TESI DOCTORAL

Source assessment of organochlorine pollutants in sediment and fish from Greenland lakes

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To the planet and its people,
may we learn to co-exist

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Abstract

The Arctic is a fragile ecosystem extremely sensitive to environmental changes and shifts, which it is currently exposed to multiple environmental stressors such as contamination or extreme warming events detrimental to the whole Arctic ecosystem equilibrium. As a consequence, the Greenlandic population has unexpectedly relatively high levels of organohalogen compounds (OHCs), which directly affect child development, immune function and reproductive abilities. Long-range atmospheric transport (LRAT) is one of the main routes for OHCs to reach Greenland, but the role of biovectors and other local sources of these contaminants, such as the emission of OCHs from airports or high populated areas, cannot be ignored. Not many studies have been done at the large-scale spatial gradient across Greenland. Most studies in Greenland have focused on time series, which are essential; however, they will give a fuller picture if combined with the spatial studies

In the thesis, three studies were conducted across temporal and spatial gradients to deepen our understanding of OHCs accumulation in the fish and sediments from Greenlandic freshwater lakes. The first chapter aimed to understand the levels of POPs arriving to the high Arctic freshwater lakes in Greenland and how the presence of the living organisms affects their depositional patterns. The role of sea birds as carriers of pollutants over long distances was evaluated. One of the three lakes selected for this purpose had a little auk (*Alle alle*) bird colony, and the other two were devoid of these seabirds. We found a strong influence of these seabirds in the transport and deposition of these hydrophobic compounds to remote sites. However, not all compounds showed the same relative increases. We found a discriminating effect in the seabird accumulation and transport of organohalogen to remote sites. The second chapter aimed to establish a record of OHCs contamination in Greenlandic freshwater lakes sediments. Airports, military bases, and research stations were important local sources for DDTs, HCB, OCS, Methoxychlor, Mirex, Chlordanes, and Heptachlors in Greenland freshwater lakes. Populated areas were essential sources for PCBs. The effect of LRAT was evident for HCHs, HCB, Chlordanes, and Heptachlors. Positive longitudinal gradients explained the arrival of HCHs and PBDEs from the Eurasian and North-eastern American continents. The concentrations of most compounds showed a decrease through the years due to the past restrictions. This study is the first to analyse a broad spectrum of OHCs, including Endosulfans, Drins, OCS, Mirex, and Methoxychlor, which were never studied in freshwater lake sediments of Greenland. The third chapter study aimed to determine the range of concentrations of PCBs,

DDTs and PBDEs in the top predator Arctic charr across Greenland freshwater lakes and understand OHCs accumulation and distribution patterns. We found that PCBs and DDTs concentrations in some Arctic charr crossed the toxicity thresholds, which may be of concern since it is an important component in the local population's diet. The most critical factors determining PCBs, PBDEs, and DDTs accumulation in Arctic charr were mean annual air temperature (indicating LRAT) and anthropogenic impact. The Arctic charr from lakes with higher anthropogenic impact also accumulated higher levels of heavier molecular weight PCBs. Total nitrogen in the lake was also an important factor determining PBDEs bioaccumulation, indicating a dilution factor of PBDEs in Arctic charr when nitrogen concentrations in the lake were higher. Some Layman metrics were significant predictors for DDTs and PBDEs bioaccumulation, providing insight into the relevance of biomagnification, trophic diversity and niche overlap effects for the cycling of these organic compounds across the freshwater food webs.

In conclusion, the thesis findings suggest that even though the OHCs are largely decreasing in Greenland, their present concentrations in freshwater lakes and particularly in the food webs top predators, such as Arctic charr, are concerning. These factors differ according to each lake's location and features and might not show up on the collective time series data. Besides, the effects of climate change may degrade the vulnerable Arctic ecosystems further and enhance revolatilisation and re-emission of these legacy compounds back into these ecosystems in concentrations high enough to be considered a "secondary source" of pollution. Due to Arctic ecosystems sensitivity, this simultaneously impacts by "multiple stressors" can seriously endanger their ecological balance.

Resum

L'Àrtic és un ecosistema fràgil extremadament sensible als canvis i variacions ambientals, que actualment està exposat a múltiples factors estressants ambientals com la contaminació o els esdeveniments d'escalfament extrem que perjudiquen tot l'equilibri de l'ecosistema àrtic. Com a conseqüència, la població groenlandesa presenta nivells relativament alts de compostos organohalogenats (OHCs), que afecten directament el desenvolupament infantil, la funció immune i les capacitats reproductives. El transport atmosfèric de llarg abast (LRAT) és una de les rutes principals perquè els OHC arribin a Groenlàndia, però no es pot ignorar el paper dels biovectors i d'altres fonts locals d'aquests contaminants, com l'emissió d'OHCs des dels aeroports o zones amb molta població. No s'han fet gaires estudis sobre el gradient espacial a gran escala de Groenlàndia. La majoria d'estudis a Groenlàndia s'han centrat en sèries temporals, que són essencials; no obstant això, donaran una imatge més completa si es combinen amb els estudis espacials

A la tesi, es van dur a terme tres estudis a través de gradients temporals i espacials per aprofundir en la nostra comprensió de l'acumulació de OHCs als peixos i sediments dels llacs d'aigua dolça de Groenlàndia. El primer capítol tenia com a objectiu comprendre els nivells de POP que arriben als alts llacs d'aigua dolça de l'Àrtic a Groenlàndia i com la presència dels organismes vius afecta els seus patrons de deposició. Es va avaluar el paper de les aus marines com a portadores de contaminants a llargues distàncies. Un dels tres llacs seleccionats amb aquest propòsit tenia una petita colònia d'aus (*Alle alle*), i els altres dos estaven desproveïts d'aquestes aus marines. Hem trobat una forta influència d'aquestes aus marines en el transport i la deposició d'aquests compostos hidròfobs a llocs remots. No obstant això, no tots els compostos van mostrar els mateixos augments relatius. Vam trobar un efecte discriminatori en l'acumulació i el transport d'organohalògens d'aus marines a llocs remots. El segon capítol tenia com a objectiu establir un registre de contaminació per OHC als sediments dels llacs d'aigua dolça de Groenlàndia. Els aeroports, les bases militars i les estacions d'investigació van ser importants fonts locals de DDT, HCB, OCS, metoxiclor, mirex, clordans i heptaclors als llacs d'aigua dolça de Groenlàndia. Les zones poblades eren fonts essencials per als PCB. L'efecte de LRAT va ser evident per a HCHs, HCB, clordans i heptaclors. Gradients longitudinals positius van explicar l'arribada de HCHs i PBDEs dels continents eurasiàtic i nord-americà. Les concentracions de la majoria dels compostos van mostrar una disminució al llarg dels anys a causa de les restriccions passades. Aquest estudi és el primer que analitza un ampli espectre d'OHCs, inclosos els endosulfans, drins, OCS, mirex i metoxiclor, que mai no s'han estudiat

en sediments de llacs d'aigua dolça de Groenlàndia. L'estudi del tercer capítol tenia com a objectiu determinar l'abast de les concentracions de PCB, DDT i PBDE en el predador àrtic superior, la truita alpina, a través dels llacs d'aigua dolça de Groenlàndia i entendre els patrons d'acumulació i distribució de OHC. Vam trobar que les concentracions de PCB i DDT en algunes truites van superar els llindars de toxicitat, cosa que pot ser preocupant, ja que és un component important en la dieta de la població local. Els factors més crítics que determinen l'acumulació de PCB, PBDE i DDT a la truita alpina àrtica van ser la temperatura mitjana anual de l'aire (que indica LRAT) i l'impacte antròpic. La truita dels llacs amb major impacte antròpic també va acumular nivells més alts de PCB de pes molecular més pesat. El nitrogen total al llac també va ser un factor important que va determinar la bioacumulació de PBDE, cosa que va indicar un factor de dilució de PBDE a l'Àrtic quan les concentracions de nitrogen al llac eren més altes. Algunes mètriques de Layman van ser predictors significatius de la bioacumulació de DDTs i PBDEs, proporcionant informació sobre la rellevància de la biomagnificació, la diversitat tròfica i els efectes de superposició de nínxols per al cicle d'aquests compostos orgànics a través de les xarxes tròfiques d'aigua dolça.

Les conclusions de la tesi suggereixen que, tot i que els OHCs estan disminuint substancialment a Groenlàndia, les seves concentracions actuals als llacs d'aigua dolça i, sobretot, als depredadors superiors de les seves xarxes tròfiques, com és la truita alpina àrtica, són preocupants. Aquests factors difereixen segons la ubicació i les característiques de cada llac i és possible que no apareguin significatuius en sèries temporals. A més, els efectes del canvi climàtic poden degradar encara més els vulnerables ecosistemes àrtics i augmentar la revolatilització i la reemissió d'aquests compostos heretats a aquests ecosistemes en concentracions prou elevades com per ser considerades una "font secundària" de contaminació. A causa de la sensibilitat dels ecosistemes àrtics, els impactes simultanis dels múltiples factors estressants ambientals poden posar en perill el seu equilibri ecològic.

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GENERAL INTRODUCTION AND OBJECTIVES

Introduction

Organohalogen Compounds (OHCs)

OHCs are a large group organic chemicals that contain at least one halogen (chlorine, bromine, fluorine or iodine) combined with carbon and other elements, widely distributed in the environment (Hull et al., 2014) (Figure 1). Several members of OHCs form a part of the well-known Persistent Organic Pollutants (POPs), which are defined as man-made compounds that are resistant to environmental degradation through chemical, biological and photolytical processes (Kodavanti & Loganathan, 2016). This persistence makes them an ideal candidate for staying in the environment (soil/sediment, biota, air, and water) for a very long duration of time. On top of it, their hydrophobic and lipophilic nature makes them partition strongly to solids, notably organic matter, mostly avoiding the aqueous phase; they also partition into lipids in organisms and bioaccumulate in the biotic components (Jones & De Voogt, 1999) with the potential to endocrine disruption, altered neurological development, immune system modulation, and even cancer (WHO, 2003).

Among the most important POPs, there are the organochlorine pesticides (Dichlorodiphenyltrichloroethane (DDT) and its metabolites, dieldrin, aldrin, endrin, mirex, heptachlor and chlordanes), polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), polybrominated diphenyl ethers (PBDEs), HCHs (α, β, γ) and pentachlorobenzene (PeCB). All of them are included in a global treaty to phase out these chemicals, popularly known as the Stockholm Convention (UNEP, 2013).

Organochlorine pesticides have been used on crops and soils to control pests and vector-borne diseases and PCBs have been used for industrial purposes such as lubricants and heat transfer fluids. DDTs and PCBs have been produced since early 20th century, while PCBs, mainly produced and used in North America and Europe, were banned in 1970s. However, DDTs are still used in some tropical countries as a disease control measure but their usage as of now has drastically been reduced than before (AMAP, 2004). HCHs were used for the first time in 1940s; again, it was banned in the western countries in the 1970s however y-HCH (Lindane) continued to be used in many places even recently for the insecticidal and disease prevention. Most of the OHCs e.g., HCB, Aldrin, dieldrin, endrin, heptachlor, Mirex and Chlordanes were started to be phased out by 1990s even before the Stockholm treaty came into being (AMAP, 2004). Endosulfan, a pesticide introduced in the 1950s, on the other hand has been used all over the world and continues to remain so in agricultural applications; although,

measures are being taken to phase it out after its inclusion under the Stockholm Convention (Weber et al., 2010). Methoxychlor, originally, developed as a replacement for DDT, is also currently under review by the Stockholm Convention (UNEP, 2019). HCB is produced as a by-product in the production of a large number of chlorinated compounds, particularly lower chlorinated benzenes, and some pesticides (AMAP, 2004). HCB one of the initial OHCs to be added to the Stockholm Convention (UNEP, 2013). PeCB was used in dielectric fluids in PCB-containing transformers, dyestuff carriers, fungicide and a flame retardant. Thus, old PCB containing devices may also be a source of PeCB so may be unintentional production in certain industrial processes (UNEP, 2017). Not much is known about the global emission of Octachlorostyrene (OCS) but in 1960s and 70s it was detected in Europe and America in maximum concentrations. Magnesium production and chlorine manufacturing were deemed important sources for OCS in the global atmosphere. OCS is being considered to be banned. PBDEs are flame retardants used in plastics, textiles, electronic circuitry, building materials, furniture and other materials to prevent fires. They are sometimes added as additives and as such are not chemically bound to the material, making them easier to leach from the products into the environment.

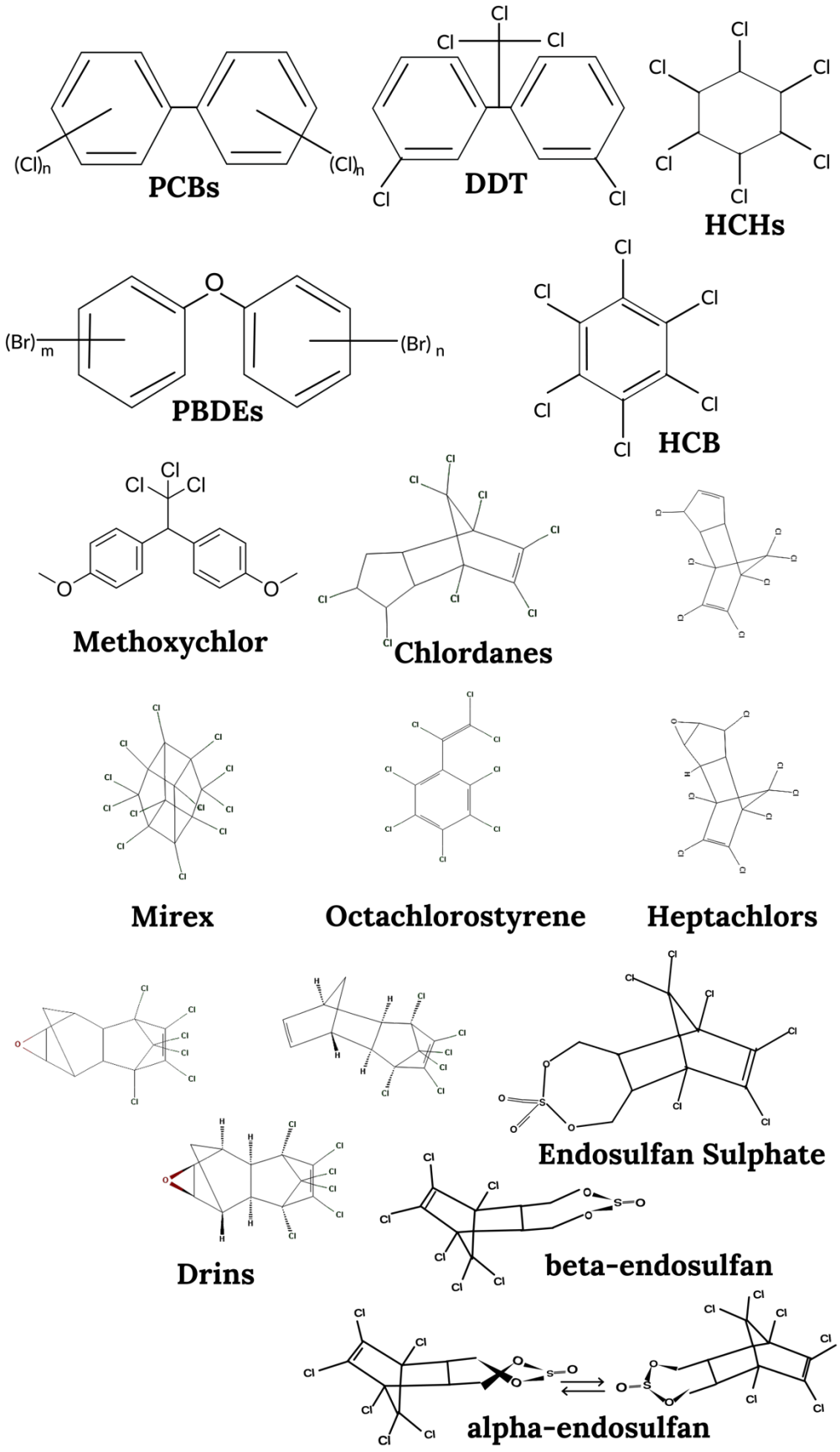


Figure 1 Chemical structure of the Organohalogen Compounds studied in this thesis
The Arctic Environment

The Arctic is synonymous with the "circumpolar North", which is depicted as remote, hostile, isolated and pristine, away from the pollution problems faced at the lower latitudes. However, this pristineness has proven to be untrue as the Arctic is closely connected to the geophysical and ecological systems at a global scale (Arctic Council, 2016). The Arctic is one of the most susceptible areas on the Earth to both natural and human induced changes (Overpeck et al., 1997). One of the biggest and initial human impacts on the Arctic has been extensively militarization during the World War II and The Cold War (Young, 1985), which turned the Arctic into one of the world's key militarized and politized zones (Young, 1985). High Arctic was strewn with such sites (especially the RADAR sites) erected at the peak of the cold war. Nonetheless, with the end of the cold war, these sites have been mandated to support scientific research on the high Arctic (Goodsite et al., 2014). The scientific research stations are not without their cons, they also release contaminants in the environment (Vecchiato et al., 2015). Currently, the other human impacts have been oil and mineral exploration, increase in tourism, increased shipping through the Arctic have all been combining to form "multiple stressors".

