodiphenyl ether	119	189084-66-0
2,2',4,5,5'-Pentachlorobiphenyl	101	37680-73-2	2,2',3,4,4',5'-Hexabromodiphenyl ether	138	182677-30-1
2,3,3',4,4'-Pentachlorobiphenyl	105	32598-14-4	2,2',4,4',5,5'-Hexabromodiphenyl ether	153	68631-49-2
2,3',4,4',5-Pentachlorobiphenyl	118	31508-00-6	2,2',4,4',5,6'-Hexabromodiphenyl ether	154	207122-15-4
2,3',4,4',5'-Pentachlorobiphenyl	123	65510-44-3	2,2',3,4,4',5',6-Heptabromodiphenyl ether	183	207122-16-5
2,2',3,3',4,4'-Hexachlorobiphenyl	128	38380-07-3			
2,2',3,4,4',5'-Hexachlorobiphenyl	138	35065-28-2	**PFAS**	**Acronym**	**CAS number**
2,2',3,4,5,5'-Hexachlorobiphenyl	141	52712-04-6	**Perfluorocarboxylates**		
2,2',3,4',5',6-Hexachlorobiphenyl	149	38380-04-0	Perfluorohexanoic acid	PFHxA	307-24-4
2,2',4,4',5,5'-Hexachlorobiphenyl	153	35065-27-1	Perfluoroheptanoic acid	PFHpA	375-85-9
2,3,3',4,4',5-Hexachlorobiphenyl	156	38380-08-4	Perfluorooctanoic acid	PFOA	335-67-1
2,3,3',4,4',5'-Hexachlorobiphenyl	157	69782-90-7	Perfluorononanoic acid	PFNA	375-95-1
2,3',4,4',5,5'-Hexachlorobiphenyl	167	52663-72-6	Perfluorodecanoic acid	PFDA	335-76-2
2,2',3,3',4,4',5-Heptachlorobiphenyl	170	35065-30-6	Perfluoroundecanoic acid	PFUnA	2058-94-8
2,2',3,4,4',5,5'-Heptachlorobiphenyl	180	35065-29-3	Perfluorododecanoic acid	PFDoA	307-55-1
2,2',3,4,4',5',6-Heptachlorobiphenyl	183	52663-69-1	Perfluorotridecanoic acid	PFTrA	72629-94-8
2,2',3,4',5,5',6-Heptachlorobiphenyl	187	52663-68-0	Perfluorotetradecanoic acid	PFTeA	376-06-7
			Perfluorosulfonates		
			Perfluorobutane sulfonate	PFBS	29420-49-3
			Perfluorohexane sulfonate	PFHxS	432-50-7
			Perfluoroheptane sulfonate	PFHpS	375-92-8
			Perfluorooctane sulfonate	PFOS	45298-90-6
			Perfluorodecane sulfonate	PFDS	335-77-3
			Perfluorododecane sulfonate	PFDoS	79780-39-5
			Perfluorosulfonamides		
			Perfluorooctane sulfonamide	PFOSA	754-91-6

Table A2. Mass transitions and quantifier/qualifier ions for all analysed compounds.

Pesticides, ECNI, SIM	**Quantifier ion**	**Qualifier ion**
^{13}C *trans*-chlordane	417.8	419.8
OCN (RSTD)	404	
α-HCH	254.8	252.8
β-HCH	254.8	252.8
γ-HCH	254.8	252.8
HCB	284.0	282.0
trans-chlordane	407.8	409.8
cis-chlordane	407.8	409.8
*oxy*chlordane	353.8	351.8
trans-nonachlor	333.8	335.8
cis-nonachlor	333.8	335.8

PCBs, PBDEs, EI, MRM	**Parent ion**	**Product ion**
^{13}C pentaPCB	338	268
^{13}C hexaPCB	372	302
^{13}C heptaPCB	406	336
OCN (RSTD)	404	334
triPCB	256	186
tetraPCB	290	220
pentaPCB	326	256
hexaPCB	360	290
heptaPCB	394	324
^{13}C triBDE	417.8	258
^{13}C tetraBDE	497.8	337.9
^{13}C pentaBDE	575.7	415.8
^{13}C hexaBDE	655.6	495.7
^{13}C heptaBDE	733.5	573.6
triBDE	408	248
tetraBDE	485.7	325.9
pentaBDE	565.6	405.8
hexaBDE	643.5	483.7
heptaBDE	723.4	563.6

PFAS, ESI, MS/MS	**Parent ion**	**Product ion**
^{13}C PFHxS	402	99/80
^{13}C PFOS	503	99/80
^{13}C PFOSA	506	78
^{13}C PFBA	217	172
^{13}C PFDcA	519	474/269
^{13}C PFDoA	615	570/169
^{13}C PFNA	468	423/219
^{13}C PFOA	417	372/169
^{13}C PFPA	268	223
^{13}C PFUnA	570	525/269
3,7dimeo-bPFDA (RSTD)	469	269
PFBS	299	99/80
PFHxS	399	99/80
PFOSlin	499	99/80
PFOSbr	499	99/80
PFOSA	498	78
PFDcS	599	99/80
PFBA	213	169
PFPA	263	219
PFHxA	313	269/119
PFHpA	363	319/169
PFOA	413	369/169
PFNA	463	419/219
PFDcA	513	469/269
PFUnA	563	519/269
PFDoA	613	569/169
PFTrA	663	619/169
PFTeA	713	669/169

