



Norwegian University  
of Life Sciences

**Master's Thesis 2019 60 ECTS**

Faculty of Chemistry, Biotechnology and Food Science

# **Riverine inputs of polychlorinated biphenyls (PCBs) and chlorobenzenes to Isfjorden, Svalbard; Implications for spatial distribution and bioavailability**

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Environment and Natural Resources



## Preface

This thesis is a part of the TerrACE project, which aims to investigate the “**effects of terrestrial inputs on contaminant dynamics in Arctic coastal ecosystems**”. The project is led by the Norwegian Institute for Water Research (project leader: Amanda Poste) in collaboration with several other research institutes. More information about the project can be found at <https://terrace-project.org/science/>.

This master project would not have been possible without financial support from TerrACE (RCN: 268458), BARELAB (RIS-ID: 10628) and the Jan Christensens scholarship, as well as all people that have helped me through the process of writing this thesis. Being a part of the TerrACE project provided a unique opportunity to get known with a lot of great and knowledgeable people from various disciplines. Together with six other master students, the PhD candidate Maeve McGovern (NIVA) and other researchers, a comprehensive sampling campaign was conducted during the summer 2018, to collect samples for all the different side projects within TerrACE. Everyone worked very hard during the field work, and everyone has been really helpful with each other, both in the field and also with data interpretation afterwards.

I would like to thank all participants and collaborators of the TerrACE project for great help and support, and especially thanks to all the students; it really helps to know that you're not alone when you feel that your thesis belongs in garbage bin. Eirik, Connor, Nathalie, Emelie, Charlotte, Emilie, Maeve, Guttorm and Amanda, you are all super-nice and talented people, good luck with everything that comes after! To my supervisors Roland, Ian and Pernilla. You are all an endless source of information when it comes to environmental chemistry and the Arctic. Thanks for all your help and support, and for your patience when I delivered my drafts a little late.

During this project, I have spent some time in the lab at NIVA. That was something I always enjoyed, because of the many nice people working there. I want to thank all the laboratory workers at NIVA that were helping me out, and especially Alfhild and Kine for spending hours teaching me about sample preparation and analysis. This project would not have been possible without your help.

I want to thank the crew on “Spitsbergen Express” for transportation and very good food during the fieldwork in September. It was an exiting experience and a nice opportunity to see the amazing areas of Isfjorden in Svalbard. Pernilla, even though we didn't find as many passive samplers as we wanted, and I was a little grumpy, it was still a really nice trip.

Finally, I want to thank my family and especially my pregnant partner, Astrid, for mental support, and for being so patient when I was working long days writing up my thesis... and for sharing my frustrations when things didn't go as planned.

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4<sup>th</sup> of May 2019

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## Abstract

Considerable amounts of deposited persistent organic pollutants (POPs); such as polychlorinated biphenyls (PCBs) and penta- and hexachlorobenzene (PeCB and HCB) are stored in the Arctic cryosphere. In recent years, more attention has been directed to the potential re-mobilization of these contaminants due to increased temperatures, change in precipitation patterns and accelerated glacier ablation, potentially leading to enhanced secondary release of legacy POPs to receiving coastal areas. However, the meltwater influence on this transport of POPs to coastal marine environments is not fully understood, and the present thesis aim to investigate this.

This study investigated the freshwater-associated contribution of selected PCBs and HCB to Isfjorden, a large Arctic fjord system on the western side of Spitsbergen (Svalbard). Rivers feeding the fjords Adventfjorden, Tempelfjorden and Billefjorden in the Isfjorden system were sampled in addition to the fjords themselves. Suspended particulate matter (SPM) from five selected rivers, and surface sediments from inner and outer parts of the receiving fjords were analyzed for PCBs, HCB and PeCB. In addition, passive samplers (PAS) were deployed at similar locations to yield information about dissolved concentrations. Sediment properties (organic matter, fine sediment fraction, chlorophyll- $\alpha$  and river catchment area characteristics (size and glacial coverage) were taken into account to assess how these factors might explain observed inputs- and distribution patterns.

Both dissolved and particulate associated chlorobenzenes and PCB congeners were detected and quantified in rivers, indicating transport from secondary POP sources to the marine receiving environment. However, the total contaminant burden from freshwater sources may still be low compared to other sources to the fjord, such as direct atmospheric deposition, oceanic current transport and local sources. Sediment concentrations of  $\sum\text{PCB}_{14}$ , HCB and PeCB in the inner fjord stations were in the range of 12-170 pg/g dry weight (dw.) and 10-106 pg/g dw., respectively. Further out in the fjords, the concentrations had increased to between 630-880 pg/g dw. ( $\sum\text{PCB}_{14}$ ) and 530-760 pg/g dw. (HCB). Sediment properties were not driving factors for explaining variation in contaminant levels between sampling stations. Instead, the lowest concentrations at the inner stations can be attributed to the larger deposition of riverine sediments at these locations, which are associated with low concentrations of contaminants. This indicate that particles have potential to sorb contaminants from the water column, potentially leading to a reduction in dissolved aqueous concentrations near the river outlets. This might lead to reduced accumulation of these contaminants in low trophic species within affected ecosystems, because dissolved concentrations are considered to play a key role regarding bioavailability and bioaccumulation of POPs.



## Sammendrag

Store mengder persistente organiske forurensninger (POPer), slik som polyklorerte bifenyler (PCBer) og penta- og heksaklorbenzen antas å være lagret i den arktiske kryosfæren. I de senere år har det blitt økt fokus på en potensiell remobilisering av disse forbindelsene, på grunn av høyere temperaturer, endring i nedbørsmønstre og økt bresmelting, noe som potensielt kan føre til større sekundære utslipp av POPer med smeltevatn til kystområdene. Men påvirkningen smeltevatn har på denne transporten av POPer til marine kystområder er lite undersøkt, og dette studiet forsøker å se nærmere på dette.

Dette studiet undersøkte ferskvanns-assosiert bidrag av utvalgte PCBer og klorbenzener til Isfjorden, et stort arktisk fjordsystem på den vestre siden av Spitsbergen (Svalbard). Det ble tatt prøver i elver som rant ut i fjordene Adventfjorden, Tempelfjorden og Billefjorden i Isfjorden-systemet. I tillegg ble det tatt prøver i fra selve fjordene. Suspendert partikulært materiale (SPM) fra fem utvalgte elver og overflatesediment fra indre og ytre deler av de mottakende fjordene ble analysert for PCBer, HCB og PeCB. Det ble i tillegg satt ut passive prøvetakere i de samme områdene for å få informasjon om løste konsentrasjoner av disse forbindelsene. Sediment-egenskaper (organisk materiale, finfraksjon og klorofyll- $\alpha$ ), og elvenes nedbørsfelt (størrelse og isdekke) ble vurdert i sammenheng med resultatene for å vurdere hvordan disse faktorene kanskje forklarer observerte tilførsels- og fordelingsmønstre.

Både løst- og partikulært- assosierte PCBer og klorbenzener ble detektert og kvantifisert i elver, noe som indikerer transport av POPer fra sekundære kilder til det marine miljø. Men den totale belastningen fra ferskvannskilder kan være liten i forhold til andre kilder til fjordene, slik som direkte atmosfærisk deposisjon, transport med havstrømmer og lokale kilder. Konsentrasjon av  $\sum\text{PCB}_{14}$  og HCB i sediment ved de indre fjordstasjonene var henholdsvis i området 12-170 pg/g tørrvekt (tv.) og 10-106 pg/g tv. Lenger ut i fjordene økte konsentrasjonene til mellom 630-880 pg/g tv for  $\sum\text{PCB}_{14}$  og 530-760 pg/g tv. for HCB. Sediment-egenskaper var ikke styrende for å forklare variasjon i konsentrasjoner mellom prøvetakningsstasjoner. I stedet så kunne de laveste konsentrasjonene i de innerste delene av fjordene tilegnes en større deponering av elvesedimenter ved disse lokasjonene, som kan assosieres med lave konsentrasjoner av forurensninger. Dette indikerer også at partiklene som kommer ut med elvene, har evne til å absorbere forbindelsene ut av vannsøylen og potensielt føre til en reduksjon av løst konsentrasjon nær elveutløpene. Dette kan føre til mindre akkumulering av disse forbindelsene i organismer lavt i næringskjeden, fordi løst konsentrasjon er en viktig faktor som styrer biotilgjengelighet og bioakkumulering av POPer.

# Table of content

List of abbreviations and scientific names.....	9
<b>1.0 INTRODUCTION .....</b>	<b>10</b>
1.1 <i>Persistent organic pollutants in Svalbard</i> .....	10
1.2 <i>Inputs, distribution and risk of POPs within an Arctic fjord</i> .....	11
1.3 <i>Scientific motivation and aim of the study</i> .....	12
<b>2.0 THEORETICAL BACKGROUND .....</b>	<b>14</b>
2.1 <i>Polychlorinated biphenyls (PCBs)</i> .....	14
2.2 <i>Hexa- and pentachlorobenzene</i> .....	15
2.3 <i>Analysis of freely dissolved concentrations in water</i> .....	15
2.4 <i>Passive sampling theory</i> .....	16
2.5 <i>Equilibrium passive sampling in sediments</i> .....	17
<b>3.0 MATERIAL AND METHODS.....</b>	<b>18</b>
3.1 <i>Material and chemicals</i> .....	18
3.2 <i>Field study</i> .....	18
3.2.1 <i>Study area</i> .....	18
3.2.2 <i>Sampling campaign</i> .....	19
3.2.3 <i>Passive water sampling in water</i> .....	20
3.2.4 <i>Sampling of river suspended particulate matter (SPM) and marine sediments</i> .....	21
3.3 <i>Analysis of sediment properties</i> .....	22
3.4 <i>Measurements of suspended particulate matter (SPM) in water</i> .....	22
3.5 <i>Ex-situ equilibrium sediment passive sampling</i> .....	24
3.6 <i>Sample preparation and analysis</i> .....	25
3.6.1 <i>Extraction of PAS and sediment/SPM samples</i> .....	25
3.6.2 <i>Clean-up of PAS and sediment/SPM samples</i> .....	26
3.6.3 <i>Instrumental Analysis</i> .....	27
3.6.4 <i>Quality assurance and control</i> .....	27
3.7 <i>Calculations of dissolved concentrations (<math>C_{free}</math>) in water from in situ passive sampling</i> .....	29
3.8 <i>Calculations of dissolved concentrations (<math>C_{free}</math>) in water from sediment partitioning</i> .....	30
3.9 <i>Estimation of fluxes</i> .....	30
3.10 <i>Data handling and statistics</i> .....	31
3.10.1 <i>Analysis of variances</i> .....	31
3.10.2 <i>Regression analysis</i> .....	31
3.10.3 <i>Principal Component Analysis (PCA)</i> .....	31
<b>4.0 RESULTS .....</b>	<b>33</b>
4.1 <i>Concentrations of PCBs and chlorobenzenes (HCB and PeCB) in sediments and river SPM</i> .....	33
4.1.1 <i>PCBs</i> .....	33
4.1.2 <i>HCB and PeCB</i> .....	33
4.2 <i>Aqueous concentrations of PCBs and chlorobenzenes</i> .....	34
4.3 <i>Relative composition</i> .....	36
4.3.1 <i>Selected ratios</i> .....	37
4.4 <i>Sediment properties (OM, fine sediment and Chl-<math>\alpha</math>)</i> .....	37
4.5 <i>Distance from nearest freshwater source</i> .....	37
4.6 <i>Principal component analysis (PCA)</i> .....	39
4.7 <i>Fluxes of contaminants from rivers to fjords</i> .....	39
4.8 <i>Partitioning between sediment and water</i> .....	40
<b>5.0 DISCUSSION.....</b>	<b>42</b>
5.1 <i>Freshwater associated contribution of contaminants to the fjords</i> .....	42
5.1.1 <i>Riverine fluxes</i> .....	42
5.1.2 <i>Mass balance between environmental media</i> .....	43
5.1.2 <i>Contaminant levels related to catchment area characteristics</i> .....	43
5.1.3 <i>Contaminant composition related to atmospheric deposition</i> .....	44
5.1.4 <i>Freshwater contribution summarized and future perspectives</i> .....	44
5.2 <i>Local sources</i> .....	45
5.3 <i>Contribution of sedimentary particle fluxes to spatial distribution of contaminants in the fjords</i> .....	45



5.3.1 Impact of sediment properties on spatial PCB and chlorobenzene distribution .....	46
<b>5.4 Terrestrial inputs - effect on dissolved concentrations.....</b>	<b>47</b>
<b>5.5 Reflections on method uncertainties and limitations.....</b>	<b>48</b>
5.5.1 Analytical considerations .....	48
5.5.2 Representativeness of sampling stations.....	48
5.5.3 Sediment properties.....	49
<b>6.0 CONCLUSIONS AND FUTURE PERSPECTIVES.....</b>	<b>50</b>
<b>References .....</b>	<b>51</b>
<b>Appendix .....</b>	<b>55</b>

## List of abbreviations and scientific names

AMAP	Arctic Monitoring and Assessment Programme
ANOVA	Analysis of variance
$C_{\text{free}}$	Freely dissolved concentration in water
Chl- $\alpha$	Chlorophyll- $\alpha$
EI	Electron ionization
GC	Gas chromatography
GPC	Gel Permeation Chromatography
HCB	Hexachlorobenzene
HVS	High volume sampling
ISTD	Internal standard
$K_{\text{oc-w}}$	Organic carbon-water partition coefficient
$K_{\text{ow}}$	Octanol-water partition coefficient
$K_{\text{sw}}$	Passive sampler-water partition coefficient
LDPE	Low density polyethylene
LOD	Limit of detection
LOQ	Limit of quantification
LRT	Long range transport
m/z	Mass to charge ratio
MRM	Multiple reaction monitoring
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
N/A	Result not available
NIVA	Norwegian Institute for Water Research
NMBU	Norwegian University of Life Sciences
OCB	Organochlorine pesticides
PAS	Passive sampling
PCA	Principal component analysis
PCB	Polychlorinated biphenyls
PeCB	Pentachlorobenzene
POP	Persistent organic pollutant
PRC	Performance reference compounds
RCN	Research council of Norway
RIS	Research in Svalbard
SPM	Suspended particulate matter
SR	Silicone rubber
SRM	Standard reference material
UNIS	The University Centre in Svalbard

## 1.0 INTRODUCTION

Persistent Organic Pollutants (POPs) such as polychlorinated biphenyls (PCBs) and hexa- and pentachlorobenzene (HCB and PeCB) are compounds that are highly resistant towards degradation and can undergo long-range transport (LRT). They bioaccumulate and biomagnify in food chains and can potentially cause adverse effects at low concentrations. These criteria were adopted in 2001 by the Stockholm Convention on Persistent Organic Pollutants, that listed 12 compounds defined as POPs, including PCBs and HCB. The usage of those 12 compounds were regulated worldwide after the ratification of the protocol in 2004. In recent years, several compounds have been added to the list, among them, PeCB. Despite their ban, these compounds are still present in the environment, due to slow degradation, but also because they are continuously released into the environment from diffusive secondary sources containing these compounds (Carlsson et al., 2018). Also, HCB and some PCB congeners (CB-11) are today produced as by-products from various industrial processes (AMAP, 2016; Barber et al., 2005; Bartlett et al., 2019)

Atmospheric- and oceanic current long-range transport (LRT) from industrial areas at lower latitudes are known to be important reasons for the occurrence of POPs in the Arctic marine environment (Burkow & Kallenborn, 2000). To coastal areas, contaminants stored in- and released as secondary emissions from terrestrial compartments, might be additional sources (Lohmann et al., 2007). That is because terrestrial environments, and particularly the vast snow- and ice-covered areas of the Arctic, are considered as a reservoir for previously deposited POPs (Garmash et al., 2013; Hermanson et al., 2005). In recent years, more attention has been directed to the potential re-mobilization of these contaminants due to increased temperatures, change in precipitation patterns and accelerated glacier ablation (Bogdal et al., 2009; Carlsson et al., 2012; Kallenborn et al., 2012), potentially leading to enhanced secondary release of legacy POPs that have been prohibited for several decades. This might have consequences for contaminant dynamics in receiving coastal areas, potentially leading to changes in food web accumulation in affected ecosystems.

### 1.1 Persistent organic pollutants in Svalbard

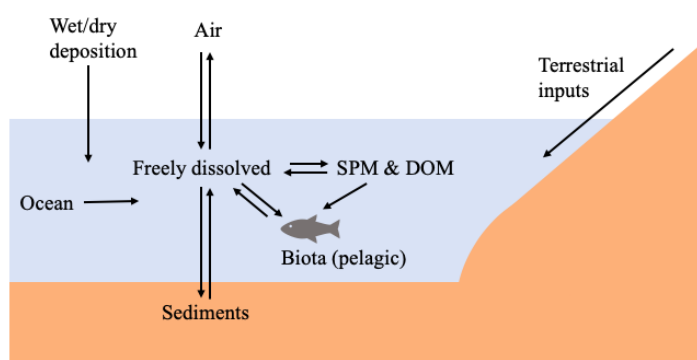
The Svalbard archipelago is located at the northern Atlantic ice-border and has experienced a notable increase in average summer temperatures since the late 1990s (0.17 °C/year; 1992-2006), together with consistent glacial withdrawal during this period (Kohler et al., 2007). Nearly 60 % of Svalbard is covered by glaciers, and the archipelago is situated far away from large industrial areas. Despite a few local PCB sources, such as the settlements Pyramiden (abandoned) and Barentsburg, the area is mainly influenced by LRT of POPs from primary sources and by remobilization and runoff from secondary sources (Gabrielsen et al., 2011). Furthermore, the area is relatively easily accessible compared to most other areas above the 76° N latitude, making the archipelago ideal for studying potential effects of changing climate conditions on contaminant dynamics within the high Arctic.

The occurrence of POPs (including PCBs and HCB) in the abiotic and biotic compartments of the Svalbard environment is well-documented through a number of studies – many of which are summarized in Gabrielsen et al. (2014) and Gabrielsen et al. (2011). In addition, these compounds have been monitored continuously at the Zeppelin station in Ny-Ålesund (Svalbard) under the Arctic Monitoring and Assessment Programme (AMAP) since the 1990s (Hung et al., 2016). Studies from glaciers in Svalbard have confirmed the occurrence of POPs (PCBs and organochlorine pesticides; OCPs) in the

snow and ice (Garmash et al., 2013; Hermanson et al., 2005), which has the potential to be released into the receiving coastal areas from ablation. Studies from Kongsfjorden and Hornsund (West Svalbard) and Wijdefjorden/Woodfjorden (North Svalbard) have reported elevating concentrations of PCBs and HCB in surface sediments due to the possible influence of meltwater runoff (Pouch et al., 2017; Pouch et al., 2018; Sapota et al., 2009). Another study reported similar trends in Kongsfjorden for currently used pesticides, but found that for legacy OCPs, such as  $\alpha$ -hexachlorocyclohexane and chlordane, oceanic current influence was more important for transport and inputs to the fjord (Ma et al., 2015).

## 1.2 Inputs, distribution and risk of POPs within an Arctic fjord

Glacial meltwaters are usually associated with transports of large amounts of sediments and freshwater within a relatively short ablation period (Wada et al., 2011). This might have implications for the movement, distribution and fate of contaminants in the receiving coastal areas, and therefore also the potential for bioaccumulation.



**Figure 1:** Schematic illustration of inputs and distribution of POPs between different environmental compartments in coastal waters.

POPs can enter the fjord system via the atmosphere (wet/dry deposition or by direct exchange), oceanic current transport and via terrestrial inputs, as shown in figure 1. In this system, the contaminants are distributed between the different environmental compartments such as sediments, suspended matter, water and biota, according to their physical chemical properties. Due to the hydrophobic nature of POPs ( $\log K_{ow} > 4$ ), the freely dissolved concentrations in the water is generally low – typically in the low nanogram-picogram per liter range. Instead, they tend to sorb to solid surfaces and thus are more frequently associated with sediments and suspended particulate matter. Marine sediments are therefore believed to be important sinks of POPs, removing the pollutants from circulation in the environment (Lohmann et al., 2007). However, disruption of the sediments, for example during sediment resuspension events, may reintroduce the contaminants into the water column, where they become available for biological uptake (Dong et al., 2016). This effect of sediment resuspension, might be of particular relevance in shallow coastal areas and estuaries, due to increased wind- and water driven turbulences (Dachs & Méjanelle, 2010)

The risk associated with sediment contamination requires knowledge of freely dissolved concentrations ( $C_{free}$ ) in water, because these are considered to play a key role in understanding biological uptake processes and bioaccumulation (Reichenberg & Mayer, 2006).  $C_{free}$  is often related to the sediments capacity to sorb the contaminants, and hence how much that is released into the water column by diffusion as freely dissolved molecules (Reichenberg & Mayer, 2006). Hydrophobic POPs mostly sorb to the organic fraction of sediments, and hence, the sediment sorption capacity is largely controlled by the amount of sediment organic carbon (Ghosh et al., 2014). Over the years, it has become evident that the sorption capacity also is dependent of the type of organic carbon, such as black carbon, which might have a stronger affinity for POPs compared to other carbon-based matters and compounds (Lohmann et al., 2005), causing bioavailable  $C_{free}$  to be lower. This illustrates how knowledge about the fate and

bioavailability of POPs in marine environments requires a sufficient understanding of the sediment sorption behavior and  $C_{\text{free}}$ . Direct measurements of  $C_{\text{free}}$  will help to better understand the POP partitioning in the environment; however, due to very low concentration in water, especially in areas with no distinct pollution sources, reliable measurements of freely dissolved concentrations of POPs are difficult. One solution to this is to use passive sampling techniques which will be further explained in section 2.3.

### **1.3 Scientific motivation and aim of the study**

The glacial influence on the total POP burden to the receiving coastal environments is not fully understood. Despite PCBs and OCPs being found in Svalbard ice caps, the representativeness of their findings is questionable due to few sampling locations far from the coastal areas of Svalbard. In addition, several factors make it difficult to assess the actual transport and fate of POPs that are stored in- and released from the ice: Firstly, the more volatile compounds (i.e., HCB and low chlorinated PCBs) are subject to re-evaporation from the glacial surface into the atmosphere (Hung et al., 2016). Secondly, the meltwater might consist of a mixture of melted ice of post- and pre-industrial origin; for example, investigations of an ice core from Lomonosovfonna (Svalbard) shows that the glacier is at least 800 years old (Kekonen et al., 2005), and should therefore not contain any POPs.

Direct measurements of meltwaters will help to better understand the importance of snow and glaciers as secondary sources of contaminants. In previous studies regarding POP distribution within Arctic fjords, sampling collection has only included water or sediments within the fjord areas, without investigation of the associated meltwater rivers. This only allows a comparison of, for example inner- with outer fjord location, with the assumption that the inner stations to a greater extent reflect terrestrial sources of contaminants. Therefore, a more comprehensive survey can be done by analyzing samples (of both dissolved- and particulate fractions) both from the fjords and the associated rivers. In addition, other factors such as different sediment properties (different organic matter content, particle size distribution) have shown to be important factors governing the spatial distribution, transport and fate of POPs (Lohmann et al., 2007). These factors might vary considerably within a fjord system due to different sources of inputs (marine, and various terrestrial inputs) and should be considered when trying to explain the spatial variability of contaminants within a certain area.