Of all the places in the world, the Arctic appears to be exceptionally vulnerable to temperature changes and contaminants whose global cycling is temperature dependent (Macdonald, 2005). Moreover, the Arctic is warming at an accelerated pace, much more than the other parts of the world. Impacts of rising temperatures, such as accelerate melting of glaciers, thawing permafrost, ocean acidification, increased precipitation and run-off, and extreme weather events are causing pronounced effects on terrestrial and marine ecosystems (Steindal et al., 2021).

All these stressors acting at the same time make the Arctic and its residents (humans as well as other biota) extremely vulnerable to the effects of the pollutants and thus making crucial to study OHCs in the different compartments of the Arctic ecosystem.

Greenland (Greenlandic: *Kalaallit Nunaat)*

Greenland is the world's largest non-continental island on the North American continent between the Arctic Ocean and the North Atlantic Ocean. Geopolitically, it is part of Europe, an autonomous territory within the Kingdom of Denmark. Most of its land mass lies within the range of the Arctic circle. The ice cap is up to 3 km thick and contains 10% of the world's resources of freshwater (Statistics Greenland, 2020).

The total area of the island is 2,166,086 km^2 of which ice-free area is 410,449 km^2 (~19% of the total area). The climate ranges from Low-Arctic in the South to Arctic in the North, while some deep fjords have sub-Arctic climate, allowing a few trees to grow. The winters are harsh and polar night lasts one to five months, and the summers are cool with midnight Sun, where the mean temperature does not exceed 10ºC. The further to the north, the colder, drier, and less windy it is. July is the warmest month while February and March are the coldest (Statistics Greenland, 2020).

There are multiple airports, military airbases and aerodromes all over Greenland. Thule Air Base is the biggest military Airbase in Greenland located in Pittufik region. The other civilian-use airports are in Kangerlussuaq, Illulisat and Nuuk of which Kangerlussuaq is the biggest one. Other areas have small airstrips and aerodromes to access via helicopters and chartered flights (Mittarfeqarfiit, 2012).

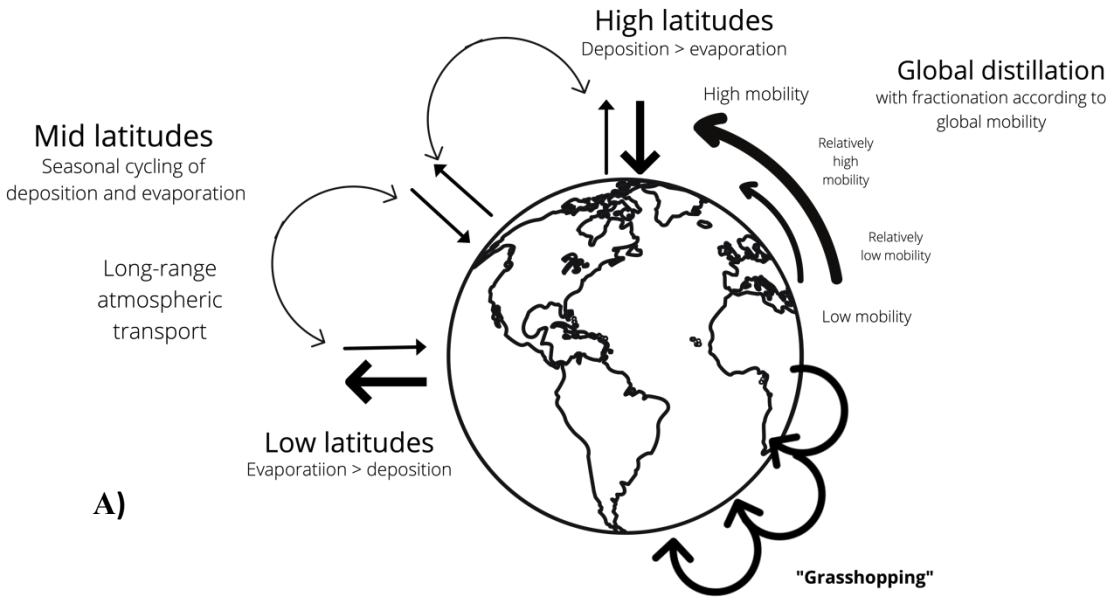
Greenland has the world's lowest population density (0.3 persons per square kilometer). The population lives exclusively at the coast in towns and settlements. Nuuk is the biggest town where almost a quarter of population lives. The other more populated towns are Sisimut, Ilulissat, Aasiaat and Qaqorrtoq. Most of the population is Indigenous Greenlandic – the Inuit population (Statistics Greenland, 2020).

The Greenlandic population, especially the Inuit population, have some of the highest levels of POPs globally (AMAP, 2015; Long et al., 2012) and are at greater risk of potentially adverse health outcomes (Lakhmanov et al., 2020), because of the exposure to the environmental contaminants through the traditional diets. These high levels of POPs in the Inuit population are linked to neurobehavioral effects, endocrine effects, cardiovascular effects, carcinogenic effects, disturbance of child development, immune function and reproductive abilities (Hjermitslev et al., 2020; Rigét et al., 2016).

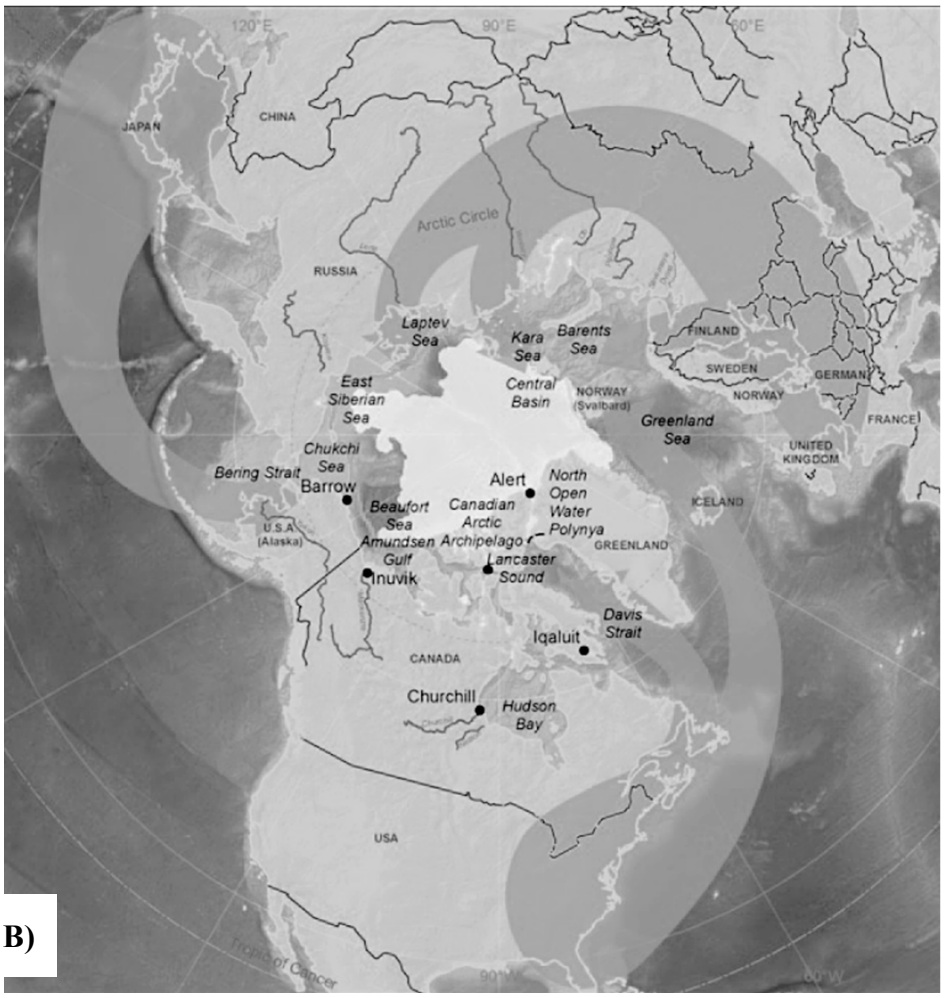
Arctic Charr *Salvelinus alpinus* (L.)

High latitude biota have to face certain major abiotic limitations, such as consistently low temperatures, extreme variations in radiant energy and nutrients on an annual basis (Christoffersen et al., 2008; Vincent & Laybourn-Parry, 2009). Lakes in Greenland are species-poor ecosystems and with a few exceptions, the existing fish community consist of Arctic charr (*Salvelinus alpinus, L.*), which is found in lakes and rivers all over Greenland (Jeppesen et al., 2017) and three-spined sticklebacks (*Gasterosteous aculeatus*) in the southern and western part. Arctic charr is the top predator fish in Greenlandic freshwater food webs (Jeppesen et al.,

2001, 2017). Non-anadromous or landlocked Arctic charr (*Salvelinus alpinus*) are usually the marine fish which no longer can migrate back to the sea, but have become established permanently in freshwater lakes and drainage basins, isolated from the ocean (Encyclopedia 2021; Power et al., 2009). For instance, in north and northeast Greenland, Arctic charr is the only fish present in freshwater lakes, while in south-west to mid regions of Greenland sticklebacks are also present in some of the lakes, together with Arctic charr (Christoffersen et al., 2008; Jeppesen et al., 2017). When fish are present in the lake, they are key players in structuring the food webs as they have a strong impact on the size, abundance, and structure of the zooplankton in the lakes (Jeppesen et al., 2017). A typical Arctic/Greenland lake has a short food web. As OHCs levels are higher in species at highest trophic position, it is only expected that Arctic char which is at the top of lake food chain will have the highest amount of OHCs in the lake compared to the other biota. Fish can accumulate high concentrations of OHCs and are an important vector of these contaminants to humans and wildlife. Arctic charr are widely distributed in the Arctic and can be an important food source for indigenous peoples. Moreover, landlocked Arctic charr (restricted to lakes and connecting streams) are relatively high in concentrations for freshwater environments due to their higher position in freshwater food webs. In Arctic charr, several factors have been propositioned to account for accumulation of OHCs: food chain structure, feeding strategy growth rate, age and lipid content as well as the trophic status of the lake (Cabrerizo, Muir, Köck, et al., 2018) .



A)



B)

Figure 2 A) POP migration processes. At high latitudes and lower temperatures global deposition processes become more pronounced than evaporation. Adapted from Wania and Mackay (1996). B) Map of the Arctic including major pathways for atmospheric contaminant transport from the source regions depicted by arrows. Adapted from Kirk and Gleason (2015).

Long Range Atmospheric Transport (LRAT) of OHCs to the Arctic Environment

For many years the polar regions were considered pristine, far away from the chemical and POPs contamination plaguing the other parts of the world. Since then, this concept has proven to be untrue/naïve. The probability of toxic contaminants reaching the polar regions was under consideration since late 1970s and early 1980s after regular experience of polluted air masses known as "Arctic Haze" which baffled the scientist and military personnel alike (Wania & Mackay, 1996). Since then, multiple studies have shown that the certain toxic chemicals are present in the Arctic (AMAP, 1998; Oehme & Manø, 1984). It has been realized that the concentrations remain present in surprising levels/concentrations even after the ban in most industrial countries of the Northern hemisphere. Although, the levels found in the Arctic are much less than the levels in temperate and tropical areas, those are enough to trigger toxicity concerns for the Polar biota and Indigenous population (AMAP, 2015).

OHCs are transported to the Arctic from its source regions via long-range atmospheric transport. These compounds are usually semi-volatile and get volatilized at the warmer temperatures of temperate and tropical regions (where they are mostly produced). They travel towards the poles via repeated cycles of deposition and evaporation, driven by seasonal, frontal, and diurnal changes in temperature aka *grasshopping* their way through the environment to arrive to the cold high latitudes, which are generally remote environments where they get condensed and deposited (aka Global distillation theory) (Kidd et al., 1998; Muir et al., 1995; Simonich & Hites, 1995; Wania et al., 1998; Wania & Mackay, 1993, 1996). Moreover, in the process of transport, these compounds with different volatilities get "fractionated" at different temperatures (which decreases with increasing latitudes), with highly volatile compounds being able to travel the farthest (Wania & Mackay, 1993) (Figure 2 A and B).