Paper I

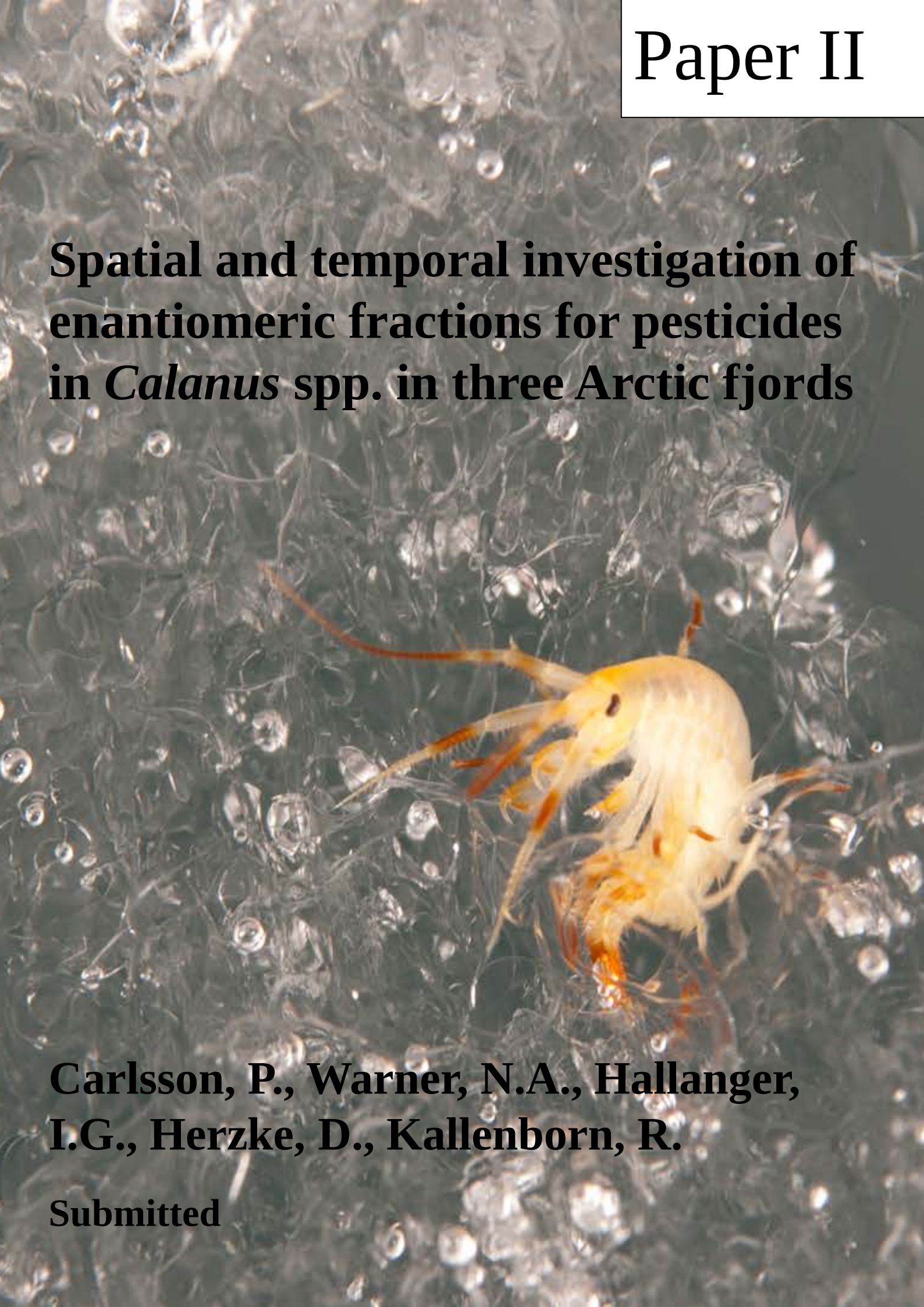
Hydrology-linked spatial distribution of pesticides in a fjord system in Greenland

Carlsson P., Cornelissen G., Bøggild C.E., Rysgaard S., Mortensen J., Kallenborn R.

Journal of Environmental Monitoring 2012, 14; 1437-1443.

Paper II

Spatial and temporal investigation of enantiomeric fractions for pesticides in *Calanus* spp. in three Arctic fjords



Carlsson, P., Warner, N.A., Hallanger, I.G., Herzke, D., Kallenborn, R.

Submitted

Paper III

Enantiomer selective and quantitative trace analysis of selected persistent organic pollutants (POP) in traditional food from western Greenland

Carlsson, P., Herzke, D., Kallenborn, R.

Submitted

Paper IV

Polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and perfluorinated alkylated substances (PFASs) in traditional sea-food items from western Greenland

Carlsson, P., Herzke, D., Kallenborn, R.

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