The overall aim of this study is to investigate the freshwater associated contribution to the contaminant profile of Isfjorden (Svalbard), a large Arctic fjord system on the western side of Spitsbergen (Svalbard). Suspended particulate matter (SPM) from selected rivers and surface sediments in the receiving fjords were collected and analyzed for 14 PCB congeners, HCB and PeCB. In addition, passive sampling techniques were applied at similar locations to yield information about dissolved contaminants. The freshwater contribution is compared with other sources to the fjord (local- and, atmospheric-, marine sources) and characteristics of the different river catchment areas (size and glacial coverage) is taken into account, to assess how this might influence the amount of freshwater associated contaminants. For rivers where discharge is available from literature, contaminant fluxes are also estimated. Sediment characteristics (organic matter-, silt and clay-, and chlorophyll- $\alpha$  content) are taken into account to assess how they might govern the spatial distribution, transport and fate of the contaminants. Furthermore, the effects of terrestrial inputs on dissolved concentrations in the coastal areas is addressed, as these concentrations are relevant in risk assessment. Analysis of target compounds was performed using state of the art gas-chromatography tandem mass spectrometry (GC-MS/MS), aiming for better quantification

limits and thus improve spatial resolution for a better comparison of sampling sites within the study area.

The main objectives in this study were to:

Generate (quantitative) information about freshwater associated contribution of PCBs and chlorobenzenes (HCB and PeCB) to the Isfjorden area on Svalbard.

**Question 1:** How much PCB and chlorobenzenes are transported by rivers to the receiving fjords, and how does these inputs compare to other sources to Isfjorden (local sources, atmospheric deposition and oceanic current transport)?

**Question 2:** Is there a relation between the amount of contaminants in the various rivers, and the size and glacial coverage of the river catchment areas?

Generate (quantitative) information about the spatial abiotic distribution of PCBs and chlorobenzenes (HCB and PeCB) in the Isfjorden area on Svalbard.

**Question 1:** How does concentrations of the target compounds vary from surface sediments closer to land compare to further out in the fjord?

**Question 2:** Are sediment characteristics (organic matter, fine sediment fraction) able to explain the spatial variation of contaminants within Isfjorden?

Assess how riverine inputs affect the dissolved concentrations of contaminants in affected coastal waters.

**Question 1:** Are the sediments acting as a sink or a source of contaminants to the water column?

## 2.0 THEORETICAL BACKGROUND

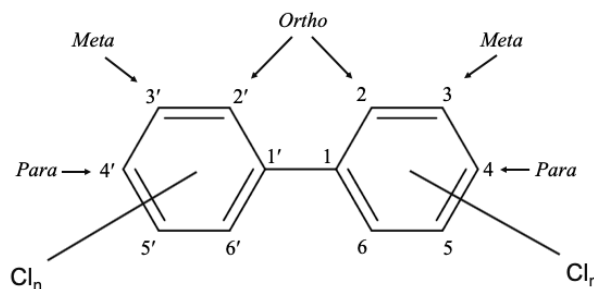
### 2.1 Polychlorinated biphenyls (PCBs)

PCBs are a group of 209 congeners which consist of a bi-phenyl structure where 1-10 hydrogens are replaced with chlorines (figure 1). Every congener is given a single identifying number ranging from 1 to 209 related to the number- and position of chlorine atoms, with higher numbers for more chlorinated congeners. PCBs were widely used during the 1950s to 1970s as coolant- and insulating fluid in electrical equipment and as additives

in plastics, paint and building materials (Gabrielsen et al., 2011). They were mainly produced as commercial, technical mixtures, consisting of a composition of different congeners, but are today commonly analyzed and quantified as separate congeners, due to their different behaviors in the environment. The degree of chlorination and where the chlorine atoms are located affects the toxicity, lipophilicity and ability to be long-range transported. In general, lower chlorinated congeners are more easily LRT through the atmosphere due to the lower vapor pressure of these compounds (Ballschmiter, 1992, cited in Gabrielsen et al., 2011). Higher chlorinated compounds are generally more lipophilic and also their resistance towards degradation increases. Congeners which have only one or no chlorine atoms in the ortho-positions (i.a. CB-105, -118 and -156) can adopt a coplanar structure, which lead to increased toxicity (Van den Berg et al., 2006).

From an analytical perspective, one challenge related to PCB-analysis is that studies may report different congeners, which makes it difficult to compare results. A suit of selected congeners is typically chosen as indicator PCBs in different studies; and possibly the most common used indicator PCBs in environmental studies are the  $\Sigma\text{PCB}_7$  (CB-28, -52, -101, -118, -138, -153, -180), often referred to as the “dutch seven” PCBs. It is important to bear in mind that reporting selected PCBs might not represent the total PCB burden to the environment. For example, measurements from AMAP have shown that  $\Sigma\text{PCB}_{10}$  represented only 11-27 % of the concentration of a total of 88 analyzed congeners (AMAP, 2004 p. 41). However, overall trends can still be assessed, as indicator PCBs often are well correlated with total concentrations (AMAP, 2004 p. 41).

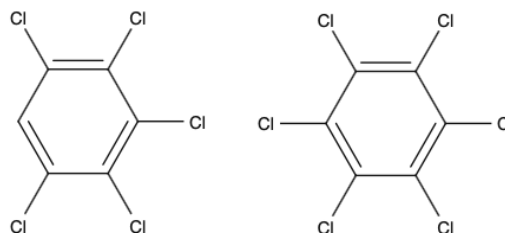
Levels of PCBs in Arctic air have shown declining trends, with exception of some slightly site specific increases of CB-52 and -101, which might be due to re-evaporation of previously atmospheric deposition of PCBs that has begun to re-mobilize (Hung et al., 2016). The overall, general temporal trend of PCBs in the Arctic is decreasing trends in both biotic and abiotic compartments (Hung et al., 2016; Rigét et al., 2019).



**Figure 2:** General structure of the PCB molecule. Made in [www.molview.org](http://www.molview.org) with modifications.

## 2.2 Hexa- and pentachlorobenzene

Hexachlorobenzene (HCB) is a volatile aromatic compound. It was commonly used as a fungicide before its production and use got banned. The structure-related compound, pentachlorobenzene (PeCB) was added later, in 2009. PeCB is not known to be manufactured for any commercial uses but is a by-product from various industrial- and combustion processes. HCB is also formed as a by-product in a large number of processes within the chemical industry (Bailey et al., 2009; Barber et al., 2005). In general, HCB levels in Arctic air has shown declining trends, but an increasing trend has been observed at Zeppelin during recent years. This might be due to re-volatilization of previously deposited HCB due to reduction in sea ice coverage in combination with continuing release of HCB from agriculture and industry (Hung et al., 2016).



**Figure 3:** Molecular structure of Penta- and hexachlorobenzene. Made in [www.molview.org](http://www.molview.org).

## 2.3 Analysis of freely dissolved concentrations in water

Freely dissolved concentrations ( $C_{\text{free}}$ ) can be determined either by direct measurements of water or by estimation from sediment partitioning by assuming equilibrium conditions between sediments and water (e.g. Persson et al. (2005)). The latter rely on accurate sediment-water partition coefficients, commonly normalized to total organic carbon and referred to as  $K_{\text{OC-w}}$  (Arp et al., 2009):

$$C_{\text{free}} = \frac{C_{\text{sed}}}{K_{\text{OC-w}} f_{\text{TOC}}} \quad (1)$$

Where  $K_{\text{OC-w}}$  is the TOC normalized sediment-water partition coefficient (L/kg),  $C_{\text{sed}}$  is the total concentration of individual compounds in the sediment,  $C_{\text{free}}$  is the dissolved concentration and  $f_{\text{TOC}}$  is the weight fraction of TOC in the dry sediment. However, it has become clear that the adsorption behavior is not only related to the organic carbon (OC) content, but also the type of carbon (such as black carbon) that can have largely different sorption capacities (Lohmann et al., 2005). Consequently, literature  $K_{\text{OC-w}}$  values for specific hydrophobic contaminants can vary up to several orders of magnitudes (Arp et al., 2009).

Due to the large uncertainty related to sediment partitioning behavior, the best way to obtain the most accurate porewater- or freely dissolved concentrations is to measure them directly. However, this face challenges due to the low concentrations of these contaminants in the water. Sampling often include high volume sampling (HVS), pumping large quantities of water through an adsorbent, with the following increased risk of contamination and loss of analytes due to handling of equipment and potential breakthrough in sample media, leading to an underestimation of the concentrations (Melymuk et al., 2014). Furthermore, HVS might become impracticable and costly due to the need for heavy equipment and frequent sampling campaigns to account for fluctuating contaminant levels. An alternative to this is passive sampling (PAS), which involves exposure of e.g. a polymer that accumulates the freely dissolved analytes from the ambient environment over time. The accumulation of a compound by the sampler is proportional to the concentration in the ambient environment (air, water, sediments) which allows for calculation of these concentrations if accurate sampler-water partition coefficients ( $k_{\text{sw}}$ ) and uptake rates are known. Furthermore, PAS results represent the average

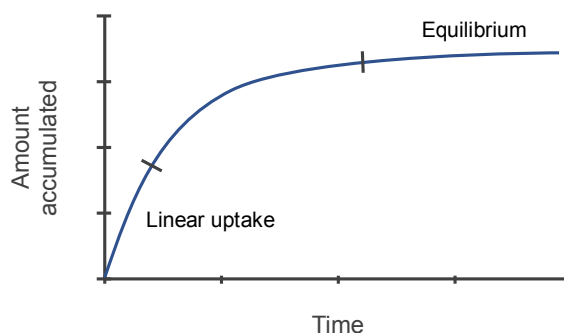


concentration in the environment during the exposure period, which is often a more relevant measurement of the contaminant concentration in the environment.

## 2.4 Passive sampling theory

A detailed description of principles, uptake models, advantages and limitations for PAS of hydrophobic organic compounds ( $\log K_{ow} > 4$ ) is described elsewhere (Rusina, 2009). Here, only a brief introduction is provided.

Accumulation of analytes onto the samplers continues until equilibrium is reached between sampler and the surrounding environment, or until the sampling period is stopped, and generally follows the uptake pattern as shown in figure 4. At equilibrium, the aqueous concentrations of a specific compound can simply be calculated from using an established sampler-water partition coefficient ( $K_{sw}$ ):



**Figure 4:** Accumulation of analytes in a passive sampler. Uptake continues toward equilibrium. In the initial uptake phase, a linear uptake of analytes is assumed.

$$C_s = C_{free} K_{sw} \quad (2)$$

Where  $C_s$  is the concentration in the sampler,  $C_w$  is the concentration in the water and  $K_{sw}$  is the sampler water partition coefficient. However, the time to reach equilibrium increases with  $K_{sw}$  and might take several years for the most hydrophobic compounds during in situ measurements (Lohmann et al., 2012). Equilibrium sampling is therefore in many cases not practically feasible, and sample collection is often done in the initial uptake stage, which generally follows a linear uptake regime, as seen from figure 4. In this uptake phase, the contaminants absorbed by the sampler is directly proportional to their aqueous concentration by the following equation:

$$M_s(t) = C_w R_s t \quad (3)$$

Where  $M_s(t)$  is the mass of analytes in the sampler at a given time (in days),  $C_w$  is the concentration in the water (pg/L) and  $R_s$  is the sampling rate (L/day).  $R_s$  is dependent on hydrodynamic conditions (temperature, flow rate etc.) and physical chemical properties of the specific compounds (molecular size, hydrophobicity).  $R_s$  can be estimated *in situ* by measuring  $R_s$  from the dissipation of Performance Reference Compounds (PRCs) which are spiked in to the sampler prior deployment (Rusina, 2009). Dissipation of the PRCs follow the same, but opposite, curve as uptake of analytes, hence the  $R_s$  can be calculated from measuring the amount of PRCs in exposed and unexposed samplers. PRCs can be isotopically labeled analytes or compounds that do not occur the current environment, but they should have similar physical-chemical properties as the target compounds (Rusina, 2009).

For this study, silicone rubber (SR) and low-density polyethylene (LDPE) were used as PAS. Well established  $K_{sw}$  values exist for these polymers for most PCB congeners and HCB (Smedes et al., 2009), which provides good estimations of  $C_{free}$ . Like most PAS, both SR and LDPE are relatively inexpensive, easy to deploy and do not require electricity, which makes them suitable for sampling of water in Arctic areas where accessibility often is restricted. Analysis of PAS requires a sufficient amount of analytes

accumulated in the samplers for detection and quantification, which involves a sufficient sampling rate and/or deployment time. A major challenge related to PAS in Arctic environments are low temperatures that slows down the uptake to the samplers. In converse, biofouling on the sampler surface which can also reduce the uptake, is less prominent compared to areas further south.

## 2.5 Equilibrium passive sampling in sediments

Passive sampling in sediments is usually performed in situ (for example: Cornelissen et al. (2008)), or ex situ in the laboratory (Smedes et al., 2012). The latter has the advantage that equilibrium sampling is possible within a reasonable time frame, because one can speed up the equilibrium time (from years to weeks or months) by shaking the sediments together with a passive sampler (Smedes et al., 2012). After equilibrium is reached,  $C_{free}$  can then be estimated using formula 2. To assure non-depletive conditions (minor absorption of sediment associated analytes), the amount of target contaminants in the sediment sample should be much higher than the mass accumulated in the sampler. As a rule of thumb, the sampler should accumulate < 5 % of the target compounds in the sediment (Smedes et al., 2012). This is not an issue for samplers deployed in situ, since the sediment pool can be considered as infinite. For laboratory experiments, the amount of sediment is limited and needs to be taken into account before the experiments starts, to avoid depletion of the sediment (Ghosh et al., 2014). An appropriate sampler-sediment ratio ( $N_s/N_{sed}$ : mass of analyte in sampler/mass of analyte in sediment) has to be determined before exposure to assure there is enough sediment mass compared to sampler mass.  $N_s/N_{sed}$  can be estimated from the formula below, which describes the distribution of a compound between the sampler and sediment at equilibrium (Smedes et al., 2012).

$$\frac{N_s}{N_{sed}} = \frac{m_s K_{sw}}{m_{sed} K_{sed-w} + m_s K_{sw}} \quad (4)$$

Where  $N_s$  and  $N_{sed}$  is the amount of a compound in the sampler and sediment respectively.  $m_s$  is the mass of sampler and  $m_{sed}$  is the mass of sediment,  $K_{sw}$  is the sampler-water partition coefficient and  $K_{sed-w}$  is the sediment-water partition coefficient.

## 3.0 MATERIAL AND METHODS

### 3.1 Material and chemicals

LDPE lay flat tubing (0.09 mm thickness) were bought from Brentwood Plastics Inc. AlteSil™ Laboratory SR sheets (thickness: 0.5 mm) were bought from Altec, UK. PCBs (analytical grade) for spiking of samplers were purchased from Dr. Ehrenstorfer GmbH, Germany (CB -1, -2, -3, -10, -14, -21, -50, -78, -104-, 145). A stock solution of these analytes was prepared in acetone and stored at 4 °C in amber vials (see appendix 5). Internal standards (PCB -30, -53, -204) and appropriate concentrations of calibration solutions for target compounds (HCB, PeCB, CB-28, -31, -44, -52, -101, -105, -118, -138, -149, -153, -156, -170, -180, -194, -209) were prepared by laboratory personnel at NIVA. All glassware was wrapped in aluminum foil and burned at 540 °C before use. Centrifuge filter tubes (0.5 mL, polypropylene 0.22 um nylon) were purchased from Costar®. Cyclohexane and acetone (J.T. Baker) pentane and dichloromethane (Rathburn), ethyl acetate (Honeywell) and methanol (Sigma Aldrich) were of HPLC-quality or better. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (Merck) and anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>3</sub>) (burned at 540 °C) was of analytical quality. Ultrapure water was produced by an Elga Maxima purification system.

### 3.2 Field study

#### 3.2.1 Study area

The present study was conducted in the Isfjorden area on West Spitsbergen (Svalbard) (78°20'N 15°20'E). The fjord system branches into several smaller fjords, including Adventfjorden, Billefjorden and Tempelfjorden (see map in figure 5). The influence of warm North-Atlantic waters to the fjords of western Spitsbergen, cause the fjords to have sub polar characteristics rather than polar, with ice free fjords during the summer months (June-September). The area around Isfjorden (and Svalbard in general) is characterized by glacial landscapes, permafrost and scarce vegetation. Consequently, the area is subject to seasonal erosion processes and transport of large amounts of sediment into the receiving coastal areas during the ablation period of June to September (Bogen & Bønsnes, 2003; Forwick et al., 2010). Precipitation is low and is around 200 mm per year in average (Eckerstörfer & Christiansen, 2011). The main sources of freshwater inputs to Isfjorden is meltwater from sea ice and river runoff from melting snow and glaciers (Nilsen et al., 2008). Sea water in Isfjorden are mainly of Atlantic origin (Nilsen et al., 2008).

The most important source of PCBs and chlorobenzenes to the study area is considered to be LRT from other places than Svalbard, and local pollution from the settlements (Gabrielsen et al., 2011). Most of the study area is uninhabited, but there are a few known local pollution sources of PCBs. This is mainly the two largest settlements on Svalbard of permanent residents, Longyearbyen in Adventfjorden and Barentsburg in Grønnfjorden (with a population of about 2000 and 500 respectively), and the abandoned Russian settlement, Pyramiden, located in Billefjorden. Concentrations of PCB within Longyearbyen soil is slightly above average Svalbard background concentrations but low compared with Pyramiden (Gabrielsen et al., 2011).

### 3.2.2 Sampling campaign

The sampling campaign was conducted between June and September 2018 as a part of the TerrACE project (RCN: 268458). Passive sampling and sampling of river suspended particulate matter (SPM) and marine sediments for analysis of POPs were carried out in selected rivers and their receiving fjords, representing different catchment areas in the Isfjorden system with regards to geochemistry and glacial cover (table 1, table 2 and figure 5). The sampling area includes Billefjorden, Sassenfjorden, Tempelfjorden and Adventfjorden with associated rivers (Sassen-, Gipsdals-, Advent-, DeGeer- and Ebbaelva) (For convenience, Tempel- and Sassenfjorden together is hereafter referred to as Tempelfjorden). Along with other student projects within TerrACE, samples were collected for determining water- and sediment characteristics which some are described in section 3.4 and 3.5. Sampling stations were chosen to take into account all research questions within TerrACE, with the overall aim of “studying effects of terrestrial inputs on contaminant dynamics in Arctic coastal ecosystems” (TerrACE, <https://terrace-project.org>)

**Table 1:** Characteristics of the different side fjords included in the present study.

Fjord	Approximate size (km)	Maximal water depth (m)	Glacial coverage of catchment area (%)	Sampled associated rivers	Local pollution sources
Sassenfjorden and Tempelfjorden	30 x 10	150	37*	Sassenelva Gipsdalselva Degeerelva	
Billefjorden**	30 x 8	200	44**	Ebbaelva	Pyramiden
Adventfjorden***	8 x 3.5	80	21***	Adventelva	Longyearbyen

\* from Forwick et al. (2010).

\*\* from Zajaczkowski et al. (2004).

\*\*\* from Hagen et al. (1993), cited in Szczuciński et al. (2009).

**Table 2:** River- and catchment characteristics of the studied rivers.

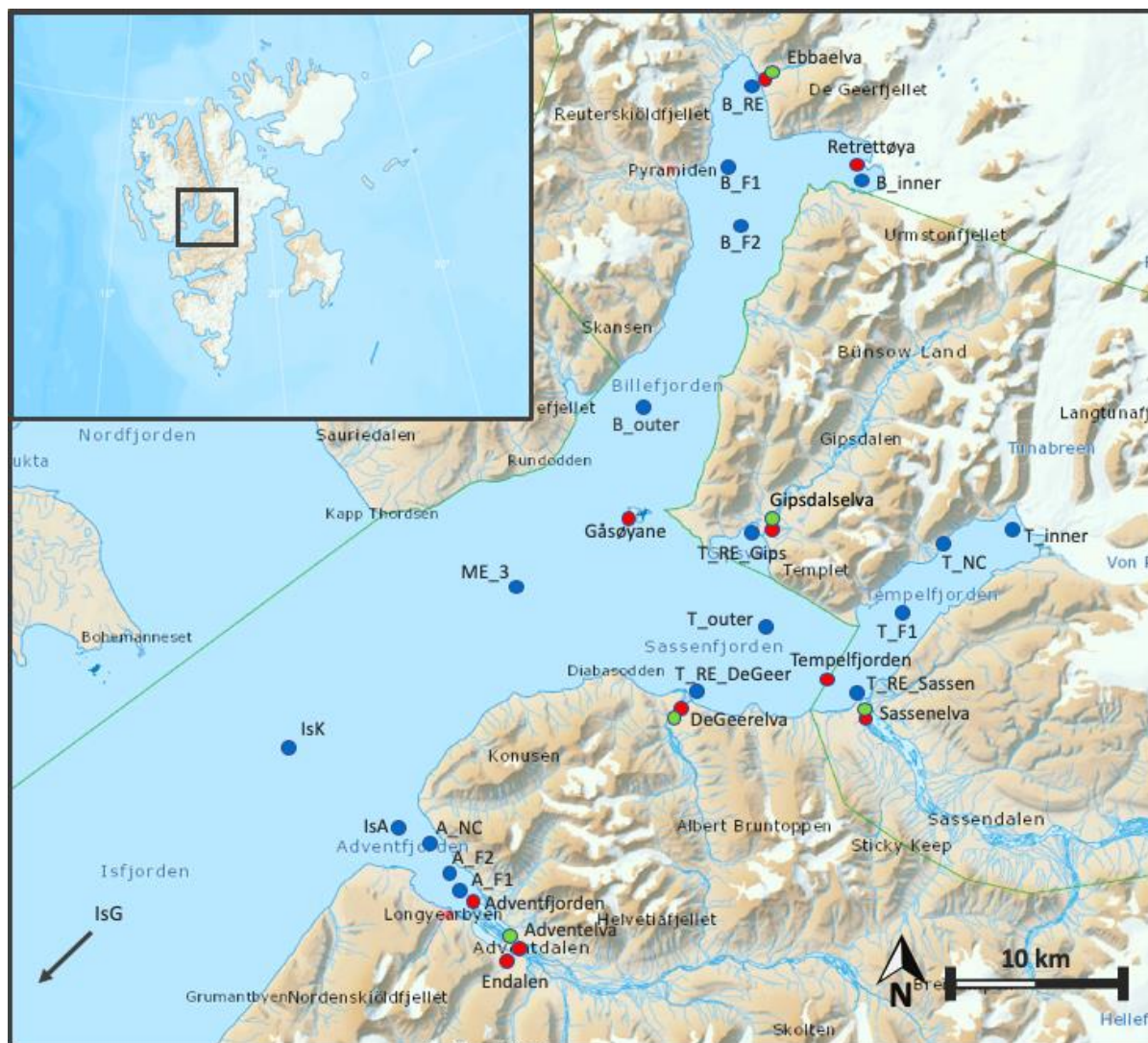
River	SPM (mg/L)*	Discharge (m <sup>3</sup> /s)	Catchment area (km <sup>2</sup> )	Glacial coverage (km <sup>2</sup> )	Glacial coverage (%)****
Adventelva	139±43	3.6**	508	~91	~18
Ebbaelva	77±55	5.0***	53	~39	~73
Degeerelva	896±718	-	79	~8	~10
Gipsdalselva	129±83	-	230	~46	~20
Sassenelva	143±89	-	810	~81	~10

\*Unpublished data, McGovern et al. (in progress). Average SPM concentration ± the standard deviation. SPM were measured monthly from May-September 2018.

\*\*From Zajaczkowski et al. (2004).

\*\*\*From Szpikowski et al. (2014); average discharge measured from 2008-2010.

\*\*\*\*Glacial coverage was estimated roughly from a map (Amanda Poste, personal communication).