General Objectives

The general aim of this thesis was to determine the patterns of OHCs distribution in Greenlandic freshwater lake across time and space. To achieve this, first, three sediment cores collected in the year 2015 were analysed for OHCs (PCBs, DDTs, PBDEs, HCHs, Endosulfans, Chlordanes, Heptachlors, Drins, HCB, Mirex, Methoxychlor, Octachlorostyrene) from lakes Q5, NOW14 and NOW5 to understand how the presence of different living organisms (humans, birds) in each of the three lake areas impacted the OHCs in them and to understand the temporal gradient of OHCs arrival to these remote sites (chapter 1: *Seabird mediated transport of OHCs to the remote Greenlandic freshwater lakes*). Secondly, surface sediments from 37 freshwater lakes across Greenland were analysed for OHCs (PCBs, DDTs, PBDEs, HCHs, Endosulfans, Chlordanes, Heptachlors, HCB, Mirex, Methoxychlor, Octachlorostyrene) to understand the patterns of OHCs distribution in the lakes and distinguish between LRAT, influence from the American continent and local pollutions sources (chapter 2: *Occurrence and distribution of organohalogen compounds in freshwater lake sediments across Greenland*). Finally, Arctic charr (*Salvelinus Alpinus*) from 25 freshwater lakes across Greenland were analysed for OHCs (PCBs, DDTs and PBDEs) to determine the range of OHCs concentrations in Arctic charr and understand the accumulation patterns of OHCs in Arctic charr (chapter 3: *Long range transport and local effects enhance OHCs accumulation in Arctic Charr (Salvelinus Alpinus) from Greenland freshwater lakes).*

Chapter 1: Seabird-mediated transport of organohalogen compounds to remote sites (Northwest Greenland)

Abstract

The role of sea birds as carriers of pollutants over long distances was evaluated by analysing organochlorine and organobromine compounds in lake sediment cores from three remote sites around the North Water polynya in Northwest Greenland. One lake, NOW5, was in the vicinity of a little auk (Alle alle L.) bird colony, whereas the other two lakes, NOW14 and Q5, were undisturbed by seabirds. The former was strongly acidic (pH=3.4) but the latter has a pH close to 8. Due to the guano loading, NOW5 exhibited higher chlorophyll concentrations (74 μg/L) than the other two lakes (1.6-3.4 μg/L), as well as higher content of total phosphorous (0.34 mg/L vs. 0.007-0.01 mg/L) and total nitrogen (3.75 mg/L vs. 0.21-0.75 mg/L). The concentrations of all organohalogen compounds were substantially greater in NOW5 than in the other lakes, indicating the strong influence of these seabirds in the transport and deposition of these compounds to remote sites. However, not all compounds showed the same increases. Hexachlorocyclohexanes and endosulfans were more than 18 times higher in NOW5, the drin pesticides and hexachlorobenzene (HCB), between 9.5-18 times and DDTs, polybromodiphenyl ethers (PBDEs), polychlorobiphenyls (PCBs) and chlordanes about 2.7-6 times. These differences demonstrated that the bird-mediated deposition have a preservation effect of the less stable and more volatile compounds, e.g., those with log Kaw < -2.4, log Koa < 9 and/or log Kow < 6.8. The results also showed that the sedimentary deposition fluxes of PCBs, HCHs, drins, chlordanes, PBDEs, HCB and endosulfans were highest in the upper sediment layer of the polynya lake, corresponding to year 2014. In contrast, the highest DDT fluxes were found in 1980. These trends indicate that despite restrictions and regulations, bird transport continues to introduce considerable amounts of organochlorine and organobromine pollutants to the Arctic regions except for DDTs, which show successful decline, even when mediated by bird metabolism.

Introduction

Organic molecules with high degrees of halogen substitution, e.g., organochlorine and organobromine compounds, were produced and used due to their high chemical stability, fire and thermal resistance, and, in some cases, pesticide activity. Unfortunately, these properties caused environmental pollution problems and human health deleterious effects. First, their high stability to environmental degradation and semi-volatility boosted their spread over long distances through the atmosphere. Second, their hydrophobic properties favoured their accumulation in flora and fauna, which led to biomagnification along the aquatic and continental trophic chains.

A substantial number of compounds with these properties have been phased out of use and production. Most organochlorine compounds such as polychlorobiphenyls (PCBs), aldrin, dieldrin, endrin, heptachlor, and other legacy pollutants listed in the Stockholm Convention's "dirty dozen" (Korosi et al., 2017) have been banned worldwide in the last decades. For instance, among the banned compounds, aldrin, dieldrin and endrin were used as insecticides from the 1950s to the early 1970s (Blais and Muir, 2005). Aldrin is readily metabolised to dieldrin in plants and animals which is more resistant to biodegradation making it more toxic (Vorkamp, Rigét, et al., 2004). Giving another example, among hexachlorocyclohexanes (HCHs), γ-HCH was widely used around the globe but the overall usage significantly decreased in the 1980s and 1990s (Hung et al., 2010) despite the fact that it is still in use in some countries. Endosulfan and methoxychlor belong to a new group of less persistent chlorinated pesticides and are still used in Europe, USA and, most likely, in other world areas.

Despite of these restrictions, many of these compounds called persistent organic pollutants (POPs) are still known to linger in the various environmental compartments from close and distant sites of human activity, reaching the most remote places of the planet, such as high mountains (Grimalt et al., 2001; Grimalt, Borghini, et al., 2004; Grimalt, Van Drooge, et al., 2004) and Arctic areas, where they were never produced or used (Ma et al., 2011; Rigét, Vorkamp, et al., 2010). In the absence of significant local anthropogenic inputs, the regional and global distributions of these compounds is increasingly reflecting phase partitioning between the environmental reservoirs such as air, water, soil, vegetation and ice, where POPs get accumulated. In general, the concentrations of phased-out or heavily restricted contaminants like PCBs, DDTs, hexachlorobenzene (HCB), chlordanes, dieldrin and their metabolites are now stabilizing or decreasing (Muir and de Wit, 2010). In contrast, many brominated flame retardants, for example, the polybromodiphenyl ethers (PBDEs), which have

the same bio-accumulative properties such as PCBs, are still in production and use and their concentrations are in fact, increasing in the Arctic (de Wit et al., 2010).

Knowledge on contamination trends and origins is critical for determining the extent of POP transport and accumulation to the Arctic (Rigét et al., 2020; 2016, 2019). In addition to atmospheric transport, some studies indicate that migratory species may also play a critical role in translocating POPs between ecosystems, increasing productivity in otherwise unproductive systems (Blais et al., 2007; Evenset et al., 2004; Michelutti et al., 2010; Michelutti, Keatley, et al., 2009; Roosens et al., 2007). This is especially true for sea birds which feed at sea and come to land to breed, bringing nutrients as well as contaminants into freshwater systems (Blais et al., 2005; Davidson et al., 2018; Evenset, Carroll, et al., 2007; González-Bergonzoni et al., 2017; Polis et al., 1997). Many avian species are migratory, travelling thousands of kilometers from breeding sites to wintering grounds, spending majority of their life in both areas (Wang et al., 2019). In recent decades, a number of surveys have indicated large accumulations of various POPs in birds all across the world, suggesting that pollutant levels in these organisms are related to their surrounding environments (Blais et al., 2007; Bustnes et al., 2012; Huertas et al., 2016; Mehlum & Daelemans, 1995; Roosens et al., 2007; Wang et al., 2019). Seabirds may be the most globally relevant bio-vectors since they are keystone species that represent the dominant form of wildlife along coastlines worldwide and form dense nesting colonies that can number in the millions of individuals (Michelutti et al., 2009a).

Local nutrient enrichment from guano has been documented, but the possibility of POP contamination in areas near seabird nesting sites has only been probed by a handful of studies (Blais et al., 2005; Choy et al., 2010; Evenset, Christensen, et al., 2007; Michelutti, Liu, et al., 2009). Most of these studies have been conducted at Cape Vera on Devon Island (Nunavut, Canada; 76º15'N, 89º15'W) where a colony of northern fulmars (*Fulmarus glacialis*, L.) was observed to release POPs and metals to the environment through their guano (Blais, 2005; Choy et al., 2010; Michelutti, Keatley, et al., 2009; Michelutti, Liu, et al., 2009). Another study was conducted in Lake Ellasjøen (Bjørnøya; Barents Sea; 74º30'N, 19º00'E) where colonies of little auk (*Alle alle*), kittiwake (*Rissa tridactyla*, L.) and glaucous gull (*Larus hyperboreus*, Gunnerus) are present (Evenset, Carroll, et al., 2007; Evenset, Christensen, et al., 2007). These studies have been focused on the transport of PCBs and DDTs, and, in the case of Lake Ellasjøen, also hexabromocyclododecanes.

In the present study, we are exploring the efficiency of transport of POPs by guano deposits in one Greenland site, at the southern end of the North Water Polynya, Northern Baffin Bay, which lies between Greenland and Canada (Figure 3). This site allocates the largest

polynya in the Arctic which covers around 85,000 km^2 with little auk. Our study focusses not only with the most hydrophobic POPs, e.g., PCBs, and DDTs, but also on more hydrophilic compounds such as aldrin, dieldrin, endrin, heptachlor, HCHs, chlordanes, endosulfans and HCB. PBDEs have also been considered. North Water Polynya (NOW) is one of the most productive marine environments in the Arctic owing to the combination of year-round nutrient rich, open waters and constant light in the summer, making it an ideal study location (González-Bergonzoni et al., 2017; Ribeiro et al., 2021). Three freshwater lakes located along the coast of NOW were selected based on their ecological conditions: one with a large migratory colony of little auk in the catchment (North Water; NOW5), one with no birds and historical human presence (Hunter gatherer Inuit-Thule people) from around 1400 AD (NOW14) and one without any interference from birds or humans (Q5).

Sediment cores were collected in each of these lakes to provide time-trend information on whether increased restrictions in the use of some products at lower latitudes may have resulted in decreasing levels in the Arctic and/or whether banned compounds are still transported to this remote environment due to possible time lags (Malmquist et al., 2003). In this regard, paleolimnological studies in remote sites provide useful information on the fate and transport processes of these pollutants (Fernández et al., 2000; Korosi et al., 2017). By using lake sediments, past atmospheric deposition rates can indirectly be estimated and compared with current contamination levels. Unfortunately, there is a dearth of information on depositional chronology of concentrations or fluxes of contaminants in freshwater lake sediments from the Arctic compared to the high altitude freshwater lakes (Grimalt et al., 2001; Grimalt, Borghini, et al., 2004; Grimalt, Van Drooge, et al., 2004). Only a few studies have provided information on concentrations and fluxes of contaminants in freshwater lakes in the European Arctic (Evenset, Christensen, et al., 2007) and Canadian Arctic (Muir et al., 1995, 1996; Stern et al., 2005), making the present study an important contribution to the available literature.

Objectives

Here, we seek to understand what the transfer of POPs has been to these reference Arctic freshwater lakes in Greenland at present and in the past, and how the presence of bird colonies may have affected their deposition pattern. Specifically, a chronological comparison of the POPs accumulation in sediment cores from the three selected lakes, starting from the industrialisation period to the present, is reported.

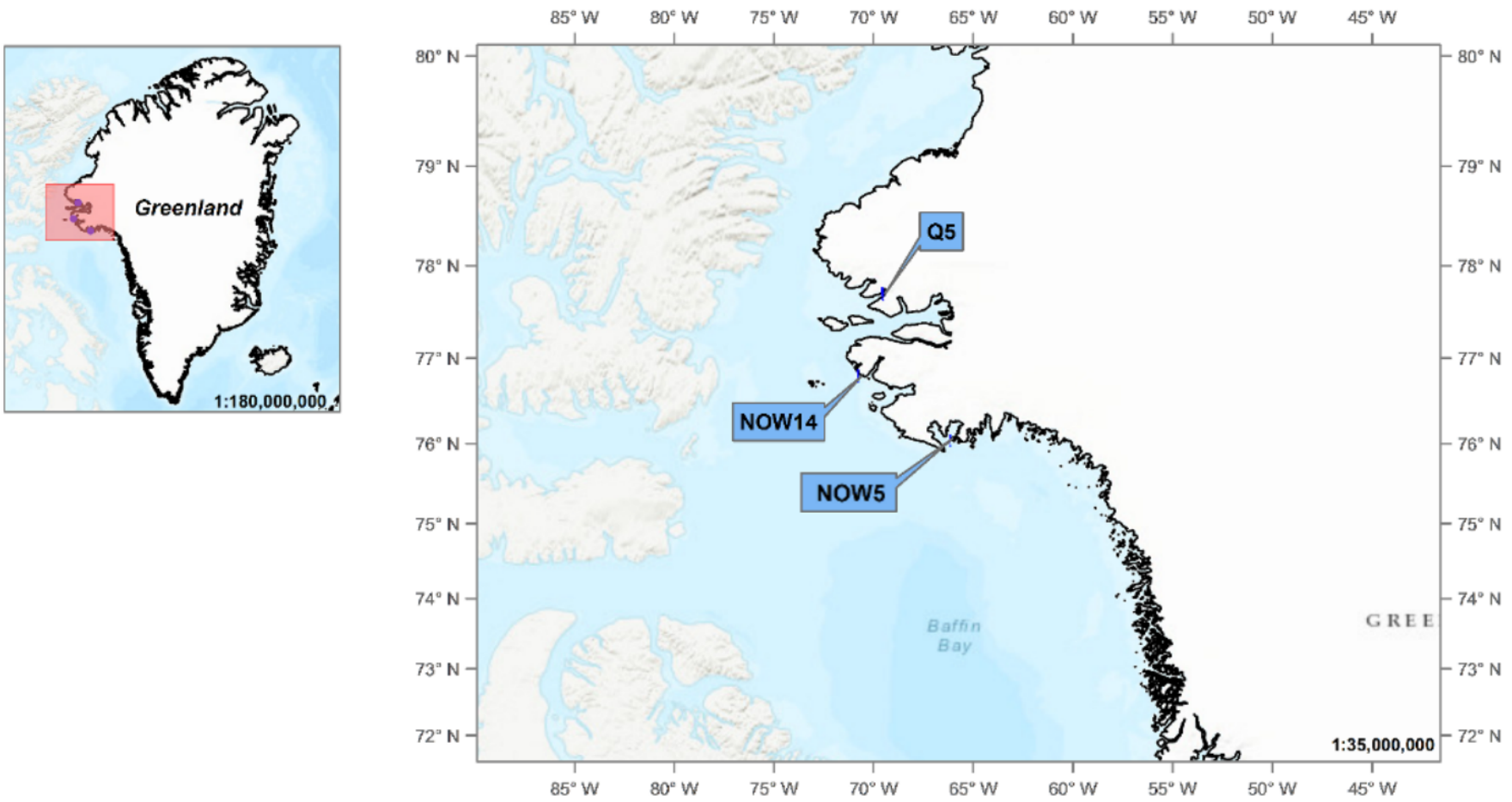


Figure 3 Map showing the location of the studied lakes. NOW5 is the lake hosting a Polynya.

Materials and Methods

Sampling

Samples were collected from the three freshwater lakes on the coast of NOW polynya in the summers of 2014 (NOW5), 2015 (NOW14), and 2016 (Q5; Figure 3). Lake coring was carried out using an HTH gravity corer with an internal diameter of 8.5 cm. The cores were sliced and stored frozen until analysis. Further details of sampling and dating of the sediment cores have been described elsewhere (Davidson et al., 2018).

Table 1 Characteristics of the studied lakes.

	NOW5 (Salve Ø)	*NOW14 (Nuuliit)*	*Q5 (Qaanaaq)*
Latitude	76.04386	76.800518	77.70713
Longitude	-65.99149	-70.60262	-69.41987
Core length to 1900 (cm)	0-12.5	0-5.5	0-12.5
Year of sampling	2014	2015	2016
Depth (m)	18	1	17
pH	3.4	8.3	7.98
Chla (μg/cm^2) or μg/l	74	3.4	1.6
T (^{o}C)	2.4	11.90	8.1
TP (mgP/l)	0.37	0.01	0.007
TN (mg/l)	3.75	0.75	0.212
Living organisms in the catchment	Birds (Little auk, thick-billed murre, common eider)	Inconsistent presence of Humans (Thule people)	None

Chemicals and Reagents

Acetone, ethyl acetate, cyclohexane, isooctane and copper (particle size < 63 μm) were from Merck (Darmstadt, Germany). The Florisil cartridges (20CC; 5 g) were acquired from Waters (Milford, MA, USA). Standards of 1,2,4,5-tetrabromobenzene (TBB), PCB 209 and the solution mixture of OCs were purchased from Dr Ehrenstoffer (Augsburg, Germany).

Solution mixtures of PBDEs, BDE 118 and [3-^{13}C] BDE-209 were acquired from Cambridge Isotope Laboratories (Andover, MA, USA).

Analytical method

The frozen sediment core slices were freeze-dried overnight. Sediments (0.1-1.0 g) were placed in a glass centrifuge tube (10 ml), spiked with surrogate standards (TBB and PCB 209) and kept in contact overnight. After that period, the samples were extracted with 10 ml ethyl acetate/cyclohexane (5:2, v/v) by vortex mixing for 1 minute and ultrasonic stirring (10 min). The extract was centrifuged (10 min; 3000 rpm) and transferred to 40 ml flasks. This procedure was repeated twice. The total extract was then concentrated to 1 ml by vacuum rotary evaporation. About 200 mg of activated copper was added to the extracts and left overnight to eliminate sulphur interference. Clean-up was performed using 5 g florisil cartridges that were eluted with 20 ml ethyl acetate/cyclohexane (5:2, v/v) after conditioning. This extract was finally concentrated to 0.5 ml.

Copper was activated by ultrasound stirring in a suspension of hydrochloric acid (25%; v/v) for 15 min. This procedure was followed by several Milli-Q washes for acid elimination until pH 7. Two rinses with acetone removed the water, and lastly, the activated copper was stored in hexane at -20 ^{o}C.

Organochlorine compound analysis

Before chromatographic analysis, an internal standard of PCB-142 was added to each sample. The OCs were identified and quantified by gas chromatography (GC; Agilent Technologies 7890N) coupled to mass spectrometry (MS, Agilent Technologies 5975C) operating in negative chemical ionisation mode (GC-NICI-MS). This instrument was provided with a HP-5MS capillary column (60 m length, 0.25 mm internal diameter, 0.25 μm film thickness; JW Scientific) protected with a retention gap. The injection was performed in splitless mode. Injector and detector temperatures were 280^{o}C and 325^{o}C, respectively. The oven temperature was held at 90^{o}C for 2 min, increased to 130^{o}C at 15^{o}C/min and 4^{o}C/min to 310^{o}C with a final holding time of 10 min. Ultrapure Helium and ammonia were used as carrier and reagent gasses, respectively.

Polybromodiphenyl ether analysis

Before chromatographic analysis, internal standards of BDE-118 and [3-^{13}C] BDE-209 were added to all the samples. A GC (Agilent Technologies 7890N) coupled to a MS (Agilent Technologies 5975C) operating in negative chemical ionisation mode (GC-NICI-MS) was used for identification and quantification of the PBDE congeners (17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190 and 209). The instrument was equipped with a low bleed fused silica capillary column (15 m length, 0.25 mm ID, 0.10 μm film thicknesses; DB-5MS) protected with a retention gap. The oven temperature was programmed from an initial temperature of 90^{o}C which was kept for 1.5 min followed by heating to 200^{o}C at 40^{o}C/min, a second increase up to 275^{o}C at 5^{o}C/min and a third increase to 300^{o}C at 40^{o}C/min. This temperature was held for 10 min and then increased to 310 ^{o}C at 10 ^{o}C/min with a final holding time of 2 min. Ammonia was used as reagent gas. Identification and quantification were performed by injection of PBDEs standard solutions (Bravo et al., 2017; Vizcaino et al., 2010).

Quality Control and Quality Assurance

Three procedural blanks were analysed with each batch of samples. Identification and quantification of OCs and PBDEs were performed by injection of external standards at different concentrations, and all the samples were blank corrected. Method detection limits were calculated from the average signals of the procedural blank levels plus three times the standard deviation. They ranged between 0.002 and 0.364 ng/g for the individual OCs and 0.001 and 0.285 ng/g for the brominated compounds. The limits of quantification were calculated from the averages of the procedural blanks plus five times the standard deviation. They ranged between 0.003 and 0.569 ng/g for the individual OCs and between 0.001 and 0.423 ng/g for PBDEs. One-half of the limits of detection were assigned to the values below the limits of detection. Pentachlorobenzene was below the LOD in most sediment sections and therefore not included in further analysis.

Results and Discussion

The lakes had a strong difference in terms of depositional setting. The waters of NOW5 were highly acidic with a pH of 3.4, whereas the pH values of NOW14 and Q5 were close to 8 (Table 1). This difference can be attributed to the influence of *A. ale* guano depositions (Davidson et al., 2018). In Spitzbergen, guano depositions of these birds also resulted in acidic lake water (Zwolicki et al., 2013). These highly acidic values have not been reported in other lakes receiving high amounts of guano depositions from other bird species.

These guano depositions are also responsible for the other observed differences between the lake waters. Thus, NOW5 has higher total phosphorous and nitrogen, 0.34 mg/L and 3.75 mg/L, respectively, than the other two lakes, 0.007-0.01 mg/L and 0.21-0.75 mg/L, respectively. Obviously, these differences led to strong contrasts in lake productivity, e.g., NOW5 show high chlorophyll concentrations (74 µg/L vs. 1.6-3.4 µg/L, respectively).

Concentrations

The concentrations of all organochlorine and organobromine compounds studied were higher in NOW5 lake than in the other two reference lakes (NOW14 and Q5; Table 2). The median concentrations of DDTs, PBDEs, PCBs, and chlordanes in the NOW5 core, 1.9 ng/g, 1.3 ng/g, 1.2 ng/g, and 0.040 ng/g, respectively, are about 2.7-6 times higher than the medians in NOW14 and Q5 lake cores, 0. 43-0. 64 ng/g, 0.22-0.37 ng/g, 0.26-0.44 ng/g, and 0-0.010 ng/g, respectively. In the case of the drin pesticides and HCB, the NOW5 medians of 0.74 ng/g and 0.36 ng/g, respectively, are about 9.5-18 times higher than in NOW14-Q5, 0.050-0.078 ng/g and 0.020-0.023 ng/g, respectively. HCHs' and endosulfans' medians in NOW5, 0.18 ng/g and 0.020 ng/g, respectively, are more than 18 times higher than in NOW14-Q5, 0-0.010 ng/g and below detection limit, respectively.

The concentrations of all POPs tested in lakes with no bird influence (NOW14 and Q5; Table 2) are lower than those reported in the lacustrine cores from high mountain European lakes (Grimalt, Van Drooge, et al., 2004), Yukon lakes (Rawn et al., 2001) and Lake Ellasjøen (Bear Island; Norway; Evenset, Christensen, et al., 2007) (Table 3). The concentrations of HCB, HCHs, endrins, and endosulfans in NOW14 and Q5 (Table 2) are also lower than those reported in cores from other Arctic lakes, including the Canadian Arctic, Alaska and Bear Island (Table 3).

However, the concentrations of DDTs in these lakes with no bird influence (max. 0.8-1.7 ng/g; Table 2) are higher than those observed in lake cores from Alaska and Devon Island

(max 0.15-0.20 ng/g; Stern et al., 2005; Allen-Gil et al., 1997) and similar to those from some Canadian Arctic lakes (Muir et al., 1995; 1996). The concentrations of PCBs (max. 0.48-0.90 ng/g; NOW14 and Q5; Table 2) are also lower than those reported in lacustrine cores from Svalbard and the Canadian Arctic (max 2.5-59 ng/g; Muir et al., 1995;1996; Rose et al., 2004), similar to those from Kangerlussuaq (Greenland; max 0.60-1.3 ng/g; Malmquist et al., 2003) and higher than in lake cores from Alaska (0.12 ng/g; Allen-Gil et al., 1997). The concentrations of PBDEs (max. 0.27-0.37 ng/g; Table 2) are comparable to those reported in lake cores from Devon Island (Nunavut, Canada; max. 0.25 ng/g; Stern et al., 2005) and higher than those reported in Kangerlussuaq (Greenland; max. 0.001-0.02 ng/g; Malmquist et al., 2003)

Except for DDT in Lake Redon, which has comparable values (max. 15-16 ng/g; Tables 2-3), the concentrations of all POPs from the core of the lake of strong bird influence, NOW5, are lower than those reported in the lake cores from remote high mountains of Europe (Grimalt, Borghini, et al., 2004; Grimalt, Van Drooge, et al., 2004). In contrast, the higher concentrations caused by guano deposition mean that these POP concentrations in the core from this lake (NOW5) which is situated very close to NOW14 and Q5 has now higher values than in many of the Arctic sites discussed above.

Similarly, the maximum concentrations of DDTs, drins, PBDEs, PCBs, HCHs, HCB, chlordanes and endosulfans, in NOW5, which are 16 ng/g, 7.9 ng/g, 6.2 ng/g, 3.8 ng/g, 1.2 ng/g, 0.65 ng/g, 0.47 ng/g, and 0.25 ng/g, respectively, are higher than those in Kangerlussuaq lakes (Greenland), where PCBs, PBDEs, chlordanes and HCB concentrations, were 0.60-1.3 ng/g, 0.001-0.02 ng/g, 0.03-0.6 ng/g, and 0.01-1.5 ng/g, respectively (Malmquist et al., 2003; Table 3). They are also higher than those in Devon Island lake cores (Canadian Arctic) for DDTs, max. 0.20 ng/g, HCHs, 0.33, ng/g, PCBs, 2.7, ng/g, PBDEs, 0.25, ng/g, chlordanes, 0.08, ng/g, dieldrin, 0.43, ng/g, and endosulfans, 0.60 ng/g (Stern et al., 2005). A comparison of the mean core concentrations in NOW5 and the mean top 2 cm from lake sediment in Alaska (Elusive, Schrader, Feniak and Desperation Lakes from the Brooks Range) shows that the concentrations of HCB, 0.17 ng/g, HCHs, 0.090 ng/g, PCBs, 0.12 ng/g, DDTs, 0.15 ng/g, endosulfans, below detection limit, and chlordanes, 0.030 ng/g (Allen-Gil et al., 1997) are higher in the seabird influenced Greenland polynya lake (Tables 2 and 3). The organohalogen concentrations in NOW5 are similar to those found in other remote Canadian Lakes such as Yukon Lakes (Rawn et al., 2001) concerning DDTs, 0.86-21 ng/g, HCB, 1.1-1.9 ng/g, and HCHs, 0.46-1.6 ng/g, or lakes located between 49ºN and 82ºN (Muir et al., 1994; 1996) for HCB, 0.3-1.8 ng/g, HCHs, 0.05-2.9 ng/g, chlordanes, 0.08-3.3 ng/g, and dieldrin, 0.05-3.2

ng/g. However, these Canadian lakes exhibit higher PCB concentrations, 2.5-59 ng/g (Tables 2 and 3). PCBs are also found in higher concentrations than NOW5 lake in cores from Svalbard, 2.6-14 ng/g (Rose et al., 2004) and Ellasjøen, 72 ng/g (Bear Island; Evenset, Christensen, et al., 2007). In this last site, the concentrations of DDTs, 4.0 ng/g, and PBDEs, 0.73 ng/g, are lower than in NOW5.

Table 2 Statistical parameters of the concentrations of the organohalogen compounds found in the studied cores (ng/g dry weight).

	NOW5						NOW14						Q5					
	Min	Max	Top[i]	Mean	Median	SD[j]	Min	Max	Top[i]	Mean	Median	SD[j]	Min	Max	Top[i]	Mean	Median	SD[j]
HCB[a]	0	0.65	0.35	0.30	0.36	0.23	0.010	0.030	0.020	0.018	0.020	0.0075	0.010	0.060	0.011	0.023	0.020	0.014
PCBs[b]	0.14	3.8	1.7	1.5	1.2	0.96	0.10	0.48	0.26	0.28	0.26	0.10	0.070	0.90	0.48	0.43	0.44	0.22
HCHs[c]	0	1.2	0.71	0.29	0.18	0.30	0	0.020	0	0.011	0.010	0.0094	0	0.010	0	0.0029	0	0.0047
Drins[d]	0.020	7.9	0.16	1.6	0.74	2.2	0.040	0.19	0.050	0.078	0.050	0.052	0.020	0.16	0.020	0.078	0.050	0.052
DDTs[e]	0.12	16	0.12	2.7	1.9	3.4	0.35	0.80	0.35	0.60	0.64	0.14	0.19	1.7	1.1	0.56	0.43	0.38
Chlordanes[f]	0	0.47	0.19	0.080	0.040	0.12	0	0.040	0.010	0.014	0.010	0.010	0	0.020	0.0060	0.048	0	0.0070
PBDEs[g]	0.22	6.2	2.5	1.6	1.3	1.5	0.27	0.48	0.37	0.35	0.37	0.061	0.11	1.1	0.27	0.29	0.22	0.26
Endosulfans[h]	0	0.25	0.25	0.062	0.020	0.083	0	0	0	0	0	-	0	0.010	0.0010	0.00071	0	0.0024

[a]Hexachlorobenzene. [b]Polychlorobiphenyls (28+52+101+118+138+153+180 congeners). [c]Hexachlorocyclohexanes (α+β+γ isomers).

[d]aldrin+dieldrin+endrin. [e]2,4'-DDE+4,4'-DDE+2,4'-DDD+4,4'-DDD +2,4'-DDT+4,4'-DDT. [f]cis+trans chlordanes.

[g]17+28+47+66+71+85+99+100+138+153+154+183+190+209 congeners.

[h]α-+β-endosulfans+endosulfan sulphate. [i]value at the top of the core. [j]standard deviation.

Table 3 Sedimentary concentrations and fluxes of organohalogen compounds from other remote lakes.