**Figure 5:** Map of Svalbard and Isfjorden with Adventfjorden (south), Sassen- and Tempelfjorden (East) and Billefjorden (North). Note that the IsG sediment station is outside the map. Red=passive sampling stations, blue=marine grab sampling and green= riverine SPM sampling stations. The map is adapted from <https://toposvalbard.npolar.no> and modified.

### 3.2.3 Passive water sampling in water

Prior deployment, LDPE tubes and SR sheets were cut into single layered strips of 1 m x 5 cm. LDPE tubes were made single layer by cutting the tubing along one edge. Prior deployment, LDPEs, and SRs were pre-cleaned and extracted in ethyl acetate to remove possible contamination and then spiked with 10 performance reference compounds (CB-1, -2, -3, -10, -14, -21, -50, -78, -104, -145), covering a  $\log K_{sw}$  range of 4.2-6.7 (Smedes et al., 2009). The spiking procedure was adapted from Smedes and Booij (2012). Briefly, 35  $\mu$ L of PRC solution (50  $\mu$ g/L) was mixed with 600 mL methanol in a 5 L glass bottle and the samplers were placed in the bottle. The bottle was shaken under stepwise addition of water every 24 hour. This was done six times, until the mixture consisted of 50/50 methanol/water. After spiking, the samplers were put in sealed metal tins and stored at -20 °C until exposure.



PAS were exposed for ~12 weeks at 10 different locations – six river stations and four marine stations (figure 5 and table 3). Marine samplers were attached to a metal mesh and deployed about 5 m below the surface. River samplers were attached directly to a metal rod that was pulled into the river bed. A total of 5 LDPEs and 2 SRs were deployed at each location (All LDPEs were collected as one pooled sample, whereas the two SRs were collected as two replicates for separate analysis and quantification). Field blanks were exposed to air during the deployment. Samplers were retrieved in mid-September. Upon recovery, samplers



**Figure 6:** Retrieving passive samplers. The samplers were washed on-site before putting them into sealed metal tins. Photographer: Pernilla Carlsson.

were washed on-site in the same water to remove particles and biofouling from the surface (except Adventfjorden samplers which were taken directly to the laboratory in Longyearbyen and cleaned with milliQ water). After cleaning, samplers were put in sealed metal tins and stored at -20 °C until further extraction at NIVAs laboratory in Oslo. Unfortunately, PAS at most of the stations were not found; only Ebbaelva-, Tempelfjorden. and Adventfjorden samplers were retrieved (see table 3).

**Table 3:** Information about passive sampler deployment.

Station	Fjord	Longitude	Latitude	Location	Deployed	Retrieved
Endalen	Adventfjorden	78°20.08'N	15°81.52'E	River	19.06.18	Not found
Adventelva	Adventfjorden	78°12.18'N	15°49.74'E	River	19.06.18	Not found
Adventfjorden	Tempelfjorden	78°13.99'N	15°40.98'E	Estuary	18.06.18	10.09.18
Tempelfjorden	Tempelfjorden	78°20.89'N	16°43.33'E	Estuary	22.06.18	10.09.18
Retrettøya	Billefjorden	78°39.11'N	16°54.61'E	Glacier front	22.06.18	Not found
DeGeerelva	Tempelfjorden	78°20.53'N	16°20.00'E	River	22.06.18	Not found
Sassenelva	Tempelfjorden	78°20.35'N	16°50.43'E	River	22.06.18	Not found
Gåsøyane	Isfjorden	78°27.06'N	16°11.42'E	Marine	22.06.18	Not found
Ebbaelva	Billefjorden	78°42.35'N	16°36.57'E	River	22.06.18	10.09.18
Gipsdalselva	Tempelfjorden	78°26.45'N	16°34.59'E	River	22.06.18	Not found

### 3.2.4 Sampling of river suspended particulate matter (SPM) and marine sediments

Information about all sampling sites for river SPM and marine sediments, including sediment characteristics, is shown in table 4.

SPM (n=5) were collected in the same rivers as the passive samplers were deployed. A stainless-steel sedimentation box (SB) was made for this purpose (figure 6) based on a design described in an earlier study (Schulze et al., 2007). The SB collects suspended sediments by reducing the incoming water flow velocity which causes particles to deposit in the container, thus providing a time-integrative collection of SPM for the exposure period. The SB was mounted in the river bed and exposed about 30 cm below the river surface for ca. 24 hours. After exposure, sediments were removed from the box using a pre-

cleaned metal spoon, transferred to clean glass jars and stored at -20 °C as soon as possible. The SB collection capacity varies with SPM concentration, water velocity and particle size, and thus the amount of sediments collected in each river varied from ca. 10 g in Ebbaelva to 2 kg in Adventelva.

Marine sediment samples from Tempel- Bille- and Adventfjorden (n=19) were collected from a boat using a Van der Veen grab. The upper 0-2 cm of the sediments were sampled from undisturbed sediments before any other samples were taken, and frozen until further analysis. Sampling locations were chosen so as they covered a gradient from close shore (or the estuaries outside the studied rivers) to outer fjord. Sampling stations were divided into categories of “Inner”, “Middle” and “Outer” stations based on their location in the fjord (see figure 5 and table 4).

**Figure 6:** Sedimentation boxes (25 x 40 x 30 cm) to collect river SPM (left). Passive samplers (silicone rubber and low density polyethylene) after exposure (middle) and collection of marine sediments with a Van der Veen grab (right).



### 3.3 Analysis of sediment properties

From each sampling station, a sub-sample was devoted to determining sediment properties which included organic matter content (OM), particle size distribution and Chlorophyll- $\alpha$  content (Chl- $\alpha$ ) (Ugelstad, in progress). OM was determined by loss on ignition (520°C) and particle size distribution using laser diffraction spectroscopy (Ugelstad, in progress). Chl- $\alpha$  in sediments were determined by fluorometric analysis as described in Holm-Hansen et al. (1965). OM content, fine sediment fraction (<63  $\mu$ m) and Chl- $\alpha$  content from these measurements are included in table 4, together with other information about the sediment/SPM-sampling stations.

### 3.4 Measurements of suspended particulate matter (SPM) in water

SPM concentrations in the rivers were measured monthly from May-September (McGovern et al., in progress). Water was collected using a stainless-steel bucket and as much as possible was filtered through a pre-weighted glass fiber filter (GF/F). Volumes ranged from 100-1000 mL depending on the particle load. Filters were then dried in the oven (60 °C for four hours or until weight stabilized) and weighted again. SPM concentration was calculated as the change in weight of the filter divided by the volume of water filtered. Average SPM concentrations in the rivers for the sampling period are shown in table 2.

**Table 4:** Information about all the sampling stations for collection of marine sediment and riverine SPM, including selected sediment properties.

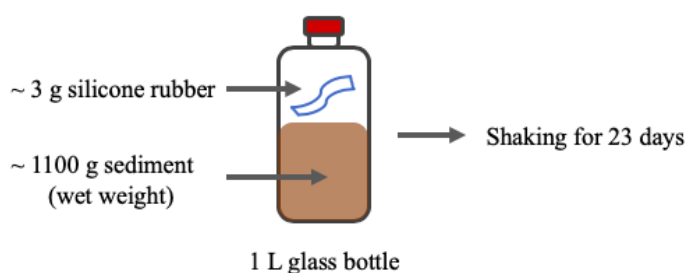
Station	Fjord	Location	Latitude	Longitude	Sampling date	Depth (m)	OM (%)	<63µm (%)	Clay (%)	Chl- <i>a</i> (µg/L)
Sassen_SPM	Tempelfjorden	River	78°20.35'N	16°50.43'E	07-08.08.18	-	6.2	N/A	N/A	N/A
DeGeer_SPM	Tempelfjorden	River	78°20.53'N	16°20.00'E	07-08.08.18	-	5.0	N/A	N/A	N/A
Gips_SPM	Tempelfjorden	River	78°26.45'N	16°34.59'E	07-08.08.18	-	1.4	N/A	N/A	N/A
T_RE_DeGeer	Tempelfjorden	Inner	78°20.92'N	16°21.16'E	20.08.18	23	7.2	94	33	630
T_RE_Gips	Tempelfjorden	Inner	78°26.24'N	16°32.85'E	22.08.18	9	6.9	99	44	2020
T_RE_Sassen	Tempelfjorden	Inner	78°20.89'N	16°48.09'E	20.08.18	10	7.7	89	32	800
T_NC	Tempelfjorden	Middle	78°25.60'N	17°05.90'E	22.08.18	16	5.9	97	43	3530
T_inner	Tempelfjorden	Inner	78°26.01'N	17°16.51'E	27.08.18	42	6.7	98	45	640
T_F1	Tempelfjorden	Middle	78°24.29'N	17°03.35'E	28.08.18	84	8.6	98	45	2080
T_outer	Tempelfjorden	Middle	78°22.71'N	16°28.22'E	27.08.18	43	9.5	99	48	1990
Ebba_SPM	Billefjorden	River	78°42.35'N	16°36.57'E	23-24.08.18	-	N/A	N/A	N/A	N/A
B_RE	Billefjorden	Inner	78°42.11'N	16°35.02'E	24.08.18	11	8.4	97	38	2320
B_inner	Billefjorden	Inner	78°38.92'N	16°54.24'E	28.08.18	46	3.8	99	39	1240
B_F1	Billefjorden	Middle	78°39.12'N	16°30.96'E	28.08.18	66	9.4	87	23	1359
B_F2	Billefjorden	Middle	78°37.63'N	16°31.22'E	29.08.18	137	10.7	93	31	682
B_outer	Billefjorden	Middle	78°30.78'N	16°14.99'E	08.08.18	104	11.0	54	18	N/A
Adv_SPM	Adventfjorden	River	78°12.18'N	15°49.74'E	02-03.08.18	-	3.0	N/A	N/A	N/A
A_NC	Adventfjorden	Middle	78°16.29'N	15°34.88'E	09.04.18	24	7.3	81	29	2100
A_F1	Adventfjorden	Inner	78°14.02'N	15°41.46'E	30.08.18	7	7.1	97	36	415
A_F2	Adventfjorden	Middle	78°14.71'N	15°40.35'E	30.08.18	43	7.7	99	43	650
IsA	Adventfjorden	Middle	78°15.80'N	15°31.80'E	18.08.18	120	6.8	97	36	5100
ME_3	Isfjorden	Outer	78°25.62'N	15°49.51'E	29.08.18	214	9.4	99	46	5690
IsK	Isfjorden	Outer	78°19.50'N	15°13.50'E	18.08.18	250	9.4	94	28	2990
IsG	Isfjorden	Outer	78°08.80'N	14°00.20'E	17.08.18	274	9.5	82	25	13090



### 3.5 *Ex-situ* equilibrium sediment passive sampling

A sediment-passive sampling experiment was conducted in the laboratory to estimate the theoretical freely dissolved aqueous concentrations ( $C_{\text{free}}$ ) based on sediment concentration (explained in section 2.5). The experiment was set up as shown in figure 7. Adventelva SPM was the only sample with sufficient amount of sample material to perform such an experiment. A rule of thumb is that a  $N_s/N_{\text{sed}}$ -ratio  $< 5\%$  yields a  $C_{\text{free}}$ . Equation 4 (from section 2.5) was used to calculate the mass of SR and the mass of sediments required to yield  $C_{\text{free}}$  (details are provided in appendix 4). It was calculated that  $> 800$  g of sediments (d.w.) and 3 g of SR was sufficient to meet these requirements. Thus,  $\sim 1100$  g of sediment (wet weight) was incubated together with 3 g of SR (pre-cleaned, non-spiked) in a 1 L clean glass bottle (water content was found to be  $\sim 20\%$  from drying 20 g of a subsample in an oven at  $60^\circ\text{C}$  for three hours, and weighing the sample until the weight was constant). After sediment and SR was transferred to the bottle, around  $\sim 50$  mL ultra-pure water was added to make a miscible slurry. The glass bottle was capped with aluminum line lid and placed on an orbital shaker (120-150 rpm) and shaken for 23 days. A blank sample was treated similarly but without sediment. After exposure, the SR sheet was removed from the bottle and cleaned with ultra-pure water to remove any remaining sediment particles. The SR-sheets were then extracted as described in section 3.6.1.

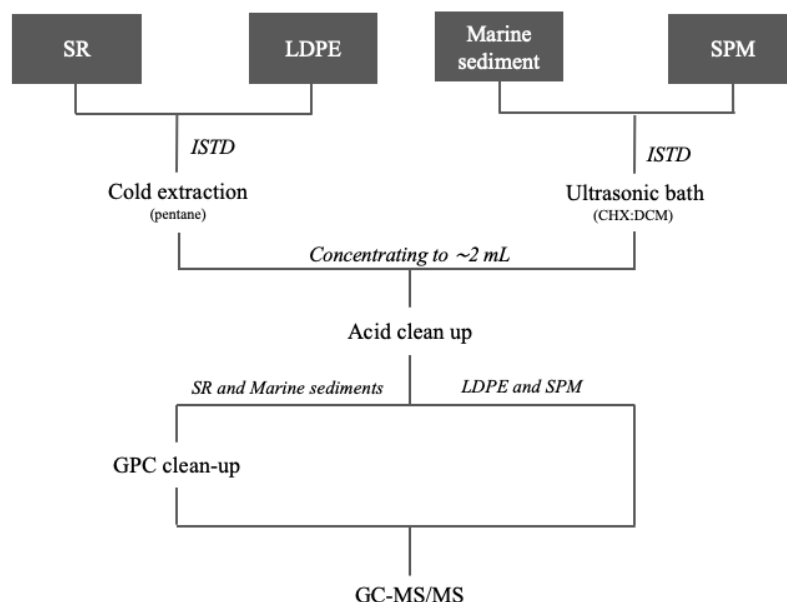
An estimate of the freely dissolved concentration was obtained from the sampler-water equilibrium formula (2) shown in section 2.4.  $K_{\text{sw}}$  values for each of the target compounds were obtained from Smedes et al. (2009).



**Figure 7:** Experimental setup for the equilibrium sediment passive sampling experiment.

### 3.6 Sample preparation and analysis

A schematic representation of the general sample preparation procedure is shown in figure 8.



**Figure 8:** Schematic representation of the sample-preparation before instrumental analysis. SR=silicone rubber. LDPE=low density polyethylene, SPM=suspended particulate matter.

#### 3.6.1 Extraction of PAS and sediment/SPM samples

##### Extraction of passive samplers (LDPE and SR)

Extraction of analytes from the passive samplers was done by cold extraction with n-pentane (Pintado-Herrera et al., 2016). Prior extraction, the sample strips were cleaned with ultra-pure water and dried with a clean tissue before transferred directly to 500 mL glass bottles. Pentane were added to the extraction bottles to cover the samplers completely, followed by addition of 50  $\mu$ L internal standard (ISTD) before the first extraction (ISTD; CB-30, -53, -204; 1  $\mu$ g/mL). Passive samplers were extracted for 24 hours before the extract was transferred to zymark tubes. This process was repeated once more while the first extract was covered properly with clean aluminum foil. Both extracts were combined, iso-octane was added as a keeper and the samples were evaporated to ca. 1 mL with TurboVap. After volume reduction, extracts were transferred quantitatively with cyclohexane to reagent tubes for acid clean-up.

##### Extraction of sediments and river SPM

Prior extraction, sediment/SPM-samples were freeze dried and homogenized, and particles >5 mm were removed. For determination of total sediment concentration, 5-12 g of each sample were transferred to 50 mL centrifuge tubes and extracted twice (2 x 60 min) in an ultrasonic bath with 40 mL cyclohexane:dichloromethane (v:v/1:1) (Zhang et al., 2015). Before the extraction started, 50  $\mu$ g of ISTDs was added to each sample. Extracts were separated from the solvent-sediment mixture by pouring the solvent into a zymark tube after centrifugation. Sequential extracts were combined and concentrated

to approximately 1 mL with TurboVap and (subsequently) transferred with a glass pipette to reagents tubes for sulfuric acid cleanup (transferred quantitatively with cyclohexane to 2 mL).

In addition, to evaluate the association of contaminants with the fine sediment fraction of sediments (<63 µm grain size), selected samples (A\_F1, A\_F2, IsA, IsK, IsG, T\_outer, me\_3, Sassen SPM, T\_RE\_Sass, T\_RE\_Deg, Advent SPM, Degeer SPM) were sieved through a clean stainless steel mesh (<63 µm) on a sieve shaker before extraction (this was done in addition to analyzing total concentration). Due to practicalities related to laboratory access, those samples were sieved and analyzed before grain size results were available (see section 3.3).

### *3.6.2 Clean-up of PAS and sediment/SPM samples*

All sediment- and passive sampler extracts contain compounds other than PCBs and chlorobenzenes, such as lipids and sulphur, which have to be removed before analysis, since they might interfere with the target compounds and/or damage analytical equipment. First, all samples were cleaned by mixing the sample extract with concentrated H<sub>2</sub>SO<sub>4</sub>. This method removes lipids and other organic molecules that are not stable in acidic conditions. SRs and marine sediment samples went through an additional clean up step with Gel Permeation Chromatography (GPC) to remove silicone oligomers (Smedes & Booij, 2012) and sulfur (Smedes & de Boer, 1997), respectively. This method is based on the size exclusion principle and separates compounds according to the size and shape of the molecules: Larger molecules like many lipids and polymers are removed as they elute before the target analytes.

#### **Acid treatment**

Acid treatment was done by mixing (and shaking) the pre-concentrated extract (approximately 2 mL) with 2 mL of concentrated sulfuric acid (96 %). Usually, a brown/yellow color was observed in the acid phase after mixing. The acid phase was removed with a glass-pipette and the treatment was repeated two more times or until coloring no longer was observed in the acid phase. As H<sub>2</sub>SO<sub>4</sub> damage the GC-instrument, this had to be removed before analysis. Accordingly, about 1 mL of ultra-pure water was added after acid-clean-up to remove remaining acid residues. Water was removed with a glass pipette and by adding sodium sulfate (NaSO<sub>4</sub>). The organic layer was then transferred with a glass pipette from the reagent tube to separate vials, depending on further treatment: LDPE- and SPM samples were transferred directly to 900 µL GC-vials and concentrated to about 100 µL with a gentle stream of nitrogen and stored at 4 °C until analysis.

After acid treatment, precipitates were observed in the LDPE extracts. It was attempted to remove it by filtration, but new precipitation was observed after a short time in the fridge. Because of this, LDPE samples were not analyzed for PCBs/chlorobenzenes.

#### **Clean up with Gel Permeation Chromatography**

For GPC clean up, SR and marine sediment extracts were solvent exchanged to 80:20-ethylacetate:cyclohexane and transferred to centrifuge filter tubes and centrifuge-filtrated at 7-12 x 10<sup>3</sup> RPM for 10 sec. If particles/precipitation was observed, samples were filtered once more. After filtration, the samples were transferred to 2 mL glass vials and stored at 4 °C until GPC-clean up. Glean up was on an Agilent 1260 Infinity II equipped with a GPC column (Agilent PLgel; inner dim: 7.5 x 300 mm; particle size: 10µm) and UV-detector. 80:20 ethyl acetate-cyclohexane was used as eluent, and the flow rate was set at 2 mL/min. Samples were injected twice (100 µL x 2) and each fraction was

collected between 4.6 min and 11.0 min in 40 mL ACE tubes. The two fractions were combined and reduced to <0.5 mL and transferred quantitatively with cyclohexane to 900  $\mu$ L GC-vials. Samples were further reduced to approximately 100  $\mu$ L and stored at 4 °C until analysis.

### 3.6.3 Instrumental Analysis

All samples were analyzed for 15 target PCBs (CB-28, -31, -44, -52, -101, -105, -118, -138, -149, -153, -156, -170, -180, -194, -209), HCB and PeCB. The listed PCBs (excluding CB-209) are hereafter referred to as  $\Sigma$ PCB<sub>14</sub>. The passive samplers were analyzed for PRCs as well (CB-1, -2, -3, -10, -14, -21, -50, -78, -104, -145).

Separation and analysis were performed on an Agilent 7890/7010B gas chromatograph coupled to a triple-quadrupole mass spectrometer (GC-MS/MS) with electron ionization (EI). The GC was equipped with two ultra-inert low polar capillary columns (15 m x 250  $\mu$ m x 0.25  $\mu$ m, Agilent HP-5ms). The helium carrier gas (purity>99%) flow was set to 1.02 mL/min in the first column and 1.23 mL/min in the second column. Splitless injection was used (1  $\mu$ L injection, injector temperature: 280 °C), and the initial GC-temperature was 60 °C (held for 1 min) before increasing to 120 °C at a rate of 40 °C/min followed by an increase to 280 °C at a rate of 5 °C/min.

The MS-detector was operated in multiple reaction monitoring (MRM) mode (explained in appendix 4), using N<sub>2</sub> as collision gas (purity >99%). For each target compound, one transition m/z was used for quantification and two other transitions for identification (see appendix 4 for details). Quantification was done using the software 'Agilent MassHunter' (Quantitative Analysis B. 09.00), and analyte concentrations were determined by measuring the peak areas of the quantification ion relative to area of the internal standard (normalization to internal standard area accounts for loss of target analytes during sample preparation, and account for variances in instrumental performance). For each compound, an external eight-point calibration curve was used (a batch of calibration solutions was run before analysis of samples). Calibration curves for all compounds were linear in a range between 0.1 ng/mL and 100 ng/mL with R<sup>2</sup> values above 0,99 for each compound (all calibration curves are found in appendix 4).

### 3.6.4 Quality assurance and control

#### **Analytical considerations**

Due to poor chromatographic separation of CB-28 and -31 in the sediment samples, these two congeners were quantified together and thus reported as CB-28/31. For the PRC-spiked passive samplers, interference (most likely from the PRC-compound – CB-50) made it difficult to quantify CB-28 and -31. CB-28 and -31 are thus not reported in the results for field exposed passive samplers. CB-209 was present in the ISTD (Kine Bæk, personal communication), resulting in blank values >95% of sample concentrations. CB-209 is therefore excluded from the results.

#### **Quantification quality control**

GC-retention time in accordance with quantification standards (with a time window of 1 min) and a deviation of the quantifier and qualifier transition ion ratio below 20% were used as identification criteria. Calibration standards were analyzed between every 10<sup>th</sup> sample to keep track of retention time and to control for changes of the analytes' responses. Drift in analyte responses were within  $\pm$ 10-20% and not considered to affect the analysis.

### Blanks, limit of detection (LOD) and limit of quantification (LOQ)

For each batch followed one or two procedural blanks that were treated exactly as the samples. Blank samples account for background contamination during sampling (field blanks), preparation, storage and analysis of the samples. It was attempted to use two blanks as long as it was practically feasible. For passive samplers followed additional field blanks and transportation blanks; these were spiked samplers and were also used to determine initial PRC concentrations in unexposed samplers.

LOD and LOQ were based on background levels in blank samples and signal to noise ratios. If two or more blanks were used, LOD was based on average blank concentration plus 3 times the standard deviation (SD) between the blank values. Limit of quantification (LOQ) was based on average blank concentration plus 10 x SD. If only one blank was used, the blank value multiplied with a factor of two and five were used for LOD and LOQ respectively. If no compounds were detected in blank samples, a signal to noise ratio (S/N; calculated by the quantification software) > 3 was used for identification and a S/N > 10 for being > LOQ.

### Analysis of replicates

A triplicate of the Adventelva SPM sample was prepared and analyzed to evaluate the variation in the method (sample preparation and analysis). The relative standard deviation between replicates was low (<10%), indicating low intra-batch variability.