Sites	Location	Compound	Concentrations (ng/g)	Flux (pg cm^{-2} y^{-1})
Pyrenees (Lake Redon) (Grimalt, Van Drooge, et al., 2004) (1942-1992)	42º38'34''N 0º46'13''E	DDTs	Max: 15; Top: 15	
		PCBs	Max: 7.3; Top: 7.3	
		HCB	Max: 1.6; Top: 1.6	
Tatras (Grimalt, Van Drooge, et al., 2004) (1942-2001)	49º10'0''-49º13'36''N 20º0'39''-20º10'0''E	DDTs	Max: 30-190; Top: 1-50	
		HCHs	Max:1-10; Top: 1	
		PCBs	Max: 36-86; Top: 5.6-45	
		HCB	Max: 0.5-3.2; Top: 1	
Canadian Arctic Devon Island (Stern et al., 2005) (1908-1997)	75º34.420'N 89º18.545'W	DDTs	Max: 0.20; Top: 0.05	Max: 1.5; Top 0.71
		HCHs	Max: 0.33; Top: 0.22	Max: 3.8; Top: 3.1
		PCBs	Max: 2.7; Top: 2.6	Max: 37; Top 37
		PBDEs	Max:0.25; Top: 0.17	Max: 2.8; Top: 2.8
		Chlordanes	Max: 0.08; Top: 0.05	Max: 1.3; Top: 1.3
		Dieldrin	Max: 0.43; Top: 0.28	Max: 4.6; Top: 4.0
		Endosulfan	Max: 0.60; Top: 0.60	Max: 0.040; Top: 0.040
Ellasjøen (Bear Island) (Evenset, Christensen, et al., 2007) (1881-1994)	74º30'N 19º00'E	PCBs	Max: 72; Top: 48	
		DDTs	Max: 4.0; Top: 1.6	
		PBDEs	Max: 0.73; Top: 0.73	
Svalbard (Rose et al., 2004) (1980-1998)	77º33'-79º48'N 9º30'-15º00'E	PCBs	Max: 2.6-14; Top: 2.6-14	
Kangerlussuaq (Greenland)	67º16'-67º02'N 51º46'-51º07'W	PCBs	Max: 0.60-1.3; Top: 0.11-1.2	Mean: 3.0

(Malmquist et al., 2003) (1940-2000)		PBDEs	Max: 0.001-0.02; Top: 0-0.02	
		Chlordanes	Max: 0.03-0.6; Top: 0-0.6	1.0-4.0
		HCB	Max: 0.01-1.5; Top: 0-0.2	0.10-2.0
Yukon Lakes (Canada) (Rawn et al., 2001)	59º47'-64º00'N 128º46'-136º10'W	PCBs	Max: 33.5-11; Top: 33.5-2.2	135-1150
		DDTs	Max: 0.86-21; Top: 0.86-3.5	6.6-1300
		HCHs	Max: 0.46-1.6; Top: 0.13-1.4	7.5-36
		HCB	Max: 1.1-1. 9; Top: 0.06-1.1	4.2-87
Canadian Arctic (Muir et al., 1995; 1996) (1895-1990)	49º42'-81º45'N 71º30'-126º16'W	PCBs	Max: 2.5-59; Top: 2.5-40	11-425
		HCB	Max: 0.3-1.8; Top: 0.1-1.8	3.2-3.9
		DDTs	Max: 0.1-12; Top: 0.1-9.5	11-69
		Chlordanes	Top: 0.08-3.3	3.8-4.2
		HCHs	Top: 0.05-2.9	3-5.3
		Dieldrin	Top: 0.05-3.2	4.3-4.7
Alaska (Allen-Gil et al., 1997)	68º16'-68º50'N 144º60'-158º45'W	HCB	Mean top 2 cm: 0.17	
		HCHs	Mean top 2 cm: 0.090	
		PCBs	Mean top 2 cm: 0.12	
		DDTs	Mean top 2 cm: 0.15	
		Endosulfans	Mean top 2 cm: 0	
		Chlordanes	Mean top 2 cm: 0.030	

Depositional fluxes

The sedimentation fluxes of all organochlorine and organobromine compounds considered for study were higher in the core of the NOW5 lake than in the cores of the other two reference lakes (NOW14 and Q5; Table 4). The medians of the fluxes of DDTs, PBDEs, PCBs, and chlordanes in NOW5 core, 10 pg cm^{-1} y^{-1}, 4.2 pg cm^{-1} y^{-1}, 5.9 pg cm^{-1} y^{-1}, and 0.15 pg cm^{-1} y^{-1}, respectively, are about 1.9-4.2 times higher than the medians in NOW14 and Q5 lake cores, 2.4-4.2 pg cm^{-1} y^{-1}, 1.3-2.2 pg cm^{-1} y^{-1}, 1.7-2.8 pg cm^{-1} y^{-1}, and 0-0.080 pg cm^{-1} y^{-1}, respectively. In the case of the drin pesticides and HCB, the NOW5 core medians of 5.2 pg cm^{-1} y^{-1} and 1.4 pg cm^{-1} y^{-1}, respectively, are about 9.5-13 times higher than in NOW14-Q5 core, 0.48-0.55 pg cm^{-1} y^{-1} and 0.11-0.12 pg cm^{-1} y^{-1}, respectively. The medians of HCHs and endosulfans in NOW5 core, 0.84 pg cm^{-1} y^{-1} and 0.070 pg cm^{-1} y^{-1}, respectively, are more than 21 times higher than in NOW14-Q5 core, 0-0.040 pg cm^{-1} y^{-1} and below detection limit, respectively.

Comparison of the data from Tables 3 and 4 shows that these sedimentation fluxes of all POPs in the lakes of the present study are lower than those described in lacustrine cores from Kangerlussuaq (Greenland; Malmquist et al., 2003), the Canadian Arctic (Muir et al., 1995; 1996) and Yukon Lakes (Rawn et al., 2001). However, there are two exceptions, the drins in the Canadian Arctic cores which have similar mean fluxes than NOW5 core, 4.3-4.7 pg cm^{-1} y^{-1} and 5.2 pg cm^{-1} y^{-1}, respectively (Tables 3 and 4), and the mean flux of PCBs in the Kangerlussuaq (3.0 pg cm^{-1} y^{-1}) which are lower than those of NOW5 core, 7.7 pg cm^{-1} y^{-1}. Comparison of the results of the present study with the POP composition in the cores from North West Greenland and Devon Island (Stern et al., 2005) shows that the latter had higher sedimentation fluxes than cores NOW14 and Q5 for of all POPs except in the case of DDTs whose maximum sedimentation rates were 1.5 pg cm^{-1} y^{-1}, 7.2 pg cm^{-1} y^{-1} and 10 pg cm^{-1} y^{-1}, respectively, and therefore higher in North West Greenland (Tables 3 and 4). Conversely, for all POPs except PCBs, sedimentation fluxes are higher in the NOW5 core, which is influenced by the bird polynya, which values are 27 pg cm^{-1} y^{-1} and 37 pg cm^{-1} y^{-1}, respectively.

Table 4 Statistical parameters of the sedimentary deposition fluxes of organohalogen compounds found in the studied cores (pg cm^{-2} y^{-1}).

	NOW5						NOW14						Q5					
	Min	Max	Top[i]	Mean	Median	SD[j]	Min	Max	Top	Mean	Median	SD[i]	Min	Max	Top	Mean	Median	SD[i]
HCB[a]	0	4.9	4.9	1.5	1.4	1.3	0.030	0.30	0.28	0.14	0.12	0.11	0.045	0.67	0.067	0.18	0.11	0.17
PCBs[b]	0.77	25	24	7.7	5.9	6.3	0.30	3.6	3.6	1.9	1.7	1.2	0.44	5.5	2.9	2.7	2.8	1.3
HCHs[c]	0	9.9	9.9	1.6	0.84	2.1	0	0.20	0	0.058	0.040	0.071	0	0.073	0	0.017	0	0.028
Drins[d]	0.080	34	2.2	7.7	5.2	8.9	0.17	0.70	0.70	0.43	0.48	0.18	0.12	0.98	0.12	0.50	0.55	0.28
DDTs[e]	1.7	47	1.7	12	10	10	1.9	7.2	7.2	3.8	4.2	1.8	1.0	10	6.4	3.6	2.4	2.3
Chlordanes[f]	0	3.6	2.7	0.53	0.15	0.94	0	0.14	0.14	0.10	0.080	0.11	0	0.44	0.036	0.048	0	0.11
PBDEs[g]	1.5	35	35	8.4	4.2	8.2	0.80	5.1	5.1	2.5	2.2	1.7	0.57	7.1	1.7	2.0	1.3	1.9
Endosulfans[h]	0	3.5	3.5	0.41	0.070	0.78	0	0	0	0	0	-	0	0.061	0.0061	0.0043	0	0.015

[a]Hexachlorobenzene. [b]Polychlorobiphenyls (28+52+101+118+138+153+180 congeners). [c]Hexachlorocyclohexanes (α+β+γ isomers). [d]aldrin+dieldrin+endrin. [e]2,4'-DDE+4,4'-DDE+2,4'-DDD+4,4'-DDD +2,4'-DDT+4,4'-DDT. [f]cis+trans chlordanes. [g]17+28+47+66+71+85+99+100+138+153+154+183+190+209 congeners. [h]α-+β-endosulfans+endosulfan sulphate. [i]value at the top of the core [j]standard deviation

Influence of birds on lacustrine POP accumulation

The specific conditions of sedimentation in NOW5 are strongly influenced by the bird population, as shown by the sedimentary concentration and flux differences between the three lakes chosen for study (Tables 2 and 4, respectively), resulting in the observed significant increase in organochlorine and organobromine compounds compared to the seabird free lakes.

Because POPs tend to partition from gas and liquid phases to organic phases, the accumulation of atmospheric POPs is also driven in part by gradients in organic carbon content of soils and sediments(Nizzetto et al., 2010). The fertilizing effects of guano deposits are the main sources of organic carbon in the lakes. Furthermore, eutrophication and the accumulation of organic matter can be related with chlorophyll a concentration. Phytoplankton in the water column is a transport driver of organohalogen compounds to the sediments both in lacustrine (Meijer et al., 2006) and marine environments (Dachs et al., 2002). In lacustrine environments, the sedimentation fluxes of the organohalogen compounds driven by phytoplankton sinking in the water column have been related to the water column chlorophyll a concentrations by equation 1 (Meijer et al., 2006),

$$F_{sed} = 1.8 \cdot C_p \cdot 10^{(1.82 + 0.62\log(Chla))}/(69Chla + 146.8) \qquad \text{eq. 1}$$

where F_{sed} is the sedimentation flux of one organohalogen compound (ng m^{-2} d^{-1}), Chla is the concentration of chlorophyll a (kg m^{-3}) and C_p is the concentration of the organochlorine compound in phytoplankton (per volume of water; ng m^{-3}).

The estimated coefficients for the C_p values in lakes NOW5, NOW14 and Q5, 0.16 m d^{-1}, 0.024 m d^{-1} and 0.015 m d^{-1}, respectively, are obtained by calculating the chlorophyll a values defined by equation 1 using the chlorophyll concentrations of Table 1. These result in ratios of 6.5 and 10 for the relative sinking rates for NOW5/NOW14 and NOW5/Q5, respectively.

These values are intermediate between the ratios of the measured concentrations or deposition rates, in the range of 1.9-21 for NOW5/NOW14 and 2.1-13 for NOW5/Q5 when calculated using the median values (Table 5). These ratios are consistent with the enhanced effect of the bird deposition. As shown in a previous study(Meijer et al., 2009), significant transport from air to water occurs in the gas phase at air to water constants, log Kaw, higher than -2.4, and in the particulate phase at octanol to air constants, log Kow, higher than 9. Accumulation from the water column into sediments is observed at octanol to water constants,

log Kow, higher than 6.8 (Meijer et al., 2009). These conditions are fulfilled by most congeners of the ΣPCBs and ΣPBDEs and DDT metabolites (Table 5). The chlordanes also have constants close to these threshold values (Table 5). Accordingly, these compounds are those having lower NOW5/NOW14 and NOW5/Q5 ratios (1.9-4.2) because their deposition and accumulation in the sediments already occurs irrespectively of bird mediation. The other compounds do not have physical chemical constants favouring transport from air to water (HCB, some HCHs, α- and β- endosulfans) or accumulation in the sediments (HCB, HCHs, drins, endosulfans) (Table 5). In these cases, the difference in the accumulation is more relevant if enhanced by bird deposition and the NOW5/NOW14 and NOW5/Q5 ratios are much higher (≥ 9.5).

Furthermore, the rates of Table 5 indicate that bird-mediated deposition has a preservation effect of the less stable compounds, e.g., endosulfans (Guerin & Kennedy, 1992), whose concentrations and fluxes are much higher in NOW5 than in the other lakes.

The effect of the birds in transporting POPs to the high arctic lakes can reflect two processes: 1) from lower to higher latitudes when they migrate and 2) from the marine environment to inland where they feed and transport meal for their chicks. This transport is in the same direction as that described in the global distillation model and the tendency for semi-volatile POP chemicals to become concentrated in cold environments (Grimalt, Borghini, et al., 2004; Grimalt, Van Drooge, et al., 2004; Wania & Mackay, 1993, 1996) but through specific biogenic mechanisms. In any case, the polynya effect leads to higher rates of POPs in the lake sediments which are not diluted by the organic matter increases due to the higher productivity associated to the increase of nutrients from the guano deposits.

Table 5 Ranges of the physical-chemical constants of the organohalogen compounds found in the lakes.

	Log Kaw[a]	Log Koa[b]	Log Kow[c]	NOW5/NOW14[d]	NOW5/Q5[d]
HCB[e]	-1.158	7.38	5.73	12	13
PCBs[f]	(-2.087, -3.388)[g]	(7.71, 11.66)	(5.62, 8.24)	3.4	2.1
HCHs[h]	-3.677	(7.82, 8.88)	(3.93, 4.14)	21	>20
Drins[i]	(-1.801, -3.388)	(7.86, 8.59)	(5.20, 6.06)	11	9.5
DDTs[j]	(-2.769, -3.468)	(9.12, 10.38)	(5.87, 6.91)	2.4	4.2
Chlordanes[k]	-2.702	8.92	6.22	1.9	-
PBDEs[l]	(-3.516, -6.131)	(9.40, 18.42)	(5.88, 12.11)	1.9	3.2
Endosulfans[m]	(-2.576, -4.877)	(6.41, 8.54)	(3.66, 3.83)	>20	>20

[a]air-water constants. [b]octanol-air constants. [c]octanol-water constants. [d]Calculated from the median values of the calculated sedimentation rates. [e]Hexachlorobenzene. [f]Polychlorobiphenyls (28 + 52 + 101 + 118 + 138 + 153 + 180 congeners). [g]range of values for the compounds included in the group. [h]α + β + γ Hexachlorocyclohexanes. [i]aldrin + dieldrin + endrin. [j]2,4'-DDE + 4,4'-DDE + 2,4'-DDD + 4,4'-DDD + 2,4'-DDT + 4,4'-DDT. [k]cis + trans chlordanes. [l]Polybromodiphenyl eters (17 + 28 + 47 + 66 + 71 + 85 + 99 + 100 + 138 + 153 + 154 + 183 + 190 + 209 congeners). [m]α- + β-endosulfans + endosulfan sulphate. Constant data from US EPA (2022) and Beyer et al., (2002).

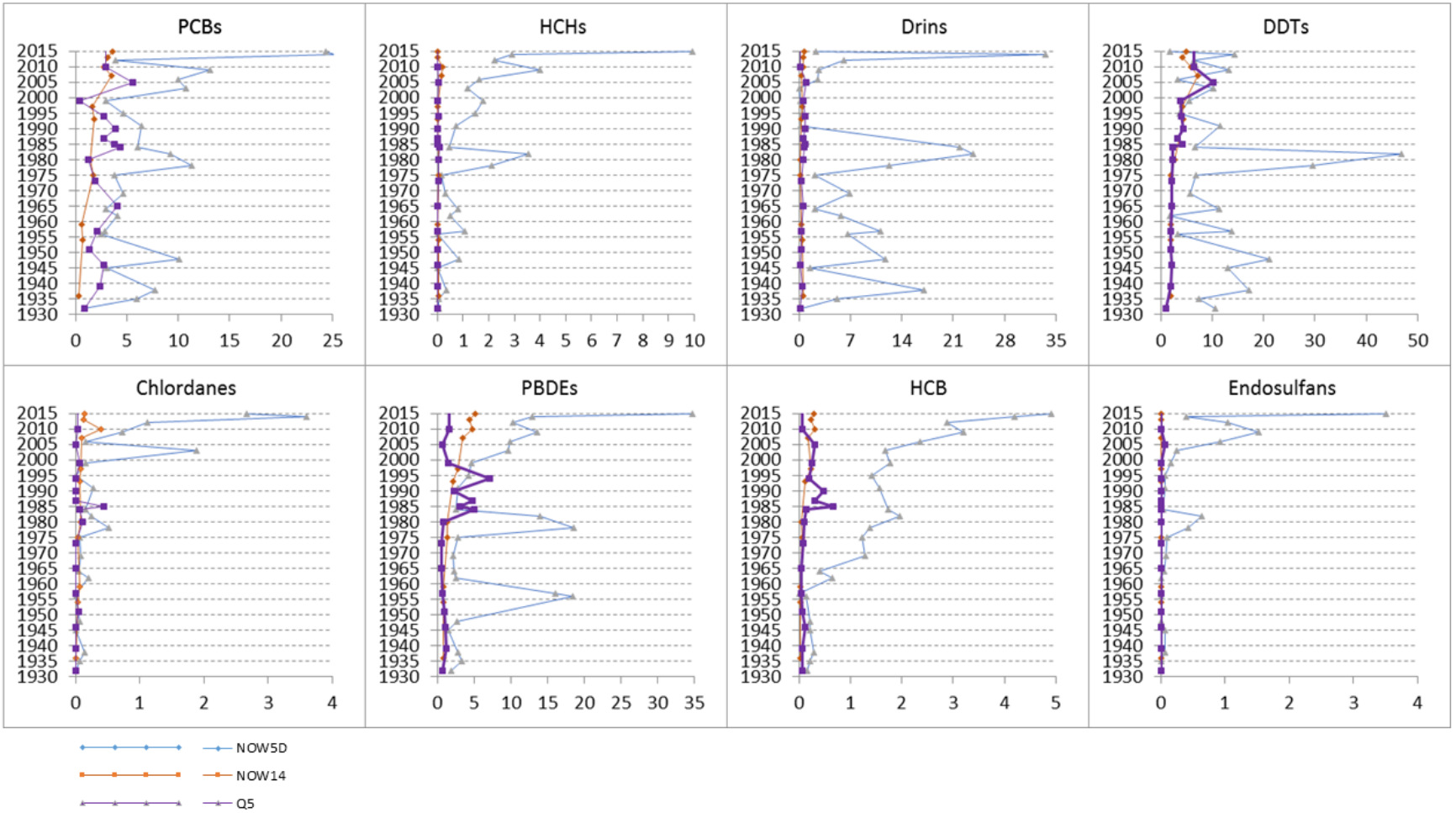


Figure 4 Downcore sedimentary deposition fluxes of the organohalogen compounds found in the studied cores (pg cm^{-2} y^{-1})

Temporal trends

With the major threat of climate change looming over the Arctic, favouring snowmelt re-emission of POPs that were deposited long ago in the various environmental compartments in the cold climate (AMAP, 2021; Arellano et al., 2011, 2015, 2018; Grimalt et al., 2009; Gustavsson et al., 2019) multiple new sources of POPs may emerge, leading to changes in transport rates and additional deposition the lakes. Consequently, monitoring lakes such as NOW5 with high sedimentation rates and supplies of contaminants from multiple sources is extremely beneficial since changes in contaminant input are reflected in the lake sediments.

Examination of the temporal trends of the sedimentary deposition fluxes of the measured pollutants (Figure 4) show much higher values for NOW5 than the other lakes. This is consistent with the overall results of Table 4 and highlights the biogenic POP transport effect linked to guano deposits once more. The most distinct feature of the majority of time profiles from this core is the increase to highest values in the most recent core sections, e.g., 2014, for many of the compounds examined, PCBs, HCHs, drins, chlordanes, PBDEs, HCB and endosulfans. Total DDTs are the lone exception showing a maximum peak in 1980. The values in the upper sections (most recent years) in the other two cores are significantly lower, with no increase. These temporal trends in core NOW5 show that despite the banning of many of the POPs, the pollutants released into the environment at lower latitudes are still transported to Arctic areas and have an impact on their ecosystems and that migratory bird activity is a main agent of long-range transport in the polynya.

In addition to this main feature, the cores from NOW5 show other patterns such as a maximum of the sedimentation fluxes of drins, PCBs, HCHs, DDTs, PBDEs, and endosulfans at 1980-1985 (Figure 4). This maximum likely reflects an episode of highest pollution by all these organohalogen pollutants and is coincident with the largest flux of DDTs recorded in this core. It is also coincident, with dating uncertainties, with a maximum of 4,4'-DDT and chlordanes in a lacustrine core from Devon Island (75º34.420'N 89º18.545'W; Stern et al., 2005). Other lower maxima reflected higher inputs from specific comments, e.g., PBDEs in 1955, PCBs, drins, and DDTs before 1955.

The fluxes of HCB followed a different pattern showing a continuous increase from 1960 to 2015 and a maximum value in this last year (Figure 4). HCB has been shown to display quite constant concentrations in the atmosphere in different remote sites, 35-85 pg m^{-3} in Europe (Van Drooge et al., 2004), 39-50 pg m^{-3} in North America (Daly et al., 2007), 56 pg m^{-3} in the Tibetan Plateau (Zhu et al., 2014) and 60 pg m^{-3} in Brazil (Guida et al., 2018) which is

close to background pollution levels, while the other organohalogen compounds identified in the lakes may reflect episodic inputs.

In general, the temporal changes of POPs in Arctic samples reported in the literature were showing decreasing trends for most organochlorine compounds and increases for the PBDEs. However, recent reports are describing that the global warming is leading to re-emission of POPs already deposited in cold areas which effects in the Arctic regions (AMAP, 2021). Concerning PBDEs, a study of sediment cores from Søndre Strømfjord, near Kangerlussuaq (West Greenland), performed in 2000 showed maximum concentrations in the top sediment sections of four of the seven cores studied (Malmquist et al., 2003). De Wit et al., (2010) also showed increasing trends for PBDEs in the freshwater sediments from the Canadian Arctic and from Greenland. In the sediment core of Lake Ellasjøen (Bear Island; Barents Sea, with a seabird colony), the PBDEs concentration of the congeners (BDE-28, 47, 99, 100, 153), 0.73 ng/g, also peaked in the surface sediments (Evenset, Christensen, et al., 2007).

PCBs concentration trends in Arctic biota have been reported to be decreasing (Rigét, Bignert, et al., 2010; Rigét, Vorkamp, et al., 2010). Decreasing trends were also identified in cores from Kangerlussuaq, West Greenland, where the concentration maximum of these pollutants peaked in 1970 (Malmquist et al., 2003). Similar decreasing trends were recorded in Lake Ellasjøen where the concentration maximum was observed in the core section of 1966 (Evenset, Christensen, et al., 2007). In other studies, i.e. Alaska (Gubala et al., 1995) and Finland (Kjeller & Rappe, 1995), PCBs were primarily found in layers starting 1950s with maxima in the 1970-1980s. A study from the Baltic, on the other hand, found PCBs appearing early in the 20th century (Muir et al., 1996). Sanders et al. (1992) also reported low levels of PCBs (mostly low molecular weight PCBs) in early 1900s. PCBs were commercially produced between the 1930s and 1980s (Bigus et al., 2014). However, on Devon Island, the concentrations of these pollutants in the sediment cores of lakes with strong bird influence (Cape Vera) show highest concentrations in the most recent core sections (Michelutti, Keatley, et al., 2009). This study likewise showed a strong contrast between the PCB concentrations in the core with bird influence (3.8 ng/g at the top) and no bird inputs (almost below limit of detection) which is consistent with the observations of the present study (Figure 2). The PCB profiles from Devon Island Lake sediment cores located at 75º34.420'N 89º18.545'W also showed maximum concentrations in the top sections (19 μg m^{-2} y^{-1}; Stern et al., 2005).

Lindane (γ-HCH) was used until recently when it was banned globally under the Stockholm Convention in 2009 (Kirk and Gleason, 2015). Arctic biota, especially seabird population, have showed decreasing trends for α- and γ-HCH (lindane) in Arctic Canada and

Greenland but increasing trends of β-HCH in East Greenland black guillemot eggs (Rigét et al., 2016). Since β-HCH has stronger affinity for organic matter than α-HCH and γ-HCH, is found in higher concentrations in biota (Li and Macdonald, 2005). However, in NOW5, the concentrations of all three isomers of HCHs were similar and showed highest concentrations in the top sections, indicating a distinct temporal trend than in the cores lacking bird influence, which showed much lower concentrations and fluxes (Figure 2). The HCH profiles in cores from Devon Island located at 75º34.420'N 89º18.545'W also showed maximum concentrations in the top sections and in the section dated in 1975 (1.95 and 2.2 μg m^{-2} y^{-1}, respectively; Stern et al., 2005).

Dieldrin, aldrin, endrin and chlordanes were banned or heavily restricted prior to the year 2000 (Kirk and Gleason, 2015). Although aldrin was widely used, it is readily degraded to dieldrin in the environment, which is the form of major concern in the Arctic. Most of the studies have focused solely on dieldrin, but in the present study all three drins were considered. Dieldrin and endrin were found in equally high concentrations in the core sections of highest sedimentation in NOW5.

HCB was first used in the 1950s with peak usage between 1970s to 1980. Despite the fact that it is currently banned it is commonly found in remote environments. For instance, in one study of freshwater lakes from Alaska, it was detected at concentrations of 0.17 ng/g dw in the top 2 cm of the sediment cores (Allen-Gil et al., 1997). In the current study, this compound is again found in highest concentration in the lake core of strong guano deposition with highest fluxes in the most recent core sections whereas the cores from the lakes free from bird influence show much lower concentrations and no discernable temporal trend.

As stated previously, the temporal profile of DDTs in the core from lake NOW5 was the only contaminant that did not show maximum values in the top sections of the core but in the section that corresponded to the year 1980. This temporal trend is in agreement with the banning policies implemented in European and north American countries. This profile is equivalent, within model age uncertainty, with the profile of 4,4'-DDT in a core from Devon Island which showed maximum concentrations in the section dated in 1988 (DV09; 1.6 μg m^{-2} y^{-1}; Stern et al., 2005). However, the lake core temporal trend of Lake Ellasjøen (Bear Island; Barents Sea) which also has a seabird colony shows the highest DDT concentrations at 1966 (4 ng/g; Evenset, Christensen, et al., 2007). These comparisons of the ages from different core records are tentative because the resolution of the time models is not the same. In any case, the NOW5 core witnesses that the DDT restrictions successfully decreased the transport of this

insecticide and metabolites to the Arctic regions which is in contrast with the observations of the other organohalogenated POPs.

Conclusions

According to the findings of this study, the levels of contamination in the lake NOW5 are positively correlated to the presence of birds in the lake catchment. The other two lakes are also polluted, albeit to a much lesser extent and mainly as a result of atmospheric deposition. The median concentrations of DDTs, PBDEs, PCBs, and chlordanes in the polynya lake are about 2.7-6 times higher than the median concentrations in the lakes with no bird influence. In the case of the drin pesticides and HCB, the former has a median that is about 9.5-18 times higher than the latter, and these ratios are more than 18 times higher for HCHs and endosulfans. When the changes in sedimentation fluxes between these lakes are considered, similar ratios are found, indicating that bird-mediated deposition has a preservation effect of the less stable and more volatile compounds. The results have also shown that the highest sedimentary deposition fluxes of PCBs, HCHs, drins, chlordanes, PBDEs, HCB and endosulfans of the polynya lake were found in the upper sediment layer, corresponding to 2014. Thus, despite the fact that many of the organochlorine and organobromine compounds have been banned, those that have already been released to the environment at lower latitudes are still being transported to Arctic areas and impacting the ecosystems there. In contrast, the maximum sedimentation fluxes of DDTs were found at the layer corresponding to 1980 which, within age model uncertainties, is consistent with the maximum sedimentation flux of this pesticide found in Devon Island (Stern et al., 2005) and could reflect that the restrictions in the use of this compound successfully decreased the transport of this insecticide and metabolite to the Arctic regions, even when mediated by bird metabolism.

Chapter 2: Occurrence and distribution of organohalogen compounds (OHCs) in freshwater lake sediments across Greenland

CHAPTER 2

Abstract

Long-range atmospheric transport (LRAT) is one of the main routes for OHCs to reach Greenland, but local sources of these contaminants exist as well. This study aims to establish a record of PCBs, DDTs, HCHs, PBDEs, Chlordanes, Heptachlors, Drins, Endosulfans, HCB, Mirex, Methoxychlor and Octachlorostyrene contamination in Greenlandic freshwater lakes sediments. We used Multi-level Models (MLMs) to discern the spatial and temporal variations of OHCs concentrations among the lakes. Airports, military bases, and research stations were important local sources for DDTs, HCB, OCS, Methoxychlor, Mirex, Chlordanes, and Heptachlors. Populated areas were important sources for PCBs. The effect of LRAT was evident for HCHs, HCB, Chlordanes, and Heptachlors when the latitudinal gradient was positive. Positive longitudinal gradients explained the arrival of HCHs and PBDEs from the Eurasian and North-eastern American continents. The concentrations of most compounds showed a decrease through the years due to the past restrictions. This study is the first to analyse a broad spectrum of OHCs, including Endosulfans, Drins, OCS, Mirex, and Methoxychlor, which were never studied in freshwater lake sediments of Greenland.

Introduction

The Arctic was long perceived as one of the last pristine environments free of pollution. However, this perception is increasingly being altered as multiple studies have shown that the Arctic, with its fragile ecosystems and sensitive fauna, is being exposed to not only the pollutants brought on by the growing urbanization in the high latitudes but also the atmospheric transport of the pollutants from the lower latitudes (Hoferkamp et al., 2010; Kirk & Gleason, 2015; Vorkamp & Rigét, 2014).

Organohalogen Compounds (OHCs), including Persistent Organic Pollutants (POPs), are halogenated organic chemicals that have been of concern in the circumpolar Arctic for decades due to their tendency to be transported long-range distances, their persistence in the environment and their toxicity (Simonich & Hites, 1995; Wania & Mackay, 1993). Moreover, they have been proven to bioaccumulate and biomagnify in food webs, exposing the organisms from the top trophic positions to doses which may cause endocrine disruption, altered neurological development, immune system modulation, and cancer (WHO, 2003). All of these overlaying properties of OHCs, in particular of POPs, cause a severe concern for the potential biological effects of these contaminants in exposed Arctic wildlife, including birds and fish, both marine and freshwater (AMAP, 2016).