### Analysis of (certified) reference material

In order to assess the quality of the method, quality control samples followed each batch. For passive samplers, an in-house reference SR-sheet, spiked with a known amount of target analytes was used. For sediments, a sample of certified reference material (SRM 1944) followed each batch. Results for SRM 1944 and the reference SR sheet is shown in table 5 and 6. The obtained average values for compounds in SRM 1944 were all within  $\pm 20\%$  of the average certified values, except HCB (which were 39% below) and CB28/31 (21 % below). Values for the reference SR-sheet (n=1) were within 85-139% of the stated average values.

**Table 5:** Results for SRM 1944 (n=5) in ng/g d.w. One sample followed each batch. Result represent the average concentrations and standard deviations are in parentheses..

Compound	Certified value	Measured	Average diff (%)
HCB	6.0 (0.4)	4 (0.6)	61
CB28/31	160	127 (13)	79
CB52	79 (2)	69 (5)	86
CB101	73 (2.5)	58 (5)	80
CB105	24 (1.1)	21 (3)	86
CB118	58 (4.3)	49 (6)	84
CB153	74 (2.9)	68 (6)	92
CB138	62 (3)	71 (8)	115
CB156	6.5 (0.7)	7 (1)	105
CB180	44 (1.2)	46 (3.5)	105

**Table 6:** Measured and stated concentrations (ng/SR sample) in the in-house reference SR sheet (n=1). Values in brackets are SD of the average values for the reference SR sheet.

Compound	Stated value	Measured	Diff (%)
HCB	8 (1)	7	85
PeCB	5 (2)	5	104
CB28+31	17 (2)	21	125
CB52	9 (1)	10	111
CB101	8 (1)	10	120
CB105	8 (1)	11	138
CB118	8 (1)	11	138
CB138	8 (1)	11	139
CB153	8 (1)	9	108
CB156	10 (2)	11	119
CB180	9 (1)	11	129

### 3.7 Calculations of dissolved concentrations ( $C_{free}$ ) in water from *in situ* passive sampling

All sampler water partition coefficients ( $K_{sw}$ ) used in this study to calculate  $C_{free}$  were obtained from Smedes et al. (2009).  $K_{sw}$  for PeCB was not found, and  $C_{free}$  in water was therefore not calculated for this compound. Aqueous concentrations of PCBs and chlorobenzenes were calculated according to Smedes and Booij (2012) based on the mass of compounds accumulated into the SR-sheets, using equation 5.

$$C_{free} = \frac{M_s}{K_{sw}m_sDEQ} \quad (5)$$

Where  $M_s$  is the mass (pg) of a target compound in the SR-sampler,  $m_s$  is the mass of the sampler (kg) and  $K_{sw}$  is the sampler-water partition coefficient (L/kg) for the specific compound. DEQ (Degree of Equilibrium) is the degree of equilibrium that each compound attained during exposure and is determined by equation 6.

$$DEQ = (1 - \exp(\frac{R_s t}{K_{sw}m})) \quad (6)$$

Where  $R_s$  is the in-situ sampling rate for each compound (expressed as L/d) and  $t$  is exposure time (d). Close to equilibrium, the DEQ-factor will approach 1 and the denominator in equation 5 will only depend on the partition coefficient and the concentration in the sampler.  $R_s$  for each compound was estimated based on the dissipation of spiked PRCs by using the model from Rusina et al. (2009), shown in equation 7.

$$R_s = \beta K_{sw}^{-0,08} \quad (7)$$

Where  $\beta$  is an adjustable parameter that depends on hydrodynamic conditions, such as temperature and flow-rate.  $\beta$  was estimated from  $R_s$ -values calculated from the dissipation of the PRCs. This was done by plotting the retained PRC-fraction as a function of  $K_{sw}$  using non-linear least squares estimation (Booij & Smedes, 2010). (details are provided in appendix 3). Then equation 7 was used to extrapolate  $R_s$  for all target compounds.

### 3.8 Calculations of dissolved concentrations ( $C_{free}$ ) in water from sediment partitioning

In order to assess the possible sorption/desorption behavior of river SPM and sediments with regards to PCBs and HCB, TOC-normalized  $C_{free}$  were calculated based on sediment concentrations. From comparing estimated  $C_{free}$  with actual measured  $C_{free}$  (with PAS), one can assess if the sediments are likely to act as a sink or a source of contaminants to the water column (Prokeš et al., 2012). For example, if estimated  $C_{free}$  is much lower than measured, one can assume non-equilibrium conditions and a net flux of contaminants from water to particles.

$C_{free}$  for all compounds based on sediment concentrations were estimated using equation 1 from section 2.3. For this particular study, only Adventfjorden were included, because TOC levels in the sediments were available from literature: Evenset et al. (2009) reported TOC-fractions in sediments in Adventfjorden to be quite consistent around 2 % from the inner to outer parts of the fjord, similar as seen for OM-content in the present study (around 7-9 %) (table 4). For Adventelva SPM, 1 % TOC content was chosen because OM content was about 3% in this sample. Literature  $K_{oc}$  values were obtained from Arp et al. (2009) who has collected several peer-reviewed  $K_{oc}$ -values for PCBs in sediments. For each compound, the average between all the available  $K_{oc}$ -values was used to calculate  $C_{free}$ . These values are listed in table 9, and results are presented in figure 13 as the ratio between sediment and PAS-based estimations of  $C_{free}$  ( $f_{sed}/f_{PAS}$ ).

In addition to estimate  $C_{free}$ , it might be useful to calculate empirical  $K_{oc-w}$  values. Such values can also help to evaluate possible equilibrium/non-equilibrium conditions. For example, if the calculated  $K_{oc-w}$ 's are low compare to literature values, it might indicate non-equilibrium conditions. Conversely, high  $K_{oc-w}$  might indicate strong sorption to sediments.

$K_{oc-w}$  was calculated from equation 1 from using the same TOC-normalized sediment concentrations as previously, and the measured  $C_{free}$  in Adventfjorden (with PAS). Results are presented in table 9.

### 3.9 Estimation of fluxes

Freshwater associated fluxes of contaminants (particulate and dissolved) were estimated for Ebbaelva and Adventelva, as river discharge for these rivers were available from literature (see table 2). The following formulas were used to calculate riverine contaminant fluxes:

$$Flux_{(particulate)} = C_{SPM} N_{SPM} D_{season} \quad (8)$$

$$Flux_{(dissolved)} = C_{free} D_{season} \quad (9)$$

Where  $C_{SPM}$  is concentration of  $\sum PCB_{14}$  or HCB found in SPM samples (mg/g),  $C_{free}$  is the concentration of  $\sum PCB_{12}$  or HCB measured with PAS in Ebbaelva (mg/L),  $D_{season}$  is discharge (L/season) and  $N_{SPM}$  is the amount of SPM measured in the river (g/L). SPM-concentrations that were used are listed in table 2. Discharge from literature was reported as m<sup>3</sup>/s, and discharge per season was derived by assuming a melting season of 120 days. Concentrations are converted to mg/g to yield fluxes in mg/season. Calculated riverine fluxes of the contaminants are shown in table 8.

### 3.10 Data handling and statistics

The free software PAST 3.24 (2019) was used for statistical analysis (Hammer et al., 2001). For data exploration and statistical analysis, all values below LOD were replaced with a random value between  $\frac{1}{2}$ -LOD and LOD using a random number generator. These values were included in statistical analysis if number of LODs were <40% for one group of samples. When calculating sums (e.g.  $\sum \text{PCB}_{14}$ ), values below LOD were set to zero. For statistical analysis, a p-value <0.05 was chosen as significant level.

#### 3.10.1 Analysis of variances

A Kruskal-Wallis test was used to check if median concentrations of  $\sum \text{PCB}_{14}$ /HCB in the different sample categories (River SPM, Inner, Middle and Outer) were significantly different from each other. A t-test was used to check if average concentrations of  $\sum \text{PCB}_{14}$ /HCB in sieved and non-sieved samples were significantly different.

#### 3.10.2 Regression analysis

Many (bio)geochemical processes affect the sediment concentration of POPs, e.g. OC/OM content, particle size distribution and sedimentation rate- and type (organic, biological or inorganic). In order to test the importance of these variables, and to follow possible sources and routes of transport of PCBs and chlorobenzenes, the impact of sediment- OM, -Chl- $\alpha$ , sediment fine fraction (<63  $\mu\text{m}$ ), clay content and distance from nearest freshwater source (as a measure of terrestrial impact) on PCBs and HCB were investigated. For this purpose, PCB and HCB concentrations were log transformed.

For regression analysis, CB-52 was chosen as a PCB-indicator instead of using the sum of PCBs. Using CB-52 as an indicator has several advantages over using the sum: CB-52 was present at higher concentrations in the river SPM and inner stations and were above LOD for all samples except DeGeer SPM. Using sums is problematic when comparing samples where many of the congeners are below LOD, which was the case for SPM- samples and inner marine stations. In addition, CB-52 is assumed to be less affected by local pollution in Isfjorden compared to other congeners (e.g. penta- and hexa chlorinated congeners) (Evenset et al., 2009), hence any local impact is reduced.

The distances from nearest freshwater source were measured using the measuring tool in <https://toposvalbard.npolar.no>, based on visual determination. A drawback of this method is that for some stations, this included other freshwater sources than the studied rivers, which might have other physical/chemical characteristics than the studied rivers. However, as a general estimate of terrestrial impact on the fjords, this was the best method available. In order to decrease any variation caused by different OM-content, OM-normalized contaminant concentrations (pg/g OM) were used.

#### 3.10.3 Principal Component Analysis (PCA)

In this study, principle component analysis (PCA) was used to visualize the contaminant-based profiles of the study area. This multivariate technique allows to visualize common similarities between sampling stations based on correlations between variables. In a simple manner, a PCA plot shows clusters of samples based on their similarity. Briefly, during PCA analysis, all variables are transformed into a new set of orthogonal variables called principal components (PC). The first component explains the largest amount of variance between the samples (in this case, the sampling stations), and the second component



explains the second most etc. A loading plot shows how strongly each variable influences a principal component and might be included in the PCA plot as vectors pinned in the origin of PC1 and PC2, pointing in one direction according to how much their influence PC1 and PC2. For example, a component (variable) pointing in a direction parallel to PC1 has stronger influence on PC1 than PC2.

For PCA analysis in PAST, log transformed, OM-normalized concentrations of all congeners, HCB and PeCB were used with the assumption that the contaminants are found mainly in the organic matter fraction of the sediments.

## 4.0 RESULTS

### 4.1 Concentrations of PCBs and chlorobenzenes (HCB and PeCB) in sediments and river SPM

#### 4.1.1 PCBs

Concentrations of all the analyzed PCB congeners, HCB and PeCB are shown in table 7. There were no significant difference between averages of sieved and non-sieved samples (<63  $\mu\text{m}$ ). However, since sieved and non-sieved samples were analyzed in different batches, there was some variation in the number of congeners detected due to different LODs. For simplicity, the sieved samples are not presented in the table, but are shown in appendix 2, together with information about all the analyzed samples and compounds, including their LODs and LOQs.

Concentrations of  $\sum\text{PCB}_{14}$  in marine sediments ranged between 18-284, 12-226 and 15-1650 pg/g dry weight (dw.) in Adventfjorden, Tempelfjorden and Billefjorden respectively. Concentrations at the outer stations (Isfjorden) were in the range of 627-875 pg/g  $\sum\text{PCB}_{14}$  dw.

Levels outside Pyramiden (B\_F1 and B\_F2) were almost a factor of two higher than median concentrations of all sediments from this study. In general, lowest concentrations were found at inner stations, that is, sediment samples taken near shore, close to glaciers and estuarine sediments, and the concentrations generally increased in samples taken further from land. Median sediment concentrations of  $\sum\text{PCB}_{14}$  for middle- and outer stations were about an order of magnitude higher compared with the inner stations (Kruskal-Wallis  $p < 0.05$ ). At inner stations, concentration of individual congeners typically ranged from <LOD up to LOQ. At middle and outer stations, > 90 % of concentrations were >LOQ. CB-52 and -153 was the only congeners that were >LOD at all sampling stations.

PCB levels in river-SPM were very low, with  $\sum\text{PCB}_{14}$  varying from 2 pg/g dw. in DeGeer SPM (two congeners detected; CB-105 and -118) to 28 pg/g dw. in Adventelva-SPM (10 congeners detected). The dominating congener in all the river SPM samples except DeGeer (<LOD) was CB-52, with an average concentration of  $10 \pm 3.6$  pg/g d.w.

#### 4.1.2 HCB and PeCB

Concentrations of HCB and PeCB in marine sediments ranged from 10 to 770 pg/g d.w. and 8.7-240 pg/g d.w., respectively. In general, they followed the same trend as for the PCBs with increasing concentrations with increasing distance from land. Similar as for the PCBs, median concentrations of PeCB and HCB were significantly higher at middle and outer stations compared to inner stations (Kruskal-Wallis  $p < 0.05$ ). Concentrations were above LOQ at all stations, except PeCB for the B\_inner station that were below LOD (appendix 2). No increase in HCB and PeCB levels were observed outside Pyramiden or Longyearbyen.

SPM related concentrations of HCB and PeCB ranged from 15-103 and 3.0-24 pg/g dw. for HCB and PeCB, respectively (Sassenelva > DeGeerelva > Adventelva > Gipsdalselva > Ebbaelva) and were > LOQ at all stations.

## 4.2 Aqueous concentrations of PCBs and chlorobenzenes

Aqueous concentrations measured with SR-samplers are shown in table 7. Due to chromatographic interferences, CB-28 and -31 was not quantified for SR samples (explained in section 3.7.4) and hence, PCB concentrations in the dissolved phase are reported as  $\sum\text{PCB}_{12}$ .  $K_{\text{sw}}$  for PeCB was not obtained, hence is not included in the results.

Tempelfjord had highest concentrations of all the detected congeners ( $\sum\text{PCB}_{12}$ : 3.2 pg/L), followed by Ebbaelva ( $\sum\text{PCB}_{12}$ : 1.9 pg/L) and Adventfjord ( $\sum\text{PCB}_{12}$ : 0.4 pg/L). CB-101 was dominating congener at both the Ebbaelva- and Tempelfjord station (1.98 pg/L and 0.86 pg/L respectively). In Adventfjorden, CB-101 was below LOD (<0.45 pg/L). HCB were dominating in samples compared with  $\sum\text{PCB}_{12}$  and were 10, 38 and 49 pg/L in Adventfjord, Tempelfjord and Ebbaelva, respectively.

Calculation of sampling rate ( $R_s$ , L/day) of individual compounds based on dissipation of PRCs is described in appendix 3. The retained fraction of CB-1, which has the lowest  $\log K_{\text{sw}}$  (4.2) among the PRCs used, ranged from 24-55%. CB-145 was the PRC with highest  $\log K_{\text{sw}}$  (6.7) and ranged between 80-95% of the original spiked concentration. All target compounds were < 20 % from equilibrium and assumed to be in the linear uptake regime. The sampling rate at  $\log K_{\text{sw}}=5$  was 7.0-8.1 L/day at the Adventfjorden station, 3.5 L/day in Tempelfjorden and 8.1-11.8 L/day in Ebbaelva, illustrating the different hydrodynamic conditions. Sampling rate generally increases with flow rate, which is probably why the highest sampling rate is observed at the river station (Ebbaelva).

**Table 7:** Concentrations of HCB, PeCB and individual PCB congeners and  $\Sigma\text{PCB}_{14}$  in marine sediments, riverine suspended particulate matter (pg/g dw.) and in water (pg/L). For water concentrations,  $\Sigma\text{PCB}_{14}$  equals to  $\Sigma\text{PCB}_{12}$  because CB-28 and CB-31 was not quantified. Concentrations labelled with a star (\*) are below limit of quantification (LOQ).

	HCB	PeCB	CB28/31	CB44	CB52	CB101	CB105	CB118
<b>ADVENTFJORD</b>								
Inner (n=1)	91	5-22	<LOD	<LOD	9.2	2.5*	<LOD	1.3
Middle (n=3)	155-413	40-99	<LOD-43*	3.3*-19	12-41	4.3*-29	1.1-15	2.8-36
<b>BILLEFJORD</b>								
Inner (n=2)	10*-54	<LOD-17	<LOD-4.1*	<LOD-7.1	5.7*-21	<LOD-24	1.1-14	2.7-32
Middle (n=3)	152-574	42-149	22-127	31-84	62-146	96-202	51-160	125-358
<b>TEMPELFJORD</b>								
Inner (n=4)	29-106	8.7-31	<LOD-5.1*	1.0*-1.9	6-10	<LOD	<LOD-0.7	<LOD-2.0*
Middle (n=3)	55-681	14-171	<LOD-46	1.2-19	8-35	<LOD-21	1.1-8.5	3.2-22
<b>ISFJORD</b>								
Outer (n=3)	532-762	205-242	145-203	51-74	91-128	56-79	25-37	62-90
<b>RIVER-SPM</b>								
Adventelva (n=1)	69	13	1.9	1.4	14.7	4.9*	0.3	0.8
Sassenelva (n=1)	103	24	2.7*	1.3	8.7	<LOD	<LOD	2.1
Degeerelva (n=1)	98	23	<LOD	<LOD	<LOD	<LOD	1.0*	1.3*
Ebbaelva (n=1)	16	3.0	<LOD	0.3*	11.3	4.9	0.3*	0.8*
Gipsdalselva (n=1)	21	3.9	<LOD	0.8*	6.3*	3.0*	0.5*	1.4
<b>WATER (pg/L)</b>								
Adventfjord (n=2)	10	-	-	0.06*	0.08*	<LOD	<LOD	0.03
Tempelfjord (n=1)	37	-	-	0.19*	<LOD	1.98*	0.04	0.20*
Ebbaelva (n=2)	49	-	-	0.15*	0.37	0.86	0.02	0.08

	CB138	CB149	CB153	CB156	CB170	CB180	CB194	$\Sigma\text{PCB}_{14}$
<b>ADVENTFJORD</b>								
Inner (n=1)	1.8*	1.2*	1.5*	<LOD	<LOD	0.6*	<LOD	18
Middle (n=3)	3.9-35	2.1-16	3.7-29	<LOD-3.9	0.7*-5.3	1.3*-11	0.4*-1.8	35-284
<b>BILLEFJORD</b>								
Inner (n=2)	2.1-28	1.2*-11	2.2-19	<LOD-3.5	<LOD-2.8	<LOD-5.0*	<LOD-0.5*	15-170
Middle (n=3)	103-286	45-96	81-170	11-44	11-25	16-36	1.5*-2.7	760-1650
<b>TEMPELFJORD</b>								
Inner (n=4)	<LOD-2.4*	<LOD-1.4*	1.1-2.9	<LOD-0.3	<LOD-0.5*	<LOD-1.2*	<LOD-0.3*	12-25
Middle (n=3)	3.5*-22	1.4*-11	5.9-25	0.6-2.3	0.8-3.4	2.3*-7.7	0.2-1.3	28-226
<b>ISFJORD</b>								
Outer (n=3)	64-90	33-45	54-76	6.2-9.7	9.6-13	19-26	3.5-4.5	630-880
<b>RIVER-SPM</b>								
Adventelva (n=1)	1.2	1.1	1.3	0.1	<LOD	<LOD	<LOD	28
Sassenelva (n=1)	1.8	1.4	1.8	<LOD	<LOD	<LOD	<LOD	20
Degeerelva (n=1)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2.3
Ebbaelva (n=1)	0.9*	0.5*	1.0*	<LOD	0.5*	<LOD	0.6*	21
Gipsdalselva (n=1)	1.8	0.8	2.8	0.2*	0.6*	1.3*	0.3*	20
<b>WATER (pg/L)</b>								
Adventfjord (n=2)	0.06	0.04	0.05	<LOD	0.04	0.05*	<LOD	0.4
Tempelfjord (n=1)	0.23	0.12*	0.36*	<LOD	0.04	0.05	<LOD	3.2
Ebbaelva (n=2)	0.12	0.14	0.15	<LOD	0.01*	0.03*	<LOD	1.9

### 4.3 Relative composition

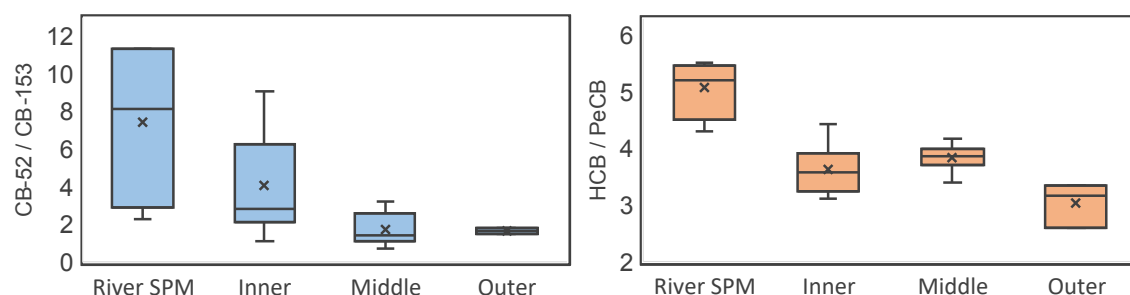
Figure 9 shows the relative abundance of  $\Sigma\text{PCB}_{14}$  and HCB (green and orange), and the relative composition of the most abundant PCB congeners in samples. For PCB-congeners, values below LOD are replaced with a random value between  $\frac{1}{2}$ -LOD and LOD. If a compound was <LOD in > 40% of the stations, this compound was excluded from the figure. CB-28/31 represented 10-20% of the total concentration in samples where they were >LOD. However, CB28/31 was <LOD in more than 40 % the sampling stations and hence was not included in the figure. The sum of the remaining congeners that are not included (CB-156, -170 and -194) represent <10% of total concentration in samples.



**Figure 9:** Relative composition HCB,  $\Sigma\text{PCB}_{14}$  and the most abundant congeners in marine sediment- and river SPM samples.

### 4.3.1 Selected ratios

Figure 10 shows ratios of CB-52/-153 and HCB/PeCB in river SPM samples and at inner, middle and outer marine stations. Note that CB-52 and -153, HCB, and PeCB were above LOQ at >90 % of the sampling stations. This is one of the reasons why these compounds were chosen for this comparison. Both ratios were decreasing from river SPM to outer sediment stations.