Long-range atmospheric transport (LRAT) is generally considered to be the main route of transport for OHCs to reach an ecologically sensitive Arctic environment (Hung et al., 2010). The transport to higher latitudes can occur via repeated cycles of deposition and evaporation, driven by seasonal, frontal, and diurnal temperature changes ("grass-hopping"). In particular, the more volatile components of mixtures are proven to hop poleward much more efficiently than the less volatile ones, leading to a compositional shift to more volatile constituents with increasing northern latitudes, also known as "global fractionation" (AMAP, 1998; Wania & Mackay, 1996; Wania & Westgate, 2008).

However, local sources of pollution in the Arctic cannot be ignored. Although, there has been apparently minimal direct use of OHCs in the Arctic, and the contaminants detected mainly have been OHCs like PCBs, DDTs and PBDEs (AMAP, 2018; Letcher et al., 2010). For example, radar sites, airports, military establishments in the Arctic, both abandoned and those still under operation, have been among the more serious sources of Arctic pollution. E.g., Alert, a Canadian Arctic military and research station has been linked to the atmospheric presence of PCBs, DDTs and PBDEs among other OHCs. Military operations impact the environment negatively; a few peer-reviewed articles deal with quantitative information about

contamination from small outposts to the surrounding environment and what we can learn from this human interaction with pristine environments (AMAP, 2004; Goodsite et al., 2014; Hung et al., 2010; Kjølholt & Hansen, 1986; Malmquist et al., 2003). Scientific research stations have also been known to contribute to the local sources of pollution for OHCs like (ppDDE, HCHs, HCB, Endosulfan, Chlordanes, Heptachlors and PBDEs); for example, North Greenland (Bossi et al., 2013, 2016), or in the Antarctic (Vecchiato et al., 2015). Towns and settlements in the Arctic as well as in Greenland can also be considered local sources of pollution (Bossi et al., 2008; de Wit et al., 2010); while chlorinated pesticides have not been known to be used at all or had a limited use, PCBs and PBDEs could originate locally via transformers, electric and electronic equipment, paint and textiles as detailed in Greenland by Vorkamp, Christensen, Glasius, et al., (2004).

Additionally, Greenland's unique spatial location is affected by weather systems, mainly from Eurasia and North America (AMAP, 2004; Bossi et al., 2008; Malmquist et al., 2003), which propitiate the input of OHCs from the North American continent as posited by various studies for the European Continent (Arellano et al., 2014; Breivik et al., 2006), especially for PBDEs.

Over the years, multiple studies have analyzed OHCs all over the Arctic (AMAP, 2004; Letcher et al., 2010; Riget et al., 2019). Most literature on OHCs studies in the Arctic has focused on air masses (Hung et al., 2010, 2016), marine mammals, birds and fish (AMAP, 1998, 2004, 2014, 2016; Muir & de Wit, 2010); but literature availability on freshwater lake sediment is scarce. It is largely agreed that it is difficult to measure OHCs in the Arctic freshwater lake sediment due to generally low levels of compounds found in there. In addition, there is a general dearth of data from Greenland amongst studies done in the Arctic (Mangano et al., 2017); and within these, some studies are available on levels and trends of OHCs bioaccumulation in marine and freshwater biota (Rigét et al., 2016, 2019; Vorkamp, Christensen, Glasius, et al., 2004) and Arctic air (Hung et al., 2010), while fewer studies have focused on abiotic compartments such as rivers, lakes and ocean. In the little information that is available in sediments from Greenland, concentrations of OHCs are reported to be low and comparable to the other areas of the Arctic (AMAP, 1998, 2004; Malmquist et al., 2003). For example, (Cleemann et al., 2000) did focus specifically on freshwater Greenland sediments and studied a few groups of compounds: PCBs, DDTs, HCHs, HCB and Chlordanes and all of the concentrations were reported to below limits of detection.

Freshwater lake sediments have high organic carbon content and are thus a significant reservoir of OHCs because the organic carbon in sediments provide stationary endpoints where

OHCs may reside for more extended periods (Ma et al., 2016). Studying remote freshwater lake sediments is essential to understand the baseline concentrations in the Arctic environments coming from both LRAT and local sources as a pollution source. In addition, as the Arctic food webs are very simple (Vincent & Hobbie, 2000), freshwater lake sediment concentrations are essential to interpret bioaccumulation and biomagnification potential in various trophic levels in freshwater Arctic food webs.

Objectives

The overarching aim of this study was (i) to establish a record of concentration of PCBs, DDTs, HCHs, PBDEs, Chlordanes, Heptachlors, Drins, Endosulfans, HCB, Mirex, Methoxychlor and Octachlorostyrene in freshwater lake sediments across the expanse of Greenland, (ii) to understand the differences between the sediment concentration patterns across latitudinal, longitudinal, altitudinal gradients and correspond them to the source of pollution to Greenland (long-range transport vs. influence from the American and Eurasian continent), and to iii) to elucidate the extent of human induced impact on freshwater ecosystems of Greenland (local sources of pollution related with population density, presence of military bases, research stations or airports).

Materials and Methods

Study Area and Sample Collection

The lake surface sediments were retrieved during the arctic summer (July-beginning of September) from the deepest point of the lake using a kayak corer or, in shallow lakes, with a core on a rod. The top half-centimeter of the core was used for the analyses. The sediment samples are based on three to six mid-lake samples that were pooled into one. Study area is depicted in Figure 5.

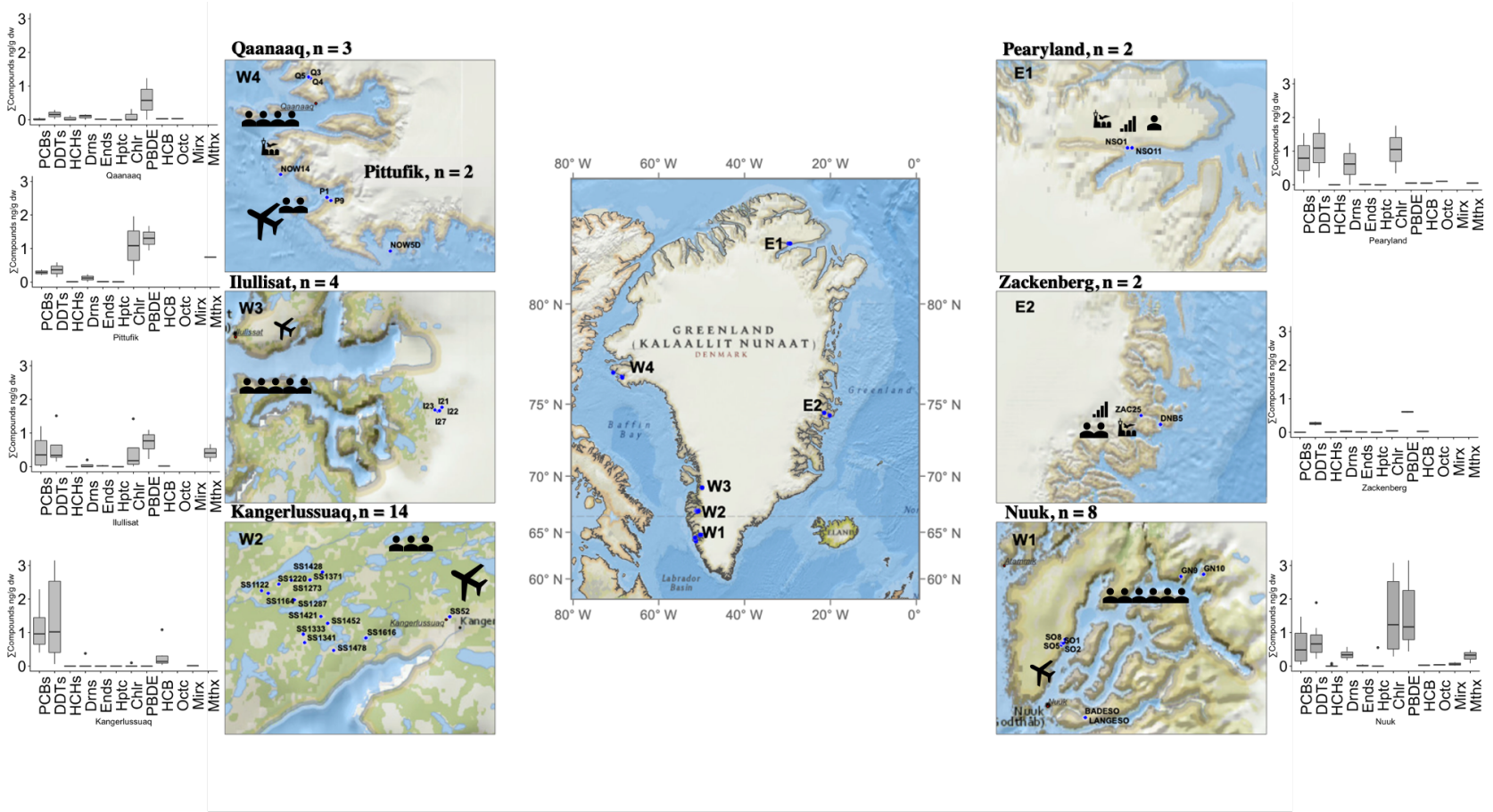


Figure 5 Map showing the locations of the lakes studied across Greenland with box plots showing the sum of the concentrations of the congeners analysed per each group of compounds in freshwater sediments in ng/g dw.

PCBs, DDTs, PBDEs, CBz, Chlordanes and Heptachlors, Endosulfans, and Drins Analysis

Chemicals

The solvents acetone, ethyl acetate, cyclohexane, isooctane, and copper (particle size < 63 μm) were all from Merck (Darmstadt, Germany) and 5g, 20CC Florisil cartridges were acquired from Waters (Milford, MA, USA). Standards of 1,2,4,5-tetrabromobenzene (TBB), PCB 209 and the solution mixture of organochlorines were purchased from Dr Ehrenstoffer (Augsburg, Germany) except for Octachlorostyrene, which was obtained from AccuStandard, Inc. (New Haven, CT, USA). A solution mixture of BDEs, BDE 118 and BDE C_3^* 209 was acquired from Cambridge Isotope Laboratories (Andover, MA, USA).

Sample Extraction and Analysis

The frozen sediment top layer from each lake was freeze-dried overnight. The extraction and clean-up was adapted from the method described in Cristale & Lacorte, (2013). 0.1-1.0 g of sediment was placed in a glass centrifuge tube (10 ml), spiked with surrogate standards (TBB and PCB 209), and kept in contact overnight. After that, the samples were extracted with 10 ml ethyl acetate/cyclohexane (5:2, v/v) by vortex for 1 minute, followed by ultrasonic extraction for 10 minutes. The extract was centrifuged (10 min at 3000 rpm) and transferred to 40 ml flasks. After repeating this procedure twice, the total extract was then concentrated to 1 ml using a Rotavapor. About 200 mg activated copper was added to the extracts and left overnight to minimize Sulphur interference on GC-MS performance. Next day, the clean-up was performed using 5g Florisil cartridges. The cartridges were conditioned with 10 ml and eluted with 20 ml ethyl acetate/cyclohexane (5:2, v/v). This extract was finally concentrated to 0.5 ml.

Copper was activated using hydrochloric acid (25%) and ultrasonicated for 15 min. Several washes of Milli-Q rinses eliminated the acid until obtaining pH 7. Two rinses with acetone removed the water, and lastly, the activated copper was stored in hexane at -20 ^{o}C.

Organochlorine Compound Analysis

Before chromatographic analysis, an internal standard of PCB-142 was added to each of the samples. Samples were identified and quantified for OCs using a GC (Agilent Technologies 7890N) coupled to a mass spectrometer (MS, Agilent Technologies 5975C)

operating in negative chemical ionization mode (GC-NICI-MS) with a HP-5MS capillary column (60 m length, 0.25 mm internal diameter, 0.25 μm film thickness; JW Scientific) protected with a retention gap. The injection was performed in splitless mode. Injector and detector temperatures were 280 °C and 325 °C, respectively. The oven temperature was held at 90 °C for 2 min, increased to 130 °C at 15 °C/min and 4 °C/min to 310 °C with a final holding time of 10 min. Ultrapure Helium and Ammonia were used as carrier and reagent gasses, respectively. The OCs analyzed were Pentachlorobenzene (PeCB), Hexachlorobenzene (HCB) together known as ΣCBz, Hexachlorocyclohexanes (ΣHCHs) (α-HCH, β-HCH, γ-HCH), ΣPCBs i.e., PCB congeners 28, 52, 101, 118, 138, 153, 180, DDTs i.e., DDT metabolites 2,4-DDD, 4,4-DDD, 2,4-DDE, 4,4-DDE, 2,4-DDT and 4,4-DDT, ΣCHLs (cis- and trans-chlordane, heptachlor, heptachlor epoxide a and b) Methoxychlor, Aldrin, Endrin, Dieldrin, Octachlorostyrene and Mirex.

Polybromodiphenyl Ether Analysis

Before chromatographic analysis, internal standards of BDE-118 and [3-^{13}C] BDE-209 were added to all the samples. A GC (Agilent Technologies 7890N) coupled to a mass spectrometer (MS, Agilent Technologies 5975C) operating in negative chemical ionization mode (GC-NICI-MS) was used for identification and quantification of the PBDE congeners (17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190 and 209). The instrument was equipped with a low bleed fused silica capillary column (15m length, 0.25 mm ID, 0.10 μm film thicknesses; DB-5MS) protected with a retention gap. The oven temperature was programmed from an initial temperature of 90 °C which was kept for 1.5 min followed by heating to 200 °C at 40 °C/min, a second increase up to 275 °C at 5 °C/min and a third increase to 300 °C at 40 °C/min. This temperature was held for 10 min and then increased to 310 °C at 10 °C/min with a final holding time of 2 min. Ammonia was used as the reagent gas. Identification and quantification were performed by injection of PBDEs standard solutions (Vizcaíno et al., 2009; Bravo et al., 2017).

Quality Assurance and Quality Control

Three procedural blanks were analysed with each batch of samples. Identification and quantification of OCs and PBDEs were performed by injection of external standards at different concentrations, and all the samples were blank corrected. The average recoveries ranged from 44.46-89.89% Method detection limits were calculated from the average signals of the

procedural blank levels plus three times the standard deviation. They ranged between 0.0004 and 0.532 ng/g for the OCs and 0.003 and 0.07 ng/g for the brominated compounds. The limits of quantification were calculated from the averages of the procedural blanks plus five times the standard deviation. They ranged between 0.002 and 2.75 ng/g for the OCs and between 0.005 and 0.098 ng/g for PBDEs. One-half of the limits of detection and limits of quantification were assigned to non-detected and non-quantified values, respectively.

Airport and population data

Airport data was obtained from Greenland Airport Authority, Mittarfeqarfiit, (2012). Airport was scaled from 0 to 3 depending on the number of passengers using it and the size of the runway at the airport (Table 15 SM[1]). Out of all the locations, Pittufik (Thule Air Base) and Kangerlussuaq (formerly Søndre Strømfjord Air Base) were given the highest weightage because of their size, current use, and historical military use. Nuuk, Zackenberg and Ilulisat were given medium weightage and Qaanaaq, Pearyland and Daneborg were given minimum weightage.