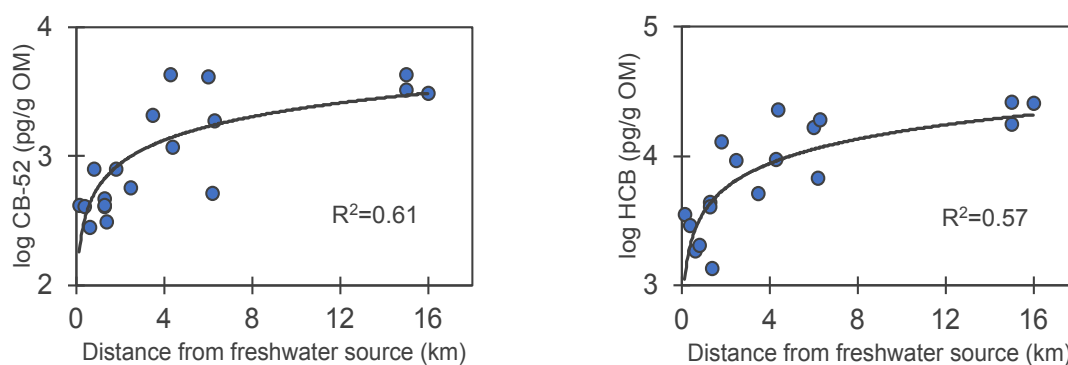
**Figure 10:** Ratio of CB-52/CB-153 (left) and HCB/PeCB (right) in river SPM- and marine sediment samples

### 4.4 Sediment properties (OM, fine sediment and Chl- $\alpha$ )

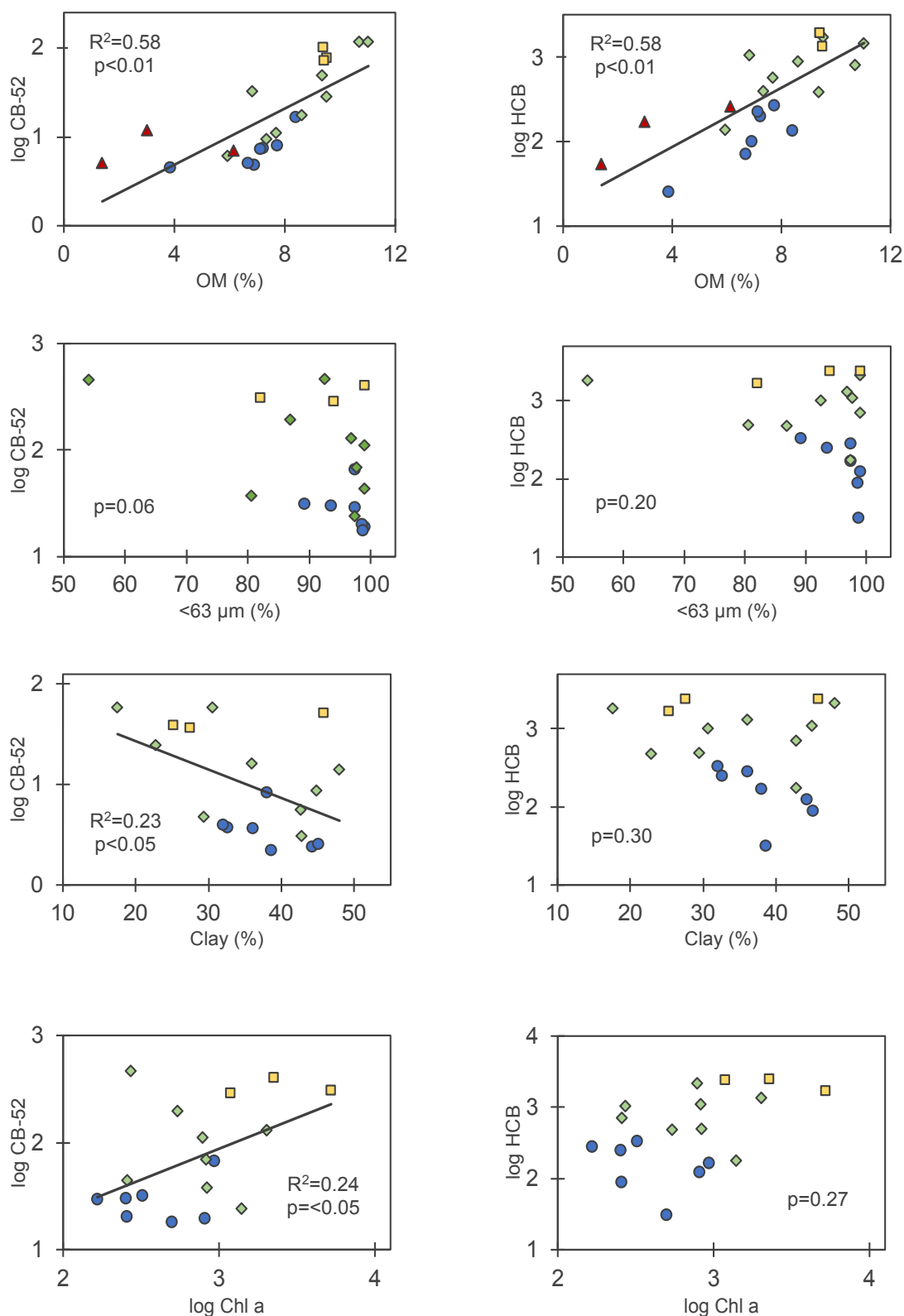
A statistically significant positive correlation was obtained for CB-52, HCB and OM content in samples ( $R^2=0.58$ ,  $p<0.01$ ). No correlation was found for sediment fine fraction (silt+clay:  $<63 \mu\text{m}$ ). However, a negative correlation was found for clay content and CB-52 ( $R^2=0.23$ ,  $p<0.05$ ). Also, for CB-52 and Chl- $\alpha$  content in sediment, a positive correlation was observed ( $R^2=0.24$ ,  $p<0.05$ ), but with a relatively large variation between samples. The relation between contaminants and sediment properties are shown graphically in figure 10 on next the page.

### 4.5 Distance from nearest freshwater source

A non-linear relationship between log transformed OM-normalized concentrations and distance from nearest freshwater source (river or glacier) were found (figure 11). The log-transformed concentrations increased the most between 0 and 3 km from the river.



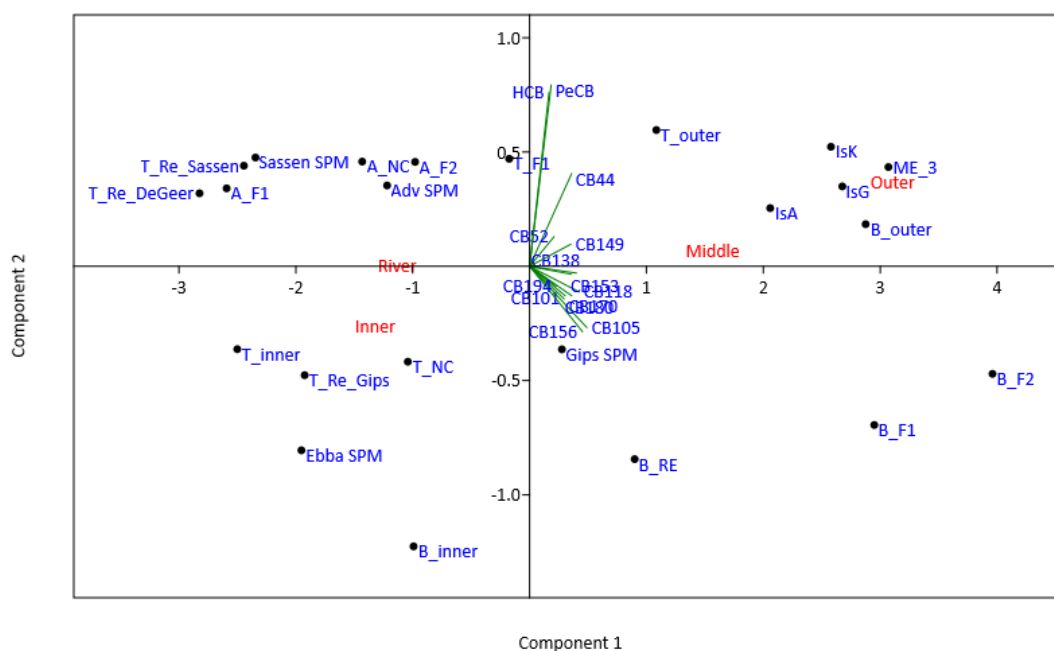
**Figure 11:** Relationship between log transformed OM-normalized concentrations of CB-52 (left) and HCB (right).



**Figure 10:** Relationship between sediment properties (OM content, fine sediment fraction (<63  $\mu\text{m}$ ), clay content, Chl- $\alpha$ ) and concentrations of CB-52 (left) and HCB (right) in marine sediments and river SPM. A regression line was fitted if linear relationship were significant ( $p<0.05$ ). Red=river SPM, blue=inner stations, green=middle stations, yellow=outer stations.

## 4.6 Principal component analysis (PCA)

Spatial variation of HCB, PeCB and 14 PCBs was analyzed by comparison of 18 marine samples and 4 SPM-samples. All concentrations were normalized for OM-content to reduce variation caused by this. PC1 explained 90 % of the variance while PC2 explained 6 % of the variance. PC1 was able to effectively separate the inner stations and SPM from the middle and outer stations. PC2 was able to separate the two stations near Pyramiden (B\_F1 and B\_F2) from the other middle/outer stations.



**Figure 12:** PCA-scatter plot of all variables included in the PCA-analysis. PC1 explained 90% of the variation while PC2 explained 5 %.

## 4.7 Fluxes of contaminants from rivers to fjords

Fluxes of SPM-associated contaminants from rivers to the receiving fjords were in the range of 36-530 mg/season (season is four months) for  $\sum\text{PCB}_{14}$  and 27-530 mg/season for HCB. Dissolved-associated fluxes of  $\sum\text{PCB}_{12}$  in Ebbaelva were in the same range, around 98 mg/season. However, dissolved HCB were dominating in Ebbaelva and were 1-2 orders of magnitude higher than particulate associated fluxes. Estimated contaminant fluxes are presented in table 8. For convenience, results from a previous study (Blais et al., 2001), which will be discussed in section 5.1, is included in the table.



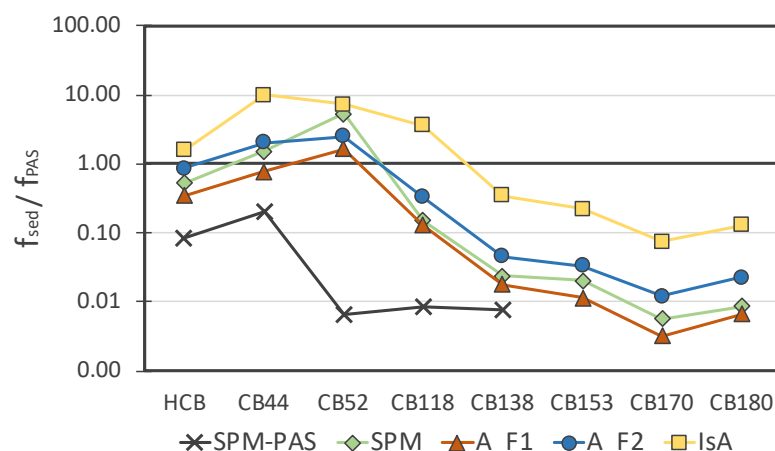
**Table 8:** Fluxes of dissolved- and SPM-associated PCBs and HCB from the studied rivers, including discharge, glacial coverage and SPM concentrations for comparison. Glacial meltwater fluxes to a high-altitude lake, Bow Lake (Canada) is included to compare results.

Location	Glacial coverage (km <sup>2</sup> )	Discharge (m <sup>3</sup> /season)	SPM (mg/L)	Compound	Flux (mg/season)	
Adventelva (this study)	91	4.7 x10 <sup>7</sup>	139±43	∑PCB <sub>14</sub>	100-210	(particulate)
				HCB	250-530	(particulate)
Ebbaelva (this study)	39	5.2 x10 <sup>7</sup>	77±55	∑PCB <sub>14</sub>	36-150	(particulate)
				∑PCB <sub>12</sub>	98	(dissolved)
				HCB	27-120	(particulate)
				HCB	2500	(dissolved)
Bow lake, (Canada)*	11	3.4 x 10 <sup>7</sup>	120±50	∑PCB <sub>104</sub>	12 000	(dissolved)
				∑PCB <sub>104</sub>	186 000	(particulate)
				HCB	150	(dissolved)

\* Blais et al. (2001)

#### 4.8 Partitioning between sediment and water

Figure 13 is showing the ratio between  $C_{\text{free}}$  which is estimated from TOC-normalized SPM/sediment concentrations (river SPM from Adventelva and Adventfjorden sediments) ( $f_{\text{sed}}$ ) and  $C_{\text{free}}$  measured with PAS in Adventfjorden ( $f_{\text{PAS}}$ ). In addition,  $f_{\text{sed}}/f_{\text{PAS}}$  based on  $C_{\text{free}}$  estimated from sediment passive sampling of Adventelva SPM (section 3.5) is included in the figure. Only compounds which were >LOD in both Adventelva PAS and all the sediments are included in the figure. An  $f_{\text{sed}}/f_{\text{PAS}}$  ratio  $\ll 1$  may indicate a net flux of the contaminants from water to particles. In converse, an  $f_{\text{sed}}/f_{\text{PAS}}$   $\gg 1$  may indicate a net flux from particles to water. The  $f_{\text{sed}}/f_{\text{PAS}}$  ratios ranged from 0.003-10 and were lower for higher chlorinated PCBs (CB-138, -153, 170 and -180).



**Figure 13:** Ratios between TOC normalized  $C_{\text{free}}$  from SPM/sediment concentrations ( $f_{\text{sed}}$ ) and  $C_{\text{free}}$  measured with PAS in Adventfjorden. In addition, the black crosses indicate the same ratio based on  $C_{\text{free}}$  estimated from equilibrium passive sampling of Adventelva SPM.

Table 9 is showing empirical sediment-water partitioning coefficients ( $K_{oc-w}$ ) based on concentrations of PCBs, HCB and PeCB in Adventelva SPM and marine sediments in Adventfjorden (A\_F1 and IsA) and  $C_{free}$  measured with PAS in Adventfjorden. For comparison, various literature  $K_{oc}$ -values from Arp et al. (2009) are included in the table.

**Table 9:** TOC normalized sediment-water partition coefficients ( $K_{oc-w}$ ) based on measured concentrations of PCBs and HCB in sediments and water in Adventfjorden. For comparison, literature  $K_{oc-w}$  values from Arp et al. (2009) are included.

Station	Calculation of various $\log K_{oc-w}$ (2% OC)			Literature $\log K_{oc-w}$ *	
	Adv SPM	A_F1	IsA	Range	Average
<b>CB44</b>	6.07	-	7.19	5.90-6.48	6.19
<b>CB52</b>	6.96	6.76	7.40	6.03-7.01	6.54
<b>CB118</b>	6.10	6.33	7.78	6.85-8.02	7.23
<b>CB138</b>	6.00	6.17	7.46	7.15-8.73	7.92
<b>CB153</b>	6.10	6.16	7.45	7.64-8.33	8.10
<b>CB170</b>	-	-	6.87		8.00
<b>CB180</b>	-	5.78	7.06	7.35-8.31	7.96
<b>HCB</b>	5.23	5.65	6.31	5.08-6.68	6.11

\*Arp et al. (2009)

## 5.0 DISCUSSION

### 5.1 Freshwater associated contribution of contaminants to the fjords.

The aqueous concentration of HCB was 50 pg/L in Ebbaelva, which is higher than measured in the marine/estuary areas in Advent- and Tempelfjorden (table 7). In addition, aqueous concentrations of selected PCBs and HCB has been measured previously in Kongsfjorden and Liefdefjorden (Hallanger et al., 2011b) and sea water outside Western Spitsbergen (Gioia et al., 2008) both from using high volume water sampling (see list of previous studies in appendix 1). They reported aqueous HCB concentrations between 2-8 pg/L, which is lower than measured with PAS in Ebbaelva. This, and considering that the Ebbaelva catchment is mostly glacial (~73%) might indicate enhanced release of HCB due to snow- and glacial melt. However, uncertainties related to the use of different sampling methodologies (passive vs. active sampling) should be considered. Allan et al. (2011) reported dissolved concentrations of HCB between 48-117 pg/L in seawater around Bjørnøya using passive sampling methodologies, which is comparable with the current results for Ebbaelva. Bjørnøya does not have any glacial cover, although it receives a large amount of snow during winter time.

Aqueous concentrations of PCBs did not show indications of elevated levels in Ebbaelva compared to the abovementioned studies (table 7 and appendix 1). Hence, the current results did not indicate enhanced rerelease from glacial runoff but seemed to rather reflect general background levels.

Comparison of dissolved concentrations should be considered carefully as several factors, such as different water characteristics (amount of particles, dissolved organic matter etc.) and inter-laboratory differences might affect the dissolved concentrations.

Concentrations of chlorobenzenes and PCBs in river SPM samples were generally low (1-2 orders of magnitude) compared to concentrations in marine surface sediments (outer fjord), and in surface sediments in the Barents Sea around Svalbard (Green et al., 2010; Zaborska et al., 2011) (table 7 and appendix 1). The difference was in general smallest for HCB, as shown by the relative larger dominance of HCB versus PCBs in river SPM samples compared to sediments from the outer marine stations (figure 9). Reasons for the relatively low levels of SPM associated contaminants might be that the samples consist of a mixture of eroded surface soil, permafrost- and particulate matter from glacial abrasion processes, that has been little exposed to the ambient environment with the possibility to accumulate local- and LRT contaminants.

#### 5.1.1 Riverine fluxes

The combination of PAS- and SPM sampling in Ebbaelva allows to investigate the contribution of particulate- and dissolved associated contaminant fluxes (mass per time) to the marine environment. Table 8 shows the estimated fluxes from Adventelva (particulate) and Ebbaelva (dissolved + particulate) during the ablation season (June-September). Considering the sorptive properties of the target compounds ( $\log K_{ow} > 4.5$ ), and the relatively large amount of particles in the studied rivers (most SPM concentrations were  $> 100$  mg particles/L) there is a likelihood that the contaminants will be mostly associated with the particulate phase (Prokeš et al., 2012). In that case, the SPM associated contaminant fluxes should be most representative for the total contribution from the rivers. However, the much higher fluxes of dissolved HCB ( $> 95$  % of total flux) in Ebbaelva (table 8), suggests that freshwater contribution of HCB is mostly linked to the dissolved fraction. Consequently, river SPM associated

contribution of HCB might not be representative for the total freshwater contribution from the other rivers where PAS-measurements are not available (see table 3). For PCBs on the other hand, dissolved fluxes in Ebbaelva constituted for a roughly 50% of total the total flux, and hence river SPM might represent a larger proportion of the total freshwater contribution of PCBs compared to HCB. This might be linked to the lower solubility of the target PCBs ( $\log K_{ow} \approx 5.7-7.8$ ) compared to HCB ( $\log K_{ow} \approx 5.5$ ), especially for the higher chlorinated congeners.

For comparison, only a few studies were found which reported glacier fed fluxes of POPs; and these were from high altitude glaciers located in the European Alps (Bizzotto et al., 2009; Bogdal et al., 2009) and in Canada (Blais et al., 2001). The two studies from the Alps reported burial flux into nearby lake sediments which is difficult to compare. The last-mentioned study from Canada, however, reported glacial meltwater fluxes (particulate + dissolved) of HCB and  $\sum PCB_{104}$  in a river feeding the high-altitude lake, Bow Lake (51°40'N, 116°28'W). Results from their study are included in table 8, together with the current results. Total flux of  $\sum PCB_{104}$  were three orders of magnitude higher into Bow Lake compared to the present study, and mostly associated with the particulate phase (>90%). HCB was only reported as dissolved fluxes and was a factor of 10 lower than in the present study. Bow Lake's position closer to potential primary sources might play an important role for the higher fluxes observed, in addition to the larger number of congeners included in the analysis, although that does not account for the large difference of PCB fluxes. Different ages of the glaciers might also be relevant; however, no such data were found for the glaciers around Bow Lake.

#### *5.1.2 Mass balance between environmental media*

Atmospheric deposition (dry deposition) to the ocean around Svalbard has been estimated to about 0.0023 kg/km<sup>2</sup> year<sup>-1</sup> for  $\sum PCB_7$  and 0.010 kg/km<sup>2</sup> year<sup>-1</sup> for HCB (Green et al., 2010). For Adventfjorden (which is about 30 km<sup>2</sup>), this would correspond to a deposition around 69 000 mg/year of  $\sum PCB_7$  and 320 000 mg/year of HCB. For Billefjorden (ca 190 km<sup>2</sup>), it would correspond to 410 000 and 1 900 000 mg/year for  $\sum PCB_7$  and HCB, respectively. These numbers are 2-3 orders of magnitude higher than the estimated fluxes from the rivers, which were in the range of 30-2500 mg during the four months of ablation (table 8). According to Green et al. (2010), the net supplies from the atmosphere is expected to be lower because the substances can also evaporate back from the sea to the atmosphere, but yet it appears that the freshwater contribution to Isfjorden is low compared to other sources such as direct atmospheric deposition. The oceanic current transport to Isfjorden is not considered here, since it is difficult to assess the magnitude of the Atlantic water influence to the fjord. However, the contribution from oceanic transport is believed to be of less importance than direct atmospheric deposition (Green et al., 2010), especially for the more volatile compounds such as HCB and low chlorinated PCBs (Burkow & Kallenborn, 2000).

#### *5.1.2 Contaminant levels related to catchment area characteristics*

The catchment areas associated with the studied rivers, vary in respect to size, topography, soil composition and glacial coverage (table 2). This will also affect the contaminant fate and mobilization between environmental compartments, and hence how much that is released into the receiving marine environment. However, the use of only one SPM sample from each river restricts the interpretation of the SPM-data. Based on this limited dataset, the size of the catchment area, or amount of glacial coverage does not seem to have any impact on the amount of analyzed contaminants in SPM samples from the

various rivers. For example, the Sassenelva catchment area is ~800 km<sup>2</sup> with ~80 km<sup>2</sup> covered with ice, while DeGeerelva catchment area is ~80 km<sup>2</sup> with ~8 km<sup>2</sup> glacial coverage, but the amount of HCB was similar in both samples. However, in the beginning of section 5.1, it was shown that HCB is likely to be more associated with the dissolved fraction, thus the SPM samples might not be representative for the total amount of HCB in the rivers. However, concentrations of PCBs (with CB-52 as indicator), did not reveal any relationship with glacial cover or catchment area size either.

### *5.1.3 Contaminant composition related to atmospheric deposition*

There was a relative higher dominance of HCB and low and mid chlorinated PCB congeners (CB-52 and -101) in the river SPM samples (figure 9 and 10). This can be related to that these compounds are relatively volatile, and hence more prone to atmospheric transport and subsequent deposition over land compared to higher chlorinated PCBs (Burkow & Kallenborn, 2000). Deposition of these compounds is likely to occur in form of snow during the colder winter months (Burkow & Kallenborn, 2000), but there is a complex interplay between deposition- and re-evaporation processes (especially during the warmer summer months) which is not fully understood. This is reflected in seasonal fluctuations in measured air concentrations.

The higher dominance of HCB and low- and mid-chlorinated compounds in the rivers is supported by air measurements at the Zeppelin station (Ny-Ålesund) where lower chlorinated PCB-congeners (such as tri- and tetra chlorinated) and other volatile compounds such as HCB are dominating (AMAP, 2004; Hung et al., 2010). Although PCB and HCB levels in air measured at Zeppelin have shown a general decline since the monitoring began in the late 1990s, the decrease of CB-52 and CB-101 has more or less stagnated, and HCB has shown increasing trends at Zeppelin in recent years. This has been attributed to re-emission of previously deposited HCB and PCBs from oceans and ice, and a continuous release of HCB from primary sources (Hung et al., 2016).

A recent study from Lomonsovfonna (Svalbard) might partly explain the large dominance of CB-52 in the river SPM samples (figure 9 and 10) (Bartlett et al., 2019). They found that CB-52 was the most abundant of all congeners in the surface snow in 2014. In addition, more CB-52 was present compared to previous measurements from 2010 from the same glacier (Garmash et al., 2013), and they argued that reasons might be transportation of recently (unintentionally) produced PCBs from pigment production. However, it is important to keep in mind that both studies are based on only one ice core each.

### *5.1.4 Freshwater contribution summarized and future perspectives*

To the authors best knowledge, this is the first study measuring actual riverine SPM- and aqueous associated concentrations of PCBs and chlorobenzenes in high Arctic fjord rivers. The detection of PCBs and chlorobenzenes in river SPM samples and in the Ebbaelva PAS, supports previous indications of secondary release of contaminants from melting snow and glaciers into the marine system (Carlsson et al., 2012). However, more investigations are needed to provide a robust quantitative understanding of the freshwater contribution of contaminants to Arctic fjord systems. This would include frequent sampling of river SPM samples to assess for temporal and spatial fluctuations within each of the rivers. This can possibly also contribute to a better comparison of the different catchment areas with regards to geochemistry and glacial coverage. Further investigations of contaminants related to SPM and transport are therefore being discussed within the TerrACE project for the continuation of the project.

PAS provided a simple estimation of time weighted average concentration for the whole ablation season, which was beneficial since they represent the contaminant situation in the river over time. However, larger peaks in contaminant levels might have been missed, for example as a result of episodic melting events of snow- and ice consisting of higher levels of contaminants.

## 5.2 Local sources

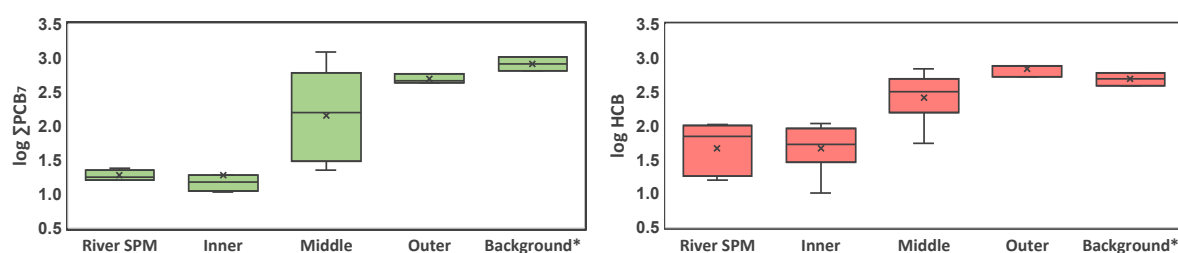
The highest concentration levels of PCBs were found in sediment samples outside Pyramiden (B\_F1 and B\_F2) and can be attributed to local pollution (Evenset et al., 2009; Jartun et al., 2009). Contaminants from this area leach into the marine environment, causing elevating levels in sediments outside Pyramiden. This was shown by Evenset et al. (2009) which found that PCB-levels in marine sediments outside Pyramiden were much higher than expected background levels (with  $\sum\text{PCB}_7$  varying from 2-20 ng/g d.w.), with the highest concentration in samples close to land (see appendix 1 for an overview of their results).

Local pollution is also indicated by the relative increase in penta-CB-101 and -118 and hexa-CB-138 at these two locations (figure 9), which is related to the use of major Soviet commercial PCB-mixtures (Sovol) which is composed of mainly mid-chlorinated compounds, such as hepta- and hexa-PCBs (Gabrielsen et al., 2011; Ivanov & Sandell, 1992). The influence of local sources is also shown by the separation of these two stations from other sampling stations in the PCA plot (figure 12). B\_F1 and B\_F2 is clearly separated from other stations that are situated further away from local settlements.

The influence of local pollution contributed to additional variation in the dataset, which can be seen from the larger range of PCB concentrations in the “Middle” category (for example as seen in figure 14 in section 5.3), since the B\_F1 and B\_F2 stations were in this category. However, the contribution of local pollution did not affect the main conclusions of this study.

## 5.3 Contribution of sedimentary particle fluxes to spatial distribution of contaminants in the fjords

The degree of terrestrial/riverine impact of sediments with associated low contaminant levels seem to be the most prevailing factor governing the spatial distribution of PCBs and chlorobenzenes within Isfjorden. This might be further enhanced by limited exchange of Atlantic sea water to the inner parts of the fjord.



**Figure 14:** Log-transformed concentrations of  $\sum\text{PCB}_7$  (left) and HCB (right) at different sampling stations in comparison with concentrations in surface sediments in the Barents sea outside Svalbard (Background\*), from Green et al. (2010). The results for River SPM, Inner, Middle and Outer stations are based on concentrations found in table 7.

Figure 14 is showing  $\Sigma\text{PCB}_7$  and HCB from the current study (based on results from table 7) in comparison with concentration levels in surface sediments of the Western Barents sea (Green et al., 2010), representing background concentrations in surface sediments around Svalbard. In general, contaminant concentrations in Isfjorden seem to increase from inner to outer stations where they are comparable with background sediment concentrations. The observed trend was most prevailing for the PCBs but also present for HCB. The observed trend is contradictory to previous studies in Svalbard fjords (Pouch et al., 2017; Pouch et al., 2018; Sapota et al., 2009). They reported higher concentrations of  $\Sigma\text{PCB}_7$  in surface sediments from the inner parts of the fjords, due to a possible influence of terrestrial/meltwater runoff. This study shows that direct atmospheric deposition and marine current influence is more important for PCB and HCB inputs to the fjord sediments, similar as found for legacy OCPs in Kongsfjorden (Ma et al., 2015).

Unlike previous studies, the current study provides an additional dimension by including SPM samples from the associated rivers that can be assessed in conjunction with spatial distribution patterns in the fjords. Sedimentation of particles from rivers is likely to decrease further from the river, for example as shown in Adventfjorden by Zajackowski et al (2004) who showed that sedimentation rates within Adventfjorden decreased from about 1.9 cm/year from inner parts of the fjord, to 0.9 cm/year in the outer parts. As a consequence, the inner stations seem to reflect river SPM with regards to both concentration levels (figure 14) and relative composition (figure 9 and 10), whereas the latter can be seen from the relative increase of CB-52 in river SPM and inner marine stations. Similarities between river SPM and inner stations is further illustrated by the clustering of these samples during the PCA analysis (figure 12).

### *5.3.1 Impact of sediment properties on spatial PCB and chlorobenzene distribution*

Although there was a fairly good agreement between the concentrations of OM and POPs-levels in sediments ( $R^2=0.58$ ), OM contents alone were not enough to explain the increasing concentration gradient observed from inner to outer stations. This is illustrated in figure 11 where OM normalized concentrations increase with distance from the nearest freshwater source. However, this is in contrast to previous studies stating that OM or organic carbon content in sediments can explain the distribution of POPs within a certain area, influenced by the same sources (Gustafsson et al., 2001). However, the differences in OM normalized concentrations of POPs in this study can rather be attributed to different sources (terrestrial vs. marine/atmospheric) as explained in the previous section.

Regarding sediment size distribution, some literature suggests that POPs mostly are associated with the sediment fine fraction (Pierard et al., 1996). It can therefore be expected that the PCB/chlorobenzene concentrations would increase with increasing distance away from the river outlet, due to longer transport of smaller riverine particles compared to e.g. gravel and larger particles, that will settle closer to the river mouth. The concentrations of PCBs and chlorobenzenes do increase from riverine SPM to outer fjord sediment stations in the present study. However, the negative correlation of CB-52 with clay content (figure 10) indicates that this is not mainly driven by the size of the sediment particles, since the inner stations, which are associated with lowest concentrations of the contaminants, had the highest clay content.

Furthermore, the analysis of fine fraction content ( $<63\ \mu\text{m}$ ; clay + silt) revealed no difference between sieved samples and bulk samples in PCB and HCB concentrations. Since the fine fraction in almost all samples were  $>80\text{-}90\%$ , any differences in PCB and HCB concentrations between sieved and bulk

samples are likely to be within the analytical uncertainties and hence, not able to attribute to grain size of the sediment.

Little research on relationships between Chl- $\alpha$  content and POP concentrations in sediment exist. This study showed a positive correlation between Chl- $\alpha$  content and CB-52 ( $R^2=0.24$ ) (figure 10). This might indicate that sedimentation of phytoplankton and their predators, zooplankton, is a transport pathway for PCBs and HCB from the water column to the sediment (Konat & Kowalewska, 2001). “Marine snow” (i.e. particulate organic carbon (POC)) is a transport pathway of OM and nutrients from the pelagic to the benthic ecosystem (Wiedmann, 2015). Hence, it is not unlikely that this would act as a transport pathway of contaminants from the water column to the bottom sediments. Earlier studies from Svalbard shows that feeding zooplankton might be important in the marine cycling of POPs, which further supports this theory (Hallanger et al., 2011a). However, this topic needs further investigations with regards to impact and volume and was outside the scope of this thesis.

With regards to spatial distribution; it is difficult to assess how sedimentation of phytoplankton and their predators is actually influencing the spatial distribution of contaminants in sediments; for example, there might be just as much sedimentation of zooplankton/phytoplankton closer to the river mouth, but this may be overshadowed by the higher sedimentation of riverine sediment at these locations.

#### 5.4 Terrestrial inputs - effect on dissolved concentrations

Comparing estimated  $C_{\text{free}}$  (based on sediment-partitioning and sediment passive sampling) with *in situ* measured  $C_{\text{free}}$  (from PAS), can provide insight to whether the solid phase particles acts a sink or a source of contaminants to the water column, or if they are in equilibrium with the ambient water. Figure 13 shows ratios between sediment based- and PAS based  $C_{\text{free}}$  ( $f_{\text{sed}}/f_{\text{PAS}}$ ) in Adventfjorden. From the Adventelva SPM and the inner station (A\_F1), a low  $f_{\text{sed}}/f_{\text{PAS}}$  ( $<0.01-0.1$ ) for mid- and low chlorinated PCBs suggest a net flux from water to particles for these compounds. This seems likely considering the low concentrations of contaminants in SPM samples compared to outer marine stations. For HCB, CB-44 and -52, higher  $f_{\text{sed}}/f_{\text{PAS}}$  ratios between 0.3-5 indicated conditions closer to equilibrium (Prokeš et al., 2012). Ratios for all compounds at the IsA station (outer Adventfjord) were between 0.1-10, indicating a fair degree of equilibrium (Prokeš et al., 2012), except for CB-44 and -52; which show slightly higher ratios (ca. 10), indicating that that the sediments may act as a source of these compounds to the water column.

Similar trends as mentioned above were also observed from the *in situ* sediment-water partition coefficients ( $K_{\text{oc-w}}$ ) from the present study (table 9). The  $\log K_{\text{oc-w}}$  for low chlorinated PCBs and HCB at inner stations and Adventelva SPM were generally within the range of literature values (Arp et al., 2009), indicating equilibrium conditions, while for the higher chlorinated PCBs,  $K_{\text{oc-w}}$  values were more than an order of magnitude below the lowest of all the literature  $K_{\text{oc-w}}$ 's, indicating low concentrations in the sediments compared to the overlying water.

However, there are some drawbacks to these two approaches. Firstly, the estimations are based on assuming 1-2 % TOC content, based on measurements from a previous study in Adventfjorden (Evenset et al., 2009). Actual measurements of TOC would have provided more accurate estimations. Secondly, estimations of  $C_{\text{free}}$  from sediment-water partitioning were based on average literature  $K_{\text{oc}}$ -values; however, sediment sorption capacities can vary greatly due to different types of organic carbon, such as black carbon, which might have a stronger affinity for POPs compared to other carbon-based matters



and compounds (Lohmann et al., 2005). This is illustrated by the range of the literature  $K_{oc-w}$  shown in table 9, that varies by up to almost two orders of magnitude.

Another attempt to avoid the uncertainties related to the use of an organic carbon/ $K_{oc}$  based approach, was to use sediment-equilibrium passive sampling, which rely on much more accurate passive sampler-water partition coefficients. Using this method, the sorption capacity of the sediments is accounted for because strong sorption to sediments causes a smaller fraction of the contaminants to be accumulated in the sampler at equilibrium. The lower  $f_{sed}/f_{PAS}$  ratios for HCB and low chlorinated PCBs for this experiment, compared with sediment  $K_{oc}$ -based ratios, might be explained by a stronger sorption to particles than expected from “classical” TOC-normalized partitioning. Svalbard and places around Isfjorden (including Longyearbyen and Pyramiden) have been subject to active coal mining activities during the last century. Hence, there is a likelihood that the black carbon fraction is higher than in sediments from other geographical areas.

However, a major weakness of the sediment-passive sampling experiment is that no method was applied to ensure equilibrium conditions. Because if equilibrium was not reached,  $C_{free}$  will be underestimated, and hence the  $f_{sed}/f_{PAS}$  ratio will be too low. This is most likely for the more hydrophobic compounds as they need more time to reach equilibrium (Smedes et al., 2012), whereas HCB and the lower chlorinated PCBs (CB-44, -52) should be closer to equilibrium. General methods to confirm equilibrium between sampler and sediments is to use PRCs, or measure the concentration in parallel samples that are extracted for different periods of time: If concentrations of a compound does not increase over time, equilibrium is reached (Ghosh et al., 2014). However, none of these were done due to laboratory practicalities and limited amount of sediment sample available.

## **5.5 Reflections on method uncertainties and limitations**

### *5.5.1 Analytical considerations*

In this study, recovery standards (RS) were not used as a part of the analytical quality assurance. The recovery of the added internal standard has to be within given limits to provide sufficient certainty related to the quantification of the target analytes (Oehme, 2007). The use of RS as a part of the quality assurance would allow to calculate the recovery of target compounds and ISTD during the sample preparation, hence discriminate samples that do not fulfill certain criteria.

In some batches, measured concentrations of certain PCBs and HCB in the certified reference material (CRM) were slightly low (especially HCB, CB-28/31 and CB-101, <80 % of reference value) even though the average CRM-results were within 20% for most of the compounds. However, samples from each fjord/gradient were analyzed in the same batch (see appendix 2), so the impact on trends of the observed concentration gradients are considered minimal.

### *5.5.2 Representativeness of sampling stations*

There is a potential bias related to the categorization of marine sampling stations into “inner”, “middle”, “outer” stations. This was done more or less visually from a map based on distances to river mouth in each fjord and not on other measurements or characteristics of the sediments. The validation of the categories is important to consider, since a lot of the discussion relies on comparing stations from these categories. However, the categories were set in coordination with other sampling within the TerrACE

project, and considered to not only practicalities related to sampling, but also biological factors, other inputs to the fjord etc. Hence, no “firm” distances to freshwater source were set, since this will vary between fjords.

Another feature is the representativeness of the samples. Firstly, the marine sediments were collected using a Van der Veen grab which collects sediments from the surface layer. However, different sampling locations might represent different age of sediments (representing other historical global emission levels) due to varying sedimentation rates at these locations. Also, the grab might collect varying amounts of sediment depending on falling speed and angle of the grab, and also on the type of sediments (if its sandy, silty etc.). An alternative to grab sampling would be to use sediment cores and date the sediment based on radioactive isotopes (i.e. Pouch et al. (2017)). However, this would have been too costly and time consuming. Instead the inclusion of many sampling stations from different side fjords within Isfjorden (Bille- Advent-, Tempelfjorden) allowed considering stations of almost equal distance to land as replicates. Since similar trends were observed in all three fjords, this strengthened the conclusions of this study.

The representativeness of the riverine SPM samples has already been briefly discussed in section 5.1.4. The use of only one SPM sample from each river limited the interpretation of the data. Furthermore, since sampling capacity of the sedimentation box is dependent on flow velocities and particle size, the amount of sediment collected from each river varied considerably, from about 2 kg in Adventelva to 10 g in Ebbaelva in 24 hours. Frequent sampling of river SPM would provide a sample collection of sediments under varying flow conditions (day to day variations), providing a more representative collection of samples. In addition, this would also account for temporal changes in contaminant levels during the ablation period.

### *5.2.3 Sediment properties*

This study would have benefitted from using total organic carbon (TOC) measurements rather than organic matter content derived from loss on ignition, which is a better predictor of both sediment concentrations and sediment-water partitioning of POPs. Presumably, an even more detailed investigation of the different types of organic carbon (such as black carbon) would have allowed to better assess the sediment adsorption capacity and how this might govern transport, distribution and fate of contaminants. Methods exist for analyzing the different types of organic carbon in sediments. Also, it is possible to separate low density coal particles from the sediments using density fractionation, for example with sodium polytungstate (Glaser et al., 2000). This would allow to determine the amount of black carbon associated contaminants from analysing this fraction.

## 6.0 CONCLUSIONS AND FUTURE PERSPECTIVES

The present study included analysis of PCBs and chlorobenzenes in marine sediments in a continuous gradient from close shore to the outer parts of Isfjorden, Svalbard. This, in combination with analysis of river SPM collected with sedimentation boxes and river passive sampling, provided useful information about freshwater associated contaminant fluxes to the fjord. A simple passive sampling method provided time weighted average aqueous concentration of sparingly soluble contaminants ( $\log K_{ow} > 5$ ) that in spite of being in the low picogram range (0.01-50 pg/L) were above detection limits for most compounds. The better selectivity from using GC-MS/MS triple quadrupole in MRM mode may have also allowed the quantification of ultra-trace level PCBs in sediment- and river SPM samples.

The detection of PCBs and HCB in river SPM- and PAS, indicate a delivery of contaminants from secondary sources. However, except from a slight indication of enhanced release of HCB from glacial meltwater (Ebbaelva), levels seem to be low compared to what is considered as background at similar latitudes. Consequently, the total PCB/HCB burden from freshwater sources seem to be low compared to other sources of inputs to the fjords (such as atmospheric deposition). However, more empirical data is needed to provide a robust quantitative understanding of freshwater contribution contaminates. Future studies should therefore focus on more frequent SPM sampling for a better elucidation of temporal variations throughout the ablation season. This in combination with a quality assured sampler deployment to avoid loss of passive samplers (which was the case in this study), will allow more robust, quantitative estimations of river associated contaminant fluxes. Furthermore, a complete mass balance budget for the fjord system should be constructed, from including the contribution from all other sources of input, such as marine current transport, sea ice transport and air-water exchange. From this, one will be able to put freshwater contribution into the “big picture” regarding coastal contaminant dynamics in high Arctic fjords.

The dominating factor that govern spatial distribution of PCBs and chlorobenzenes within Isfjorden is sediment loadings from the rivers, that are associated with very low concentrations of contaminants compared to sediments that are mainly of atmospheric/marine influence. Due to the low contaminant levels associated with them, the riverine sedimentary loads might have the potential to sorb these contaminants from the water column as they are entering the marine environment, potentially leading to a reduction in aqueous concentrations. This is especially relevant in a toxicology perspective, as the dissolved fraction can be a key factor explaining biological uptake processes and accumulation in aquatic food chains. Further work within the TerrACE project aims to focus on how this might have implications for bioaccumulation in affected ecosystems in Isfjorden.

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## Appendix 1

### Selected previous studies in- and around Svalbard regarding PCB and HCB in sediments and water.

Table 1: List of selected previous studies in and around Svalbard.

	HCB	CB28	CB52	CB101	CB118	CB138	CB153	CB180	Reference
<b>SEDIMENTS</b>									
Adventfjorden (n=7)	209-431	6-69	8-88	11-56	7-59	15-43	21-48	11-42	Evanset et al. (2009)
Billefjorden (n=7)	91-443	22-97	199-2428	395-4505	513-5859	337-3910	273-2964	49-471	Evanset et al. (2009)
Kongsfjorden (n=4)*	-	186-285	22-239	6-51	0.3-47	0.02-50	0.01-128	dl-7.60	Pouch et al. (2017)
Hornsund (n=5)*	-	20-353	11-750	17-145	10-195	9-73	15-122	dl-28	Pouch et al. (2017)
Barents Sea (n=2)** (background)	388-611	159-284	146-217	101-140	68-76	76-122	75-116	30-91	Green et al., (2010)
<b>WATER</b>									
Kongsfjorden (n=1)	5.2	0.63	0.65	0.31	0.13	0.08	0.10	N/A	Hallanger et al. (2011b)
Liefdefjorden (n=2)	2.2-7.8	0.3-1.1	0.4-1.4	0.2-0.9	0.1-0.5	0.0-0.7	0.0-0.8	N/A	Hallanger et al. (2011b)
Outside Kongsfjorden (n=1)	5.3	1.02	0.95	0.43	0.18	0.13	0.19	N/A	Gioia et al. (2008)
Svalbard (west) (n=4)	2.6-4.0	-	0.10-0.17	0.02-0.03	0.01	dl.0.02	-	-	Allan et al. (2011)
Bjørnøya (n=1,2)***	48-117	<2	<2	<24	<5	<3	<4	<5	Sobek and Gustafsson (2004)
Svalbard (East) (n=2)****	N/A	0.05-0.3	dl-0.32	dl-0.27	0.07-0.13	0.09-0.19	dl-0.16	dl-0.06	

\* Used sediment cores, results from the upper 0-2 cm is included in the table.

\*\*Station 19 (76.62°N, 34.46°E) and 24 (76.22°N, 18.57°E). Used sediment cores, results from the upper 0-2 cm is included in the table.

\*\*\* PCBs were only reported for one sample location, while HCB from two sampling locations around Bjørnøya was reported.

\*\*\*\* Station 4 (77.49°N, 29.53°E) and 5 (78.20°N, 27.17°E). Reported concentrations as particulate + dissolved.



## Appendix 2

### Concentrations of PCBs, HCB and PeCB in sediments and suspended particulate matter (SPM)

Table 1: Analysis of sediments/suspended particulate matter. Concentrations are in ng/g sediment dry weight. Yellow is <LOD, green is <LOQ. Orange is <LOD because of too much noise in the chromatogram. Blue is analysis of certified reference material (SRM 1944).

Sample ID	Location	CB-28/31	CB-44	CB-52	CB-101	CB-105	CB-118	CB-138	CB-149	CB-153	CB-156	CB-170	CB-180	CB-194	CB-209	HCB	Penta-CB
spm 27 bl-1	BLANK	0.00047	0.00017	0.00415	0.00213	0.00009	0.00011	0.00010	0.00006	0.00017	0.00005	0.00007	0.00031	0.00005	0.01063	0.00080	0.00018
spm 28 bl-2	BLANK	0.00067	0.00009	0.00465	0.00232	0.00009	0.00013	0.00021	0.00015	0.00032	0.00002	0.00005	0.00031	0.00010	0.01102	#N/A	0.00028
	LOD	0.00172	0.00029	0.00545	0.00264	0.00026	0.00035	0.00040	0.00029	0.00057	0.00011	0.00018	0.00093	0.00023	0.01166	0.00160	0.00044
	LOQ	0.00572	0.00068	0.00791	0.00360	0.00087	0.00118	0.00095	0.00070	0.00133	0.00037	0.00061	0.00311	0.00075	0.01361	0.00401	0.00091
spm 20	Sassen SPM (1)	0.00268	0.00153	0.00830	0.00219	0.00254	0.00212	0.00190	0.00133	0.00176	0.00008	0.00028	0.00048	0.00015	0.00845	0.10217	0.02337
spm 21	Sassen SPM (2)	0.00269	0.00110	0.00918	0.00194	0.00148	0.00204	0.00179	0.00142	0.00180	0.00003	0.00028	0.00073	0.00015	0.00853	0.10469	0.02466
spm 24	Ebba SPM	0.00105	0.00031	0.01128	0.00490	0.00032	0.00078	0.00091	0.00052	0.00100	0.00009	0.00055	0.00074	0.00059	0.02315	0.01551	0.00304
spm 25	Gips SPM (1)	0.00133	0.00054	0.00614	0.00270	0.00047	0.00136	0.00166	0.00066	0.00250	0.00021	0.00060	0.00122	0.00034	0.01235	0.01960	0.00365
spm 26	Gips SPM (2)	0.00190	0.00104	0.00643	0.00338	0.00053	0.00152	0.00197	0.00086	0.00302	0.00025	0.00051	0.00141	0.00036	0.01243	0.02324	0.00411
spm 29 srm1944	SRM 1944	123.1	56.5	71.8	59.9	20.6	44.8	71.5	50.1	73.2	7.2	20.2	47.9	13.3	7.4	4.1	2.2
sed 37 bl-1	BLANK	0.00247	0.00030	0.00440	0.00173	0.00015	0.00021	0.00023	0.00024	0.00030	0.00008	0.00010	0.00008	0.00010	0.01202	0.00190	0.00135
sed 38 bl-2	BLANK	0.00820	0.00083	0.00438	0.00128	0.00019	0.00045	0.00044	0.00038	0.00058	0.00009	0.00011	0.00028	0.00013	0.01230	0.00317	0.00278
	LOD	0.01748	0.00168	0.00443	0.00247	0.00025	0.00085	0.00078	0.00062	0.00105	0.00012	0.00031	0.00054	0.00035	0.01276	0.00522	0.00509
	LOQ	0.04583	0.00429	0.00453	0.00472	0.00042	0.00206	0.00181	0.00133	0.00248	0.00020	0.00103	0.00180	0.00117	0.01414	0.01148	0.01216
sed 30	A_F1	0.00378	0.00164	0.00925	0.00251	0.00056	0.00130	0.00176	0.00115	0.00148	0.00011	0.00029	0.00057	0.00022	0.01002	0.09082	0.02051
sed 31	A_F2	0.01093	0.00376	0.01392	0.00531	0.00128	0.00332	0.00445	0.00276	0.00428	0.00035	0.00085	0.00194	0.00049	0.01105	0.22342	0.05795
sed 32	A_NC	0.00845	0.00326	0.01188	0.00433	0.00108	0.00284	0.00385	0.00211	0.00375	0.00022	0.00068	0.00130	0.00037	0.01149	0.15503	0.04047
sed 33	IsA	0.04326	0.01849	0.04074	0.02904	0.01517	0.03621	0.03420	0.01558	0.02889	0.00389	0.00532	0.01109	0.00180	0.01231	0.41340	0.09935
sed 34	IsK	0.14496	0.05143	0.09133	0.05554	0.02485	0.06239	0.06442	0.03328	0.06061	0.00617	0.00957	0.01912	0.00347	0.01539	0.76220	0.24155
sed 36 srm1944	SRM 1944	106.01	50.35	64.25	56.03	18.01	44.79	66.31	47.30	66.06	5.65	18.46	46.06	12.14	6.59	3.79	2.24

Sample ID	Location	CB-28/31	CB-44	CB-52	CB-101	CB-105	CB-118	CB-138	CB-149	CB-153	CB-156	CB-170	CB-180	CB-194	CB-209	HCB	Penta-CB
sed 58 bl-1	BLANK	0.00303	0.00046	0.00466	0.00252	0.00004	0.00019	0.00013	0.00100	0.00030	0.00005	0.00003	0.00027	0.00006	0.01032	0.00108	0.00120
sed 59 bl-2	BLANK	0.00355	0.00058	0.00466	0.00349	0.00013	0.00053	0.00059	0.00109	0.00040	0.00008	0.00008	0.00016	0.00005	0.01026	0.00449	0.00195
	LOD	0.00439	0.00076	0.00466	0.00508	0.00028	0.00108	0.00133	0.00122	0.00056	0.00012	0.00017	0.00065	0.00016	0.01041	0.01003	0.00315
	LOQ	0.00695	0.00132	0.00467	0.00992	0.00072	0.00277	0.00360	0.00163	0.00105	0.00025	0.00058	0.00217	0.00055	0.01069	0.02693	0.00683
sed-50	T_F1	0.01972	0.00700	0.02185	0.00854	0.00288	0.00850	0.00855	0.00375	0.01124	0.00101	0.00139	0.00343	0.00039	0.01061	0.34747	0.08821
sed-51	T_inner	0.00316	0.00097	0.00646	0.00344	0.00044	0.00128	0.00129	0.00078	0.00230	0.00014	0.00026	0.00108	0.00013	0.01166	0.02857	0.00873
sed-52	T_NC	0.00380	0.00119	0.00759	0.00401	0.00110	0.00321	0.00350	0.00137	0.00585	0.00056	0.00082	0.00226	0.00023	0.01138	0.05493	0.01383
sed-53	T_outer	0.04643	0.01908	0.03517	0.02118	0.00855	0.02224	0.02247	0.01093	0.02503	0.00227	0.00345	0.00771	0.00127	0.01128	0.68093	0.17060
sed-54	T_Re_DeGeer	0.00354	0.00140	0.00955	0.00386	0.00155	0.00095	0.00099	0.00092	0.00106	0.00011	0.00009	0.00042	0.00032	0.01084	0.07980	0.02131
sed-55	T_Re_Gips	0.00278	0.00097	0.00612	0.00365	0.00071	0.00199	0.00241	0.00108	0.00292	0.00025	0.00053	0.00120	0.00028	0.01173	0.04013	0.01072
sed-56	T_Re_Sassen	0.00511	0.00191	0.00999	0.00243	0.00067	0.00161	0.00193	0.00143	0.00221	0.00017	0.00020	0.00079	0.00020	0.01059	0.10621	0.03105
sed-57 srm1944	SRM 1944	131.4	56.3	71.9	58.9	19.7	49.5	69.7	49.9	70.8	6.6	20.3	47.5	12.6	6.9	4.1	8.2
sed-67 bl-1	BLANK	0.0005	0.00052	0.00487	0.00316	0.00011	0.00014	0.00020	0.00037	0.00022	0.00013	0.00015	0.00035	0.00025	0.01082	0.00139	0.00119
sed-68 bl-2	BLANK	0.0017	0.00074	0.00458	0.00380	0.00013	0.00033	0.00032	0.00059	0.00022	0.00018	0.00014	0.00105	0.00020	0.01082	0.00303	0.00208
	LOD	0.00357	0.00111	0.00534	0.00484	0.00018	0.00063	0.00050	0.00094	0.00022	0.00047	0.00044	0.00210	0.00068	0.01083	0.00568	0.00353
	LOQ	0.00930	0.00222	0.00679	0.00800	0.00032	0.00157	0.00106	0.00203	0.00023	0.00155	0.00148	0.00699	0.00227	0.01085	0.01376	0.00794
sed-60	B_F1	0.02151	0.03073	0.06155	0.09616	0.07514	0.17031	0.12758	0.04577	0.08687	0.01747	0.01114	0.01612	0.00148	0.01247	0.15174	0.04219
sed-61	B_F2	0.04802	0.07472	0.14648	0.20205	0.16042	0.35845	0.28598	0.09598	0.16992	0.04350	0.02474	0.03582	0.00274	0.01205	0.32017	0.09385
sed-62	B_inner	0.00116	0.00097	0.00567	0.00461	0.00106	0.00272	0.00211	0.00124	0.00215	0.00008	0.00010	0.00042	0.00017	0.01140	0.01007	0.00332
sed-63	B_outer	0.12715	0.08424	0.14499	0.09838	0.05098	0.12457	0.10252	0.04538	0.08099	0.01121	0.01084	0.02031	0.00236	0.01263	0.57426	0.14933
sed-64	B_RE	0.00408	0.00707	0.02116	0.02401	0.01358	0.03238	0.02787	0.01066	0.01900	0.00348	0.00279	0.00496	0.00049	0.01173	0.05381	0.01726
sed-65	IsG	0.15681	0.05594	0.09759	0.06581	0.02959	0.07365	0.07595	0.03709	0.05386	0.00709	0.01043	0.01982	0.00357	0.01595	0.53180	0.20538
sed-66 srm1944	SRM 1944	138.3	58.2	73.4	65.6	25.3	59.7	85.1	53.4	72.9	8.0	22.6	50.0	13.5	6.7	3.7	2.1

Sample ID	Location	CB-28/31	CB-44	CB-52	CB-101	CB-105	CB-118	CB-138	CB-149	CB-153	CB-156	CB-170	CB-180	CB-194	CB-209	HCB	Penta-CB
84 blank	BLANK	0.00324	0.00094	0.00732	0.00545	0.00022	0.00051	0.00046	0.00210	0.00053	0.00012	0.00018	0.00044	0.00019	0.01359	0.00146	0.00144
	LOD	0.00649	0.00188	0.01463	0.01089	0.00044	0.00101	0.00091	0.00419	0.00159	0.00037	0.00054	0.00133	0.00056	0.02719	0.00292	0.00288
	LOQ	0.01621	0.00470	0.03659	0.02723	0.00110	0.00253	0.00228	0.01049	0.00531	0.00122	0.00179	0.00444	0.00188	0.06797	0.00731	0.00720
spm 22	DeGeer SPM	0.00240	0.00075	0.00750	0.00314	0.00101	0.00134	0.00082	0.00066	0.00043	0.00009	0.00009	0.00038	0.00015	0.00768	0.09714	0.02185
spm 23	DeGeer SPM	0.00266	0.00096	0.00771	0.00275	0.00090	0.00129	0.00092	0.00062	0.00042	0.00012	0.00013	0.00031	0.00011	0.00780	0.09878	0.02400
spm 70	A_F1 <63	0.00752	0.00281	0.01080	0.00767	0.00190	0.00391	0.00508	0.00330	0.00466	0.00046	0.00120	0.00221	0.00030	0.01247	0.04699	0.01404
spm 71	A_F2 <63	0.03574	0.01086	0.02783	0.01538	0.00307	0.00710	0.00901	0.00790	0.00786	0.00038	0.00219	0.00424	0.00075	0.02286	0.14933	0.04038
spm 72	IsA <63	0.03088	0.01140	0.02550	0.01990	0.01096	0.02499	0.02899	0.01190	0.02263	0.00391	0.00519	0.00929	0.00147	0.01324	0.23495	0.06707
spm 73	IsK <63	0.11065	0.03705	0.06560	0.05090	0.02181	0.05382	0.05474	0.02872	0.04639	0.00562	0.00861	0.01630	0.00281	0.02388	0.47670	0.16104
spm 74	IsG <63	0.11120	0.04188	0.07513	0.06512	0.02975	0.07153	0.06907	0.03397	0.05425	0.00738	0.00892	0.01702	0.00290	0.02553	0.36200	0.12573
spm 75	T_outer <63	0.04756	0.01708	0.03964	0.02084	0.00699	0.01812	0.01916	0.00960	0.02073	0.00217	0.00322	0.00714	0.00111	0.01868	0.56439	0.12831
spm 76	ME_3 <63	0.17115	0.06312	0.12679	0.07416	0.03311	0.07710	0.07555	0.03840	0.06433	0.00821	0.01119	0.02218	0.00410	0.04143	0.65060	0.18648
spm 78	T_RE_Sass <63	0.00678	0.00214	0.01166	0.00516	0.00066	0.00163	0.00202	0.00172	0.00232	0.00010	0.00032	0.00095	0.00022	0.01081	0.08426	0.02272
spm 79	T_RE_Deg <63	0.00747	0.00291	0.01241	0.00574	0.00114	0.00226	0.00210	0.00158	0.00191	0.00012	0.00032	0.00076	0.00023	0.01242	0.11082	0.02642
spm 80	ME_3	0.20339	0.07371	0.12819	0.07876	0.03654	0.08946	0.08954	0.04512	0.07606	0.00972	0.01334	0.02628	0.00453	0.01473	0.76866	0.22973
spm 83 srm1944	SRM 1944	134.80	48.08	61.52	51.60	21.17	45.93	63.43	41.69	58.31	6.92	17.73	40.71	10.91	5.80	2.73	1.64
85 spm blank	BLANK	0.000282	0.000600	0.004600	0.001873	0.000070	0.000158	0.000160	0.000196	0.000151	0.000038	0.000137	0.000317	0.000041	0.007591	0.000536	0.000419
	LOD	0.000564	0.001200	0.009200	0.003747	0.000140	0.000316	0.000319	0.000392	0.000303	0.000076	0.000275	0.000633	0.000083	0.015182	0.001072	0.000837
	LOQ	0.001410	0.003000	0.023000	0.009367	0.000349	0.000791	0.000798	0.000979	0.000757	0.000189	0.000687	0.001583	0.000206	0.037956	0.002680	0.002094
spm 81	Adv SPM <63	0.003182	0.001290	0.007799	0.004468	0.000683	0.001628	0.001460	0.001084	0.001141	0.000016	0.000210	0.000402	0.000157	0.009480	0.046531	0.010504
spm 82	DeGeer SPM <63	0.003966	0.000921	0.008330	0.003549	0.000408	0.000608	0.000803	0.000617	0.000516	0.000017	0.000134	0.000203	0.000150	0.008977	0.077559	0.019486
spm 77	Sass_SPM <63	0.002855	0.001252	0.007365	0.003747	0.000987	0.001317	0.001213	0.000963	0.001088	0.000173	0.000204	0.000369	0.000189	0.007052	0.060812	0.017523

## APPENDIX 3

### Calculation of sampling rate and dissolved concentrations in water using AlteSil™ silicon rubber sheets

#### 1.0 Calculation of retained fraction (f) of spiked performance reference compounds

Retained fraction were calculated using formula 1:

$$f = \frac{C_{SR}}{\text{Average } C_{bl}} \quad (1)$$

Where  $C_{SR}$  is concentration of the PRC in exposed sample (ng/g) and “Average  $C_{bl}$ ” is the average concentration of the PRC in blank samples (ng/g).

Table 1: Concentrations of spiked performance reference compounds (PRCs) in exposed and non-exposed samplers (blank samples) and retained fraction based on average blank concentration of PRCs.

Sample	CB1	CB2	CB3	CB10	CB14	CB2Ta1	CB50	CB78	CB104	CB145
Advent_blank	1.7	2.5	2.1	2.1	3.2	2.8	2.5	8.1	2.6	2.6
Ebba_blank	1.3	1.9	1.8	1.8	3.0	2.6	2.4	7.6	2.6	2.5
Transp_blank	1.5	2.5	2.0	2.0	3.4	2.8	2.6	8.4	2.7	2.6
Ebba_1	0.4	1.2	0.9	1.0	2.6	2.3	2.1	6.4	2.1	2.1
Ebba_2	0.4	1.1	0.9	1.0	2.6	2.4	2.3	7.9	2.4	2.5
Advent_1	0.4	1.2	0.9	1.6	3.0	2.5	2.4	7.1	2.4	2.4
Advent_2	0.4	1.2	0.9	1.4	2.9	2.5	2.4	7.3	2.4	2.4
Tempel	0.8	1.8	1.4	1.6	3.1	2.7	2.5	7.0	2.4	2.4
Retained fraction (f)										
f_Ebba_1	0.25	0.50	0.46	0.50	0.82	0.83	0.84	0.80	0.81	0.80
f_Ebba_2	0.24	0.46	0.45	0.50	0.83	0.89	0.93	0.98	0.92	0.95
f_Advent_1	0.29	0.52	0.47	0.78	0.93	0.93	0.97	0.88	0.93	0.91
f_Advent_2	0.27	0.52	0.44	0.72	0.92	0.92	0.94	0.91	0.92	0.91
f_Temp	0.6	0.8	0.7	0.8	1.0	1.0	1.0	0.9	0.9	0.9

#### 2.0 Calculation of aqueous concentrations

All sampler water partition coefficients ( $K_{sw}$ ) used in this study was obtained from Smedes et al. (2009). Aqueous concentration the target compounds was calculated using the formula below:

$$C_w = \frac{M_s}{K_{sw} m_s DEQ} \quad (2)$$

Where  $M_s$  is the mass (in kg) of a target compound in the SR-sampler,  $m$  is the mass of the sampler (kg) and  $K_{sw}$  is the sampler-water partition coefficient (L/kg) for the specific compound. DEQ (Degree of Equilibrium) is the degree of equilibrium that each compound attained during exposure and is determined by

$$DEQ = (1 - \exp(-\frac{R_s t}{K_{sw} m})) \quad (3)$$

Where  $R_s$  is the in-situ sampling rate for each compound (expressed as L/d) and  $t$  is exposure time (d).  $R_s$  for each compound was estimated based on the dissipation of spiked PRCs by using the model from Rusina et al. (2009)

$$R_s = \beta K_{sw}^{-0.08} \quad (4)$$

Where  $\beta$  is an adjustable parameter that was estimated from  $R_s$ -values calculated from the dissipation of the PRCs. This was done by plotting the retained PRC-fraction as a function of  $K_{sw}$  using non-linear least squares estimation (Booij & Smedes, 2010). Then equation 4 was used to extrapolate  $R_s$  for all target compounds.

## 2.1 Ebbaelva.

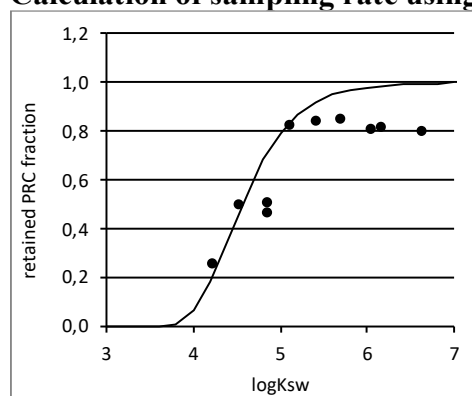
- Two replicates (#1 and #2).

### 2.1.1 Replicate #1

Table 2: Mass (ng sampler) accumulated in blank silicon rubber samples (pink) and exposed samples (blue) Ms\_Ebba bl is mass accumulated in field blank exposed during sampler deployment. Ms\_Tr bl. is transportation blank. Green columns show the percentage of the compound detection in blank compared to exposed samples.

CB	Ms_Ebba bl	Ms_tr bl	Ms	Ebba bl (%)	Tr bl (%)
CB28	0.15	0.30	1.687	9	17
CB31	1.02	0.99	0.853	119	116
CB44	0.03	0.02	0.129	24	13
CB52	0.16	0.17	0.416	39	42
CB101	0.16	0.18	0.730	23	24
CB105	0.00	0.00	0.018	9	16
CB118	0.01	0.01	0.056	14	17
CB138	0.02	0.02	0.088	18	18
CB149	0.02	0.01	0.093	18	15
CB153	0.02	0.02	0.100	17	16
CB156	0.00	0.00	0.008	14	41
CB170	0.00	0.00	0.010	34	28
CB180	0.01	0.01	0.026	30	39
CB194	0.00	0.00	0.002	60	180
HCB	0.09	0.08	34.071	0	0

### Calculation of sampling rate using non-linear regression



Ebbaelva\_1

Output summary	
m(kg)	0.028
t (d)	81
logBeta) est.	1.306
logBeta SE	0.115
residual SE	0.134
df	9
Rs (L/d) at logKsw=5	8.057
Vw (L) at logK5w=5	583.0

Table 3: All calculated parameters for individual target compounds in Ebbaelva 1

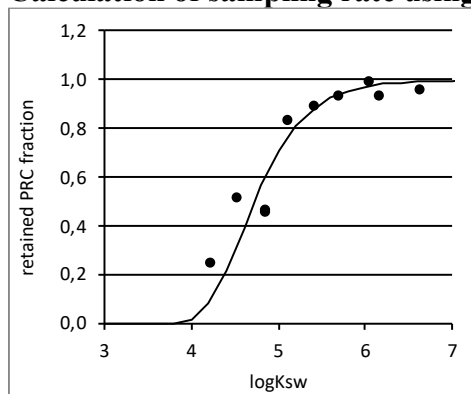
CB	logKsil-w	Rs	Ms	Cw (pg/L)	DEQ	Cw (pg/L)	Cw bl.substr
CB28	5.53	7.31	1.687	2.85	0.060	2.94	2.55
CB31	5.49	7.36	0.853	1.43	0.066	1.48	-0.26
CB44	5.82	6.93	0.129	0.23	0.029	0.23	0.19
CB52	5.81	6.94	0.416	0.74	0.030	0.75	0.45
CB101	6.28	6.36	0.730	1.42	0.009	1.42	1.09
CB105	6.42	6.20	0.018	0.04	0.007	0.04	0.03
CB118	6.42	6.20	0.056	0.11	0.007	0.11	0.09
CB138	6.77	5.81	0.088	0.19	0.003	0.19	0.15
CB149	6.64	5.96	0.093	0.19	0.004	0.19	0.16
CB153	6.72	5.87	0.100	0.21	0.003	0.21	0.17
CB156	6.72	5.87	0.008	0.02	0.003	0.02	0.01
CB170	7.10	5.47	0.010	0.02	0.001	0.02	0.02
CB180	6.99	5.58	0.026	0.06	0.002	0.06	0.04
CB194	7.59	5.00	0.002	0.00	0.000	0.00	0.00
HCB	5.06	7.97	34.071	52.79	0.180	58.19	58.05

## 2.1.2 Replicate #2

Table 4: Mass (ng sampler) accumulated in blank silicon rubber samples (pink) and exposed samples (blue) Ms\_Ebba bl is mass accumulated in field blank exposed during sampler deployment. Ms\_Tr bl. is transportation blank. Green columns show the percentage of the compound detection in blank compared to exposed samples.

CB	Ms_Ebba bl	Ms_Tr bl.	Ms	Ebba bl (%)	Tr bl (%)
CB28	0.15	0.30	1.364	11	22
CB31	1.02	0.99	0.993	102	100
CB44	0.03	0.02	0.119	26	15
CB52	0.16	0.17	0.395	41	44
CB101	0.16	0.18	0.646	26	27
CB105	0.00	0.00	0.015	11	19
CB118	0.01	0.01	0.063	13	15
CB138	0.02	0.02	0.081	19	20
CB149	0.02	0.01	0.095	17	15
CB153	0.02	0.02	0.098	18	17
CB156	0.00	0.00	0.004	24	72
CB170	0.00	0.00	0.009	38	31
CB180	0.01	0.01	0.023	33	43
CB194	0.00	0.00	0.004	23	68
HCB	0.09	0.08	32.048	0	0

### Calculation of sampling rate using non-linear regression



Ebbaelva\_2

#### Output summary

m(kg)	0.028
t (d)	81
logBeta) est.	1.472
logBeta SE	0.063
residual SE	0.087
df	9
Rs (L/d) at logKsw=5	11.80
Vw (L) at logK5w=5	808.4

Table 5: All calculated parameters for individual target compounds in Ebbaelva\_2

CB	logKsil-w	Rs	Ms	Cw (pg/L)	DEQ	Cw (pg/L)	Cw bl.substr
CB28	5.53	10.70	1.364	1.57	0.086	1.65	1.37
CB31	5.49	10.78	0.993	1.14	0.095	1.19	-0.01
CB44	5.82	10.15	0.119	0.14	0.043	0.15	0.12
CB52	5.81	10.16	0.395	0.48	0.044	0.49	0.28
CB101	6.28	9.32	0.646	0.86	0.014	0.86	0.63
CB105	6.42	9.08	0.015	0.02	0.010	0.02	0.02
CB118	6.42	9.08	0.063	0.09	0.010	0.09	0.07
CB138	6.77	8.52	0.081	0.12	0.004	0.12	0.10
CB149	6.64	8.72	0.095	0.13	0.006	0.13	0.11
CB153	6.72	8.60	0.098	0.14	0.005	0.14	0.12
CB156	6.72	8.60	0.004	0.01	0.005	0.01	0.00
CB170	7.10	8.01	0.009	0.01	0.002	0.01	0.01
CB180	6.99	8.18	0.023	0.03	0.002	0.03	0.02
CB194	7.59	7.32	0.004	0.01	0.001	0.01	0.00
HCB	5.06	11.67	32.048	33.90	0.252	39.1	38.95

## 2.2 Adventfjorden

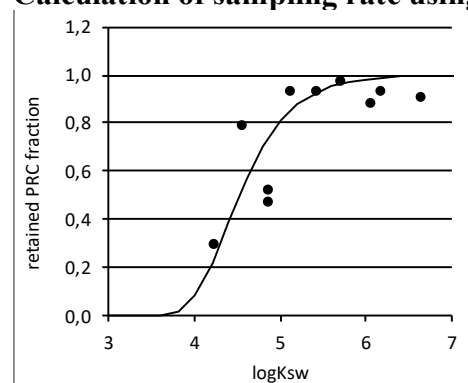
- Two replicates (#1 and #2)

### 2.2.1 Replicate #1

Table 6: Mass (ng sampler) accumulated in blank silicon rubber samples (pink) and exposed samples (blue) Ms\_Adv bl is mass accumulated in field blank exposed during sampler deployment. Ms\_Tr bl. is transportation blank. Green columns show the percentage of the compound detection in blank compared to exposed samples.

CB	Ms_Adv bl.	Ms_Tr bl.	Ms	Adv bl (%)	Tr bl (%)
CB28	0.17	0.30	0.261	64	113
CB31	0.88	0.99	0.990	89	100
CB44	0.02	0.02	0.048	37	36
CB52	0.15	0.17	0.205	75	84
CB101	0.18	0.18	0.183	101	96
CB105	0.00	0.00	0.006	38	46
CB118	0.01	0.01	0.026	40	37
CB138	0.02	0.02	0.050	35	32
CB149	0.01	0.01	0.034	40	43
CB153	0.02	0.02	0.045	40	36
CB156	0.00	0.00	0.006	62	55
CB170	0.00	0.00	0.021	13	14
CB180	0.01	0.01	0.033	17	31
CB194	0.00	0.00	0.010	21	29
HCB	0.05	0.08	5.620	1	1

### Calculation of sampling rate using non-linear regression



Adventfjord\_1

Output summary	
m(kg)	0.0278
t (d)	84
logBeta) est.	1.242
logBeta SE	0.115
residual SE	0.128
df	9
Rs (L/d) at logKsw=5	6.957
Vw (L) at logK5w=5	527.0



Table 7: All calculated parameters for individual target compounds in Adventfjorden 1

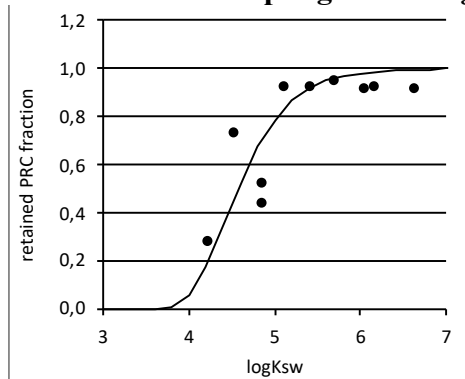
CB	logKsil-w	Rs	Ms	Cw (pg/L)	DEQ	Cw (pg/L)	Cw bl.substr
CB28	5.53	6.31	0.261	0.49	0.054	0.51	0.06
CB31	5.49	6.36	0.990	1.85	0.059	1.91	0.11
CB44	5.82	5.98	0.048	0.10	0.026	0.10	0.06
CB52	5.81	5.99	0.205	0.41	0.027	0.41	0.08
CB101	6.28	5.50	0.183	0.40	0.008	0.40	0.01
CB105	6.42	5.36	0.006	0.01	0.006	0.01	0.01
CB118	6.42	5.36	0.026	0.06	0.006	0.06	0.04
CB138	6.77	5.02	0.050	0.12	0.003	0.12	0.08
CB149	6.64	5.14	0.034	0.08	0.003	0.08	0.05
CB153	6.72	5.07	0.045	0.10	0.003	0.10	0.06
CB156	6.72	5.07	0.006	0.01	0.003	0.01	0.01
CB170	7.10	4.73	0.021	0.05	0.001	0.05	0.05
CB180	6.99	4.82	0.033	0.08	0.001	0.08	0.06
CB194	7.59	4.32	0.010	0.03	0.000	0.03	0.02
HCB	5.06	6.88	5.620	9.72	0.162	10.6	10.49

## 2.2.2 Replicate #2

Table x: Mass (ng sampler) accumulated in blank silicon rubber samples (pink) and exposed samples (blue) Ms\_Adv bl is mass accumulated in field blank exposed during sampler deployment. Ms\_Tr bl. is transportation blank. Green columns show the percentage of the compound detection in blank compared to exposed samples.

CB	Ms_Adv bl.	Ms_Tr bl.	Ms	Adv bl (%)	Tr bl (%)
CB28	0.17	0.30	0.289	58	102
CB31	0.88	0.99	0.868	101	114
CB44	0.02	0.02	0.050	35	35
CB52	0.15	0.17	0.207	74	84
CB101	0.18	0.18	0.190	97	92
CB105	0.00	0.00	0.006	41	50
CB118	0.01	0.01	0.023	46	42
CB138	0.02	0.02	0.036	50	44
CB149	0.01	0.01	0.026	51	55
CB153	0.02	0.02	0.036	50	45
CB156	0.00	0.00	0.003	112	98
CB170	0.00	0.00	0.014	19	20
CB180	0.01	0.01	0.024	23	43
CB194	0.00	0.00	0.007	29	40
HCB	0.05	0.08	6.007	1	1

### Calculation of sampling rate using non-linear regression



Adventfjord\_2

Output summary	
m(kg)	0.029
t (d)	84
logBeta) est.	1.306
logBeta SE	0.103
residual SE	0.122
df	9
Rs (L/d) at logKsw=5	8.057
Vw (L) at logK5w=5	602.4

Table 8: All calculated parameters for individual target compounds in Adventfjorden\_2

CB	logKsil-w	Rs	Ms	Cw (pg/L)	DEQ	Cw (pg/L)	Cw bl.substr
CB28	5.53	17.65	0.289	0.47	0.062	0.49	0.10
CB31	5.49	17.66	0.868	1.40	0.068	1.45	-0.11
CB44	5.82	17.58	0.050	0.09	0.031	0.09	0.06
CB52	5.81	17.58	0.207	0.36	0.031	0.36	0.08
CB101	6.28	17.47	0.190	0.35	0.010	0.36	0.02
CB105	6.42	17.44	0.006	0.01	0.007	0.01	0.01
CB118	6.42	17.44	0.023	0.04	0.007	0.04	0.02
CB138	6.77	17.37	0.036	0.07	0.003	0.07	0.04
CB149	6.64	17.39	0.026	0.05	0.004	0.05	0.02
CB153	6.72	17.38	0.036	0.07	0.003	0.07	0.04
CB156	6.72	17.38	0.003	0.01	0.003	0.01	0.00
CB170	7.10	17.30	0.014	0.03	0.001	0.03	0.03
CB180	6.99	17.32	0.024	0.05	0.002	0.05	0.03
CB194	7.59	17.21	0.007	0.02	0.000	0.02	0.01
HCB	5.06	17.78	6.007	8.97	0.186	9.9	9.82

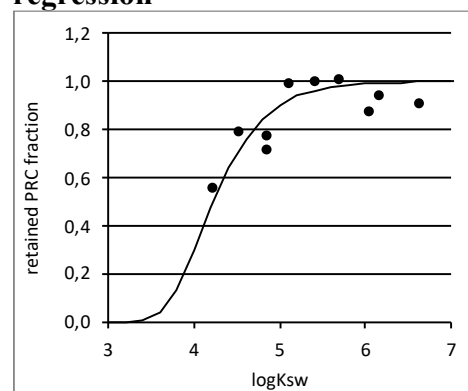
## 2.3 Tempelfjorden

- One sample

Table 9: Mass (ng sampler) accumulated in blank silicon rubber samples (pink) and exposed samples (blue) Ms\_Tr bl is mass accumulated in transportation blank The green column show the percentage of the compound detection in blank compared to exposed sample.

CB	Ms_Tr bl.	Ms	Tr bl (%)
CB28	0.30	1.509	20
CB31	0.99	1.152	86
CB44	0.02	0.065	27
CB52	0.17	0.260	67
CB101	0.18	0.632	28
CB105	0.00	0.013	23
CB118	0.01	0.054	18
CB138	0.02	0.064	25
CB149	0.01	0.039	36
CB153	0.02	0.092	17
CB156	0.00	0.005	66
CB170	0.00	0.010	28
CB180	0.01	0.021	48
CB194	0.00	0.003	101
HCB	0.08	10.409	1

### Calculation of sampling rate using non-regression



### linear

#### Tempelfjord

Output summary	
m(kg)	0.029
t (d)	84
logBeta) est.	0.943
logBeta SE	0.108
residual SE	0.073
df	9
Rs (L/d) at logKsw=5	3.488
Vw (L) at logK5w=5	278.7

Table 10: All calculated parameters for individual target compounds in Tempelfjord

CB	logKsil-w	Rs	Ms	Cw (pg/L)	DEQ	Cw (pg/L)	Cw bl.substr
CB28	5.53	3.16	1.509	5.68	0.027	5.8	4.63
CB31	5.49	3.19	1.152	4.30	0.030	4.4	0.62
CB44	5.82	3.00	0.065	0.26	0.013	0.3	0.19
CB52	5.81	3.00	0.260	1.03	0.014	1.0	0.35
CB101	6.28	2.76	0.632	2.73	0.004	2.7	1.98
CB105	6.42	2.69	0.013	0.06	0.003	0.1	0.04
CB118	6.42	2.69	0.054	0.24	0.003	0.2	0.20
CB138	6.77	2.52	0.064	0.30	0.001	0.3	0.23
CB149	6.64	2.58	0.039	0.18	0.002	0.2	0.12
CB153	6.72	2.54	0.092	0.43	0.001	0.4	0.36
CB156	6.72	2.54	0.005	0.02	0.001	0.0	0.01
CB170	7.10	2.37	0.010	0.05	0.001	0.1	0.04
CB180	6.99	2.42	0.021	0.10	0.001	0.1	0.05
CB194	7.59	2.16	0.003	0.02	0.000	0.0	0.00
HCB	5.06	3.45	10.409	35.92	0.085	37.5	37.26

## APPENDIX 4

### Sediment equilibrium passive sampling to estimate aqueous concentrations from Adventelva suspended particulate matter

$C_{free}$  from sediment passive sampling of Adventelva SPM was estimated using formula 1:

$$C_{free} = \frac{C_s}{K_{sw}} \quad (1)$$

Where  $C_s$  is the concentration in the sampler and  $C_w$  is the concentration in the water. To assure non-depletive conditions (minor absorption of sediment associated analytes), the amount of contaminants in the sediment should be < 5% of the mass accumulated by the sampler, that is, a  $N_s/N_{sed}$  ratio (Mass of analyte in sampler/mass of analyte in sediment) < 5%.  $N_s/N_{sed}$  was estimated from the formula below, which describes the distribution of a compound between the sampler and sediment at equilibrium.

$$\frac{N_s}{N_{sed}} = \frac{m_s K_{sw}}{m_{sed} K_{sed-w} + m_s K_{sw}} \quad (2)$$

Where  $N_s$  and  $N_{sed}$  is the amount of a compound in the sampler and sediment respectively.  $m_s$  is the mass of sampler and  $m_{sed}$  is the mass of sediment. and  $K_{sw}$  is the sampler-water partition coefficient.  $K_{sed-w}$  is the sediment-water partition coefficient. As a substitute for  $K_{sed-w}$ , TOC normalized organic carbon partition coefficients were used, assuming that most of the contaminants are associated with the organic carbon fraction of the sediments. TOC content was assumed to be 1%. It was desirable to have a rate corresponding to levels above >1ng in the passive sampler ( $N_s$ ) to It was desirable to have a rate corresponding to levels above > 1 ng / sample so that levels were quantifiable with GC-MS/MS.

## 1.0 Calculation of N<sub>s</sub>/N<sub>sed</sub> ratio

Table 1: Calculation of N<sub>s</sub>/N<sub>sed</sub> ratio. %OC, m<sub>sed</sub> and m<sub>s</sub> were adjustable parameters.

% OC	1	%
m sed dw	800	g
msil (g)	3	g

CB	logsw	logKoc-w (L/kg)	m oc (g)	C sed (ng/g)	C oc (ng/g OC)	Cfree pg/L	Csil (ng/g)	Ns (ng)	Nsed (g)	Ns/Nsed (%)
CB28	5.53	-	8	0.001	0.14	-	-	-	1.14	-
CB31	5.49	-	8	0.056	5.60	-	-	-	44.8	-
CB44	5.82	6.2	8	0.001	0.14	0.090	0.060	0.18	1.12	16
CB52	5.81	6.5	8	0.015	1.47	0.423	0.273	0.82	11.8	7
CB101	6.28	7.1	8	0.005	0.49	0.043	0.082	0.24	3.95	6
CB105	6.43	7.8	8	0.000	0.03	0.001	0.001	0.00	0.26	2
CB118	6.42	7.2	8	0.001	0.08	0.005	0.012	0.04	0.61	6
CB138	6.77	7.9	8	0.001	0.12	0.001	0.008	0.02	0.94	3
CB149	6.64	-	8	0.001	0.11	-	-	-	0.85	-
CB153	6.72	8.1	8	0.001	0.13	0.001	0.005	0.02	1.04	2
CB156	6.73	7.8	8	0.000		0			0.09	0
CB170	7.11	8.0	8	0.000	0.02	2E-07	0.002	0.01	0.12	5
CB180	7	8.0	8	0.000	0.05	5E-07	0.005	0.02	0.39	4
CB194	7	-	8	0.000	0.03	-	-	-	0.21	-
HCB	5.06	6.1	8	0.069	6.86	0.005	0.611	1.83	54.9	3

## 2.0 Results from quantification

Table 2: Concentration of analyte in sample (ng/g SR). Yellow is values >LOD. LOD was defined as blank value x 2.

Sample ID	Advent SPM	SPM blank
Name	Advent SPM	SPM blank
g sed	830	0
g SR	3	6.5
CB28+31	0.0069	0.0086
CB44	0.0028	0.0004
CB52	0.0110	0.0052
CB101	0.0117	0.0045
CB105	0.0007	0.0002
CB118	0.0014	0.0003
CB138	0.0034	0.0004
CB149	0.0031	0.0005
CB153	0.0033	0.0007
CB156	0.0002	0.0003
CB170	0.0005	0.0002
CB180	0.0013	0.0006
CB194	0.0005	0.0004
HCB	0.038	0.0015
PeCB	0.013	0.0015

## 3.0 Estimation of $C_{\text{free}}$

$C_{\text{free}}$  was estimated from using formula 1 as shown in table 3. Samples are not blank subtracted.

Table 3: Estimation of  $C_{\text{free}}$  in water based on sediment passive sampling of Adventelva SPM.

	logK <sub>sw</sub>	K <sub>sw</sub> L/kg	m SR	m (ng/sample)	pg/kg sil	C <sub>free</sub> (pg/L)
CB44	5.75	562341	3	0.0083	3	0.0049
CB52	5.84	691831	3	0.0330	11	0.0159
CB101	6.38	2398833	3	0.0350	12	0.0049
CB105	6.65	4466836	3	0.0000	0	0.0000
CB118	6.74	5495409	3	0.0041	1	0.0002
CB138	6.83	6760830	3	0.0101	3	0.0005
CB149	6.67	4677351	3	0.0094	3	0.0007
CB153	6.92	8317638	3	0.0099	3	0.0004
HCB	5.50	316228	3	0.1154	38	0.1216

## Appendix 4

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### Information about GC-MS/MS analysis

#### **1.0 About GC-MS/MS in environmental trace analysis.**

Nowadays, GC-MS is the most powerful and common technique for the identification and quantification semi-volatile POPs in environmental samples. An MS-detector separates ionized molecules (from an ion source) by their mass to charge ratio ( $m/z$ ), allowing a further separation of compounds with different masses that coelute from the GC-column. This leads to increased selectivity and ability to detect compounds at very low concentrations.

One of the working horses in many environmental laboratories is the GC-MS single quadrupole with electron ionization. Working in selective ion monitoring (SIM) mode focus the MS-filter on pre-selected masses, which entails better sensitivity and higher signal to noise ratios compared to scan-modes that scans over a range of masses. However, the single quadrupole still struggles with matrix interference (e.g. natural organic matter) when analyzing ultra-trace contaminant levels in complex mixtures such as marine sediments (e.g. natural organic matter, lipids) (Zhang et al. 2015). Solutions to this can be to use so called tandem-MS instrumentations, which minimizes the matrix interference by improved selectivity from using two mass filters instead of one. Ions passing the first mass-filter are broken down into smaller fragments by collision with an inert gas in a collision cell, before they are transported through the second mass filter. The equivalent of SIM-mode in a triple quadrupole is multiple reaction monitoring (MRM) mode, where the two mass filters are set to selected  $m/z$ -ratios where only selected fragments of the precursor ion is allowed to pass the second mass filter.

#### Reference

Zhang, H., Bayen, S. & Kelly, B. C. (2015). Co-extraction and simultaneous determination of multi-class hydrophobic organic contaminants in marine sediments and biota using GC-EI-MS/MS and LC-ESI-MS/MS. *Talanta*, 143: 7-18.





Table 1: MRM setup for all analyzed compounds in the present study.

Name	TS	Transition	Scan	Type	Precursor Ion	Product Ion	RT	Ion Polarity
2-Chlorobiphenyl (BZ #1)	1	188,0 -> 152,1	MRM	Target	188,0	152,1	10,38	Positive
Pentachlorobenzene	2	249,9 -> 215,0	MRM	Target	249,9	215,0	10,85	Positive
3-Chlorobiphenyl (BZ #2)	3	188,0 -> 152,1	MRM	Target	188,0	152,1	11,77	Positive
4-Chlorobiphenyl (BZ #3)	3	188,0 -> 152,1	MRM	Target	188,0	152,1	11,92	Positive
2,6-Dichlorobiphenyl (BZ #10)	4	222,0 -> 152,1	MRM	Target	222,0	152,1	12,69	Positive
3,5-Dichlorobiphenyl (BZ #14)	6	222,0 -> 152,1	MRM	Target	222,0	152,1	14,88	Positive
Hexachlorobenzene	5	283,8 -> 213,9	MRM	Target	283,8	213,9	14,61	Positive
2,4,6-Trichlorobiphenyl (BZ #30)	7	256,0 -> 186,0	MRM	ISTD	256,0	186,0	15,41	Positive
2,2',4,6-Tetrachlorobiphenyl (BZ #50)	8	289,9 -> 219,9	MRM	Target	289,9	219,9	17,68	Positive
2,3,4-Trichlorobiphenyl (BZ #21)	9	256,0 -> 186,0	MRM	Target	256,0	186,0	18,1	Positive
2,4',5-Trichlorobiphenyl (BZ #31)	8	186,0 -> 151,0	MRM	Target	186,0	151,0	17,72	Positive
2,2',5,6'-Tetrachlorobiphenyl (BZ #53)	9	289,9 -> 219,9	MRM	ISTD	289,9	219,9	18,12	Positive
2,4,4'-Trichlorobiphenyl (BZ #28)	9	256,0 -> 186,0	MRM	Target	256,0	186,0	17,76	Positive
2,2',5,5'-Tetrachlorobiphenyl (BZ #52)	10	289,9 -> 219,9	MRM	Target	289,9	219,9	19,07	Positive
2,2',3,5'-Tetrachlorobiphenyl (BZ #44)	11	255,0 -> 220,0	MRM	Target	255,0	220,0	19,84	Positive
2,2',4,6,6'-Pentachlorobiphenyl (BZ #104)	11	325,9 -> 255,9	MRM	Target	325,9	255,9	19,65	Positive
2,2',4,5,5'-Pentachlorobiphenyl (BZ #101)	12	325,9 -> 255,9	MRM	Target	325,9	255,9	22,35	Positive
3,3',4,5-Tetrachlorobiphenyl (BZ #78)	13	289,9 -> 219,9	MRM	Target	289,9	219,9	23,01	Positive
2,2',3,4,6,6'-Hexachlorobiphenyl (BZ #145)	14	359,9 -> 289,9	MRM	Target	359,9	289,9	23,29	Positive
2,2',3,4',5,6-Hexachlorobiphenyl (BZ #149)	15	287,9 -> 217,9	MRM	Target	287,9	217,9	24,57	Positive
2,3',4,4',5-Pentachlorobiphenyl (BZ #118)	15	325,9 -> 253,9	MRM	Target	325,9	253,9	24,67	Positive
2,2',4,4',5,5'-Hexachlorobiphenyl (BZ #153)	16	359,9 -> 289,9	MRM	Target	359,9	289,9	25,48	Positive
2,3,3',4,4'-Pentachlorobiphenyl (BZ #105)	16	325,9 -> 253,9	MRM	Target	325,9	253,9	25,61	Positive
2,2',3,4,4',5'-Hexachlorobiphenyl (BZ #138)	17	359,9 -> 289,9	MRM	Target	359,9	289,9	26,46	Positive
2,2',3,4,4',5,6,6'-Octachlorobiphenyl (BZ #204)	18	427,8 -> 357,8	MRM	ISTD	427,8	357,8	28,51	Positive
2,3,3',4,4',5-Hexachlorobiphenyl (BZ #156)	18	287,9 -> 217,9	MRM	Target	287,9	217,9	28,3	Positive
2,2',3,4,4',5,5'-Heptachlorobiphenyl (BZ #180)	19	395,8 -> 325,8	MRM	Target	395,8	325,8	28,87	Positive
2,2',3,3',4,4',5-Heptachlorobiphenyl (BZ #170)	20	393,8 -> 323,8	MRM	Target	393,8	323,8	29,88	Positive
2,2',3,3',4,4',5,5'-Octachlorobiphenyl (BZ #194)	21	427,8 -> 357,8	MRM	Target	427,8	357,8	32,08	Positive
Decachlorobiphenyl (BZ #209)	22	497,7 -> 427,7	MRM	Target	497,7	427,7	34,31	Positive

## Appendix 5

### Preparation of PRC stock solution and PRC calibration solutions

Multicomponent stock solution conc = 50 µg/mL

ID	Stock (mg)	Purity %	Mass (mg)	Con (mg/mL)	proportion	0.05 mg/mL vol (mL)
1	50	99.0	21.7	2.17	0.023	1.152
2	50	99.0	25.6	2.56	0.020	0.977
3	50	99.0	21.5	2.15	0.023	1.163
10	25	97.0	8.9	0.89	0.056	2.809
14	50	99.8	20.8	2.08	0.024	1.202
21	10	98.0	9.7	0.97	0.052	2.577
50	10	99,9 ± 0,05	7.5	0.75	0.067	3.333
78	5	99.9	5.6	0.56	0.089	4.464
104	5	99.1	5.7	0.57	0.088	4.386
145	5	99.6	6.2	0.62	0.081	4.032
Sum						26.096

Figure 1: Lab notes from preparation of PRC stock solutions. Solid form PCB compounds were weighted and dissolved in acetone.

		clo-xx		clo-yy		istd clo-94			
ng/ml	ng/ml	100	2000	1000	ch	totalvolum			
komponent	istd	ml	ml	ml	ml	ml	ch		
0,2	100	0,01		0,5	4,49	5			
0,5	100	0,025		0,500	4,475	5			
1	100	0,050		0,500	4,450	5			
4	100	0,200		0,500	4,300	5			
20	100	0,050		0,500	4,450	5			
50	100	0,125		0,500	4,375	5			
120	100	0,300		0,500	4,200	5			

clo-94 = pcb-30, pcb-53, pcb-204  
 clo-xx og yy = pcb-1, -2, -3, -10, -14, -21, -50, -78, -104, -145  
 clo-106 = 50 µg/ml

clo-xx	400 µl av clo-106 fort til 10ml	= 2000 ng/ml
clo-xx	100 µl av clo-106 fort til 50ml	= 100 ng/ml

Figure 2: Lab notes from preparation of PRC calibration solutions.



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