Population data was obtained from Statistics Greenland (Statistics Greenland, 2020) and rounded off to the closest higher value (for e.g., if the population was 18757, it was rounded off to 19000) (Table 16 SM). Areas were divided as per current Greenland map demarcation based on Statistics Greenland (Statistics Greenland, 2020).

Statistical Analyses

To assess the differences among different areas in Greenland, among the samples created by presence of an airport or high population in the vicinity of the lakes, we used analysis of Kruskal Wallis and Pairwise Wilcox test on sum of congeners per group of compounds, as the concentrations did not pass the Shapiro-Wilks normality test and Levene's test for heteroscedasticity, even after transformation of the variables. To both simultaneously quantify the distribution patterns of OHCs in addition to the abundance of the constituent congeners on the sites, we used MLMs (Multi-level Models) (Bartrons et al., 2016; Jackson et al., 2012). This analysis provided simultaneous information about the drivers of OHC concentrations and the response of individual congeners to these drivers. The data was divided into groups of compounds (PCBs, DDTs, PBDEs, Endosulfans, Drins, ΣCBz, Chlordanes and Heptachlors)

[1] SM: Supplementary Material in Annex

and the models can be interpreted as several regressions in which differences in slopes and intercept among different congeners are random variables. Using predictor (independent) variables enables this approach to assess the effects of abiotic drivers on OHCs concentrations and congener compositions, while considering spatial correlations in the residuals. Without using predictor variables, this approach tests for spatial correlations in OHC concentrations and congener composition. Concentrations of PCBs, DDTs, PBDEs, HCHs, Chlordanes, Heptachlors, HCB, OCS, Methoxychlor and Mirex were the dependent variables in each model. They were logarithmically transformed to control for heteroscedasticity. The predictor variables we tested in each model were geographic variables, namely, latitude, longitude, altitude, and year when the samples were obtained from each lake, and population and presence of an airport in the lake vicinity. To remove the effects of airport that had high median concentrations we redid the models without the lakes with direct airport influence (in the vicinity of the major Greenlandic airports) and just showed the MLMs without these locations close to the airport in the Supplementary Materials. All independent variables were centred and scaled to determine what predictors have the largest effect on the dependent variable. Latitude and population were negatively correlated more than 65% and thus, population was therefore excluded in the models, so that all variables listed above had pairwise correlations < 0.65 (Cohen's scale). In the results where latitude was negatively related to the compounds (no LRAT effect observed), we redid the models using population as a predictor variable to understand the difference between latitudinal pattern and effect of populated areas as local sources of pollution; we kept the other variables the same as when using latitude as independent variable. We checked for normality and homogeneity of residuals with Shapiro-Wilks and Levene's tests. Variance structure with a constant variance function (VarIdent, form=~1|Congener function in the *nlme* package, Pinheiro et al. 2019) was added to the model as there was no homogeneity of variances. Finally, a spatial autocorrelation term was added in the model by adding a covariance matrix that depends on the Euclidean distance between sites in the residual variation equation (corExp/corGaus function in the *nlme* package, Pinheiro et al. 2019). The different congeners per each group of compounds were used as random effects but were not found to be significant in any of the cases and thus they were not included in the final models. In the models for PCBs, DDTs and HCB, where we had two different sampling campaigns, data source was used as an additional fixed effect as we used two different data sources for these compounds. Data source was not selected or not significant in any of the models.

Data were analysed using R, v. 4.1.1 (R Development Core Team 2021).

Results

Concentrations in Greenland freshwater lake sediments were low for most compounds analysed (Table 6, three first rows). More than half (57%) of all the concentrations reported were below the limit of detection (LOD). In the following sections, we will discuss only the patterns in the samples where concentrations were greater than LOD.

General trends of OHCs in freshwater-lake sediments

The total concentrations in sediments from Greenland lakes for PCBs ranged from 0-5.595 ng/g dw with median concentrations 0.62 ng/g dw (Figure 5, Table 17 SM, Figure 12-14 SM). Maximum concentrations were found in lake Badeso in Kobbefjord area in Nuuk, a major Greenlandic town, and the second highest concentrations were detected in Kangerlussuaq area with Greenland's biggest airport. However, the median levels were the highest in Kangerlussuaq, Pearyland (the Northernmost area in this study) and Nuuk.

The total concentrations for the DDTs ranged from 0.023-63.96 ng/g dw with median concentrations of 0.505 ng/g dw among all the samples (Figure 5, Table 17 SM, Figure 12-14 SM). The highest concentration was found in one of the lakes of Kangerlussuaq area, which houses one of the largest Greenlandic Airport (63 ng/g dw). In addition, ppDDE in lakes SS1616 and SS1452 from the same regions, exceeded toxicity thresholds (threshold at 5.28 ng/g dw (Environment and Climate Change Canada, 2019; US EPA, 2014)). The median concentrations were the highest in Kangerlussuaq and Pearyland.

The total concentrations in the HCHs ranged from 0-0.13 ng/g dw in all the samples (Figure 5, Table 17 SM, Figure 12-14 SM). The maximum concentrations were found in Qaanaaq (~700 people) area followed by Nuuk (~19000 people). However, the median concentrations in samples from Pearyland were the highest, followed by Pittufik/Thule and Zackenberg. Lakes in all the other areas had median values below limit of detection.

The total concentrations for the PBDEs ranged from 0-4.3 ng/g dw with maximum concentrations found in Kangerlussuaq and Nuuk (Figure 5, Table 17 SM, Figure 12-14 SM) but with median concentrations found to be highest in Pittufik and Nuuk, areas with big airports and relatively highly populated, and lowest in Pearyland and in Kangerlussuaq (Figure 5, Table 17 SM, Figure 12-14 SM).

The total concentrations for Chlordanes ranged from 0-1.96 ng/g dw with the highest value found in Nuuk (highly populated area, ~19000 people), followed by Pittufik (Thule US airbase), Pearyland (Station Nord- A scientific research station) and Ilulisat (a town of ~5000 people) (Figure 5, Table 17 SM, Figure 12-14 SM). The median values followed the same trend

as the maximum values, with Nuuk having the highest median concentrations, followed by Pittufik, Pearyland and Ilulisat. The lowest concentrations were detected in Zackenberg (<50 people) on the east coast and in Kangerlussuaq and Qaanaaq where there is a small village (<700 people).

The total concentrations in Heptachlors ranged from 0-0.55 ng/g dw (Figure 5, Table 17 SM, Figure 12-14 SM). These group of compounds were only detected in Nuuk and Pittufik. Most median values in the regions were below limit of detection, except Pittufik, the American airbase, where the median concentrations were 0.0096 ng/g dw.

The total concentrations in Drins ranged from 0-1.24 ng/g dw with the highest concentrations in the northernmost Pearyland lakes, followed by Nuuk and Kangerlussuaq (Figure 5, Table 17 SM, Figure 12-14 SM). The median concentrations trends coincided with the maximum concentration trend. The lowest median values were detected in Zackenberg on the North-eastern Greenlandic coast.

The total concentrations for Endosulfans ranged from <LOD-0.055 ng/g dw with the maximum concentrations found in Ilulisat and Nuuk: the two areas with towns where human population is ~5000 and ~19000 people, respectively (Figure 5, Table 17 SM, Figure 12-14 SM). Kangerlussuaq was the only area where the Endosulfans were not detected i.e., the concentrations were <LOD. Endosulfan sulphate was the most often detected Endosulfan metabolite found in sediments, over α or ß Endosulfan.

Octachlorostyrene ranged from 0-0.11 ng/g dw with the highest values in the northernmost lake of NSO1 (Figure 5, Table 17 SM, Figure 12-14 SM). Other lakes with OCS present in concentrations higher than LOD were SO2 and SO5 in Nuuk and Q4 in Qaanaaq.

Out of CBz (PeCB and HCB), PeCB was found in concentrations <LOD in all the samples (Figure 5, Table 17 SM, Figure 12-14 SM). The total concentrations for HCB ranged from 0-1.085 ng/g dw with maximum concentrations found in Kangerlussuaq area, followed by Pearyland. Median concentrations were also highest in Kangerlussuaq and in Pearyland (the northern most lake). The median concentrations were significantly higher in Kangerlussuaq area with airport than in other areas. HCB was <LOD in Pittufik area (with the US military airbase) in all the samples.

Mirex was detected only in Kangerlussuaq and Nuuk areas (Figure 5, Table 17 SM, Figure 12-14 SM). Median concentrations were <LOD for all areas. For Methoxychlor, the maximum concentrations were detected in Pittufik and Ilulisat, followed by Nuuk. The median

concentrations followed the same trend as described for maximum concentrations. No Methoxychlor was detected in the rest of the lakes.

Contaminant Spatial Patterns: With and Without Airport

To understand the differences between the sediment concentration patterns across latitudinal, longitudinal, altitudinal gradients versus local sources of OHCs related with population density, presence of military bases or airports, we built MLM with all lakes analysed (Table 7), as well as with just the sites without major airport impact (Table 18 SM). The model containing all sites showed multiple significant variables, explaining the most variability (Table 7). The presence of big military bases or airports was the strongest factor determining the accumulation of most OHCs in Greenland freshwater sediments, which showed a positive trend with Chlordanes and Heptachlors, ß = 0.372, HCB, ß = 0.56 and on the other hand PCBs, ß =-0.469, and PBDEs, ß =-0.238 were negatively correlated. Year showed a negative trend for PCBs, ß = -0.444, HCHs, ß = -0.15 and PBDEs, ß = -0.25. Longitude showed positive relationship with DDTs, ß = 0.153, and negative relationship with HCHs, ß = -0.355 and PBDEs, ß = -0262. Altitude showed negative relationship with DDTs, ß = -0.12, HCHs, ß = -0.231, Chlordanes and Heptachlors, ß = -0.238. Latitude showed a positive with HCHs, ß = 0.2, HCB, ß = 0.332, Chlordanes and Heptachlors, ß = 0.311, but a negative trend with PCBs, ß = -0.188 and PBDEs, ß = -0.302. Since latitude was negatively correlated with population density (r=>-0.65), population density was initially excluded from this analysis to avoid collinearity issues. To further disentangle the relationship between concentrations and latitude/population density, we ran the models again, this time replacing latitude with population (Table 19 SM). Population was significant and positively related to PCBs (ß = 0.291) and negatively related to HCHs (ß = -0.276). The rest of the compounds did not show any significant relationship with population (Table 19 SM).

Given the high significance of the big airports, we rerun again the models but removing the effects of big airports (i.e., Kangerlussuaq and Pittufik/Thule) as a pollutant point source to discern the long-range transport of OHCs (Table 18 SM). In this case, much reduced significance of explanatory variables was observed in the models, suggesting high impact of local pollution sources nearby all lake sediments analysed. Year was still negatively related with PCBs (ß = -0.669) and PBDEs (ß =-0.209). Longitude was still significant in the cases of DDTs (ß =0.145) and PBDEs (ß =-0.288), and altitude was significant in cases of PCBs (ß =0.25) and DDTs (ß =-0.145).

Table 6 Concentration of organohalogen compounds (sum of congener per group of compounds in ng/g dw) reported in surface freshwater sediment in the Arctic region. The three first rows of the table correspond to the values analysed within this study. <D indicates values are lower than the limits of detection.

Area	Ref	PCBs	DDTs	PBDEs	HCHs	Mirex	Chlordanes	Heptachlors	Endosulfans	Drins	HCB	PeCB	OCS
Greenland *All samples*	This study	0.62 (<D-5.59)	0.505 (0.023-63.96)	0.43 (<D-4.3)	<D (<D-0.13)	<D	0.33 (<D-3.07)	<D (<D-0.55)	0.011 (<D-0.055)	<D	0.069 (0.011 - 1.084)	<D	<D (<D-0.11)
Samples without Airport presence	This study	0.07 (<D-5.59)	0.32 (0.023-1.91)	0.63 (<D-3.99)	<D (<D-0.13)	<D	0.344 (<D-3.07)	<D (<D-0.55)	0.013(<D-0.055)	<D	0.0268 (0.011 - 0.065)	<D	<D (<D-0.11)
Samples with only big Airport presence	This study	0.91 (<D-3.37)	0.824 (0.06-63.96)	<D (<D-4.3)	0.006 (<D-0.015)	<D	0.2 (<D-1.96)	<D (<D-0.019)	0.009 (<D-0.014)	0.1	0.137 (0.035 - 1.084)	<D	<D
Greenland (Kangerlussuaq)	(Malmquist et al., 2003)	0.04-0.922		BDE 47 0.002-0.03			0.001-1.5					0.005-0.35	
Greenland	(Cleemann et al., 2000)	<0.1	<0.1		<0.1						<0.1		

Canadian Arctic	(Blais et al., 2005)		1-60				1-10
Canadian Arctic	(Stern et al., 2005)	2.56		0.17	0.17	Dieldrin: 0.28	0.36
Bear Island European Arctic	(Evenset, Christensen, et al., 2007)	2-72	0.1-4.0	0-0.73			
	(Evenset et al., 2004)	Ellasjoen: ∑7PCB = 60 Oyangen: ∑7PCB = 4.4	Ellasjoen: ∑DDT = 6.9 Oyangen: ∑DDT = 0.8		Ellasjoen :HCHs = 0.4 Oyangen :HCHs = 0.2	Ellasjoen: cis-chlordane = 0.17 Oyangen: cis-chlordane = 0.08	
Svalbard European Arctic	(Rose et al., 2004)	2.58-13.52					
Norwegian Arctic	(de Wit et al., 2010)			0.11(0.025 to 9.6)			
Alaskan lakes	(Blais et al., 1998)	0.3 – 30					

Yukon Lakes, Canada	(Rawn et al., 2001)	33.5-11.1	0.86-21.4		0.46-1.57				1.1-1.89
Canadian Arctic	(Muir et al., 1995, 1996)		0.11-9.96		0.05-2.88		< 0.01-1.04	Dieldrin: 0.05-3.17	0.09-1.8
Lake AJ-AX, Canada	(de Wit et al., 2006)			BDE 209 0.07					
Lake Romulus, Canada	(de Wit et al., 2006)			BDE 209 <0.1					
Lake Char, Canada	(de Wit et al., 2006)			BDE 209 0.042					
Alaska (St Lawrence Island)	(Scrudato et al., 2012)	3-31 ug/kg dw	DDE 0-0.6 ug/kg dw			Mirex0.6-1.7 ug/kg dw			
Alaska	(Allen-Gil et al., 1997)	0.12	0.15		0.09		ND		0.17
Russian arctic	(AMAP, 2004)	1.58-2.48	0.85-69.4		0.09-0.96	CHLs <0.05-0.26		HCB:0.14-0.21	

								CBz:0.44-0.56
Bjornoya, Norway	(AMAP, 2004)	Lake Ellasjoen ∑PCBs10: 60*; Lake Oyangen ∑PCBs10: 4.4 *	Lake Ellasjoen 6.9;Lake Oyangen 0.8		Lake Ellasjoen <0.2;Lake Oyangen <0.4	Lake Ellasjoen 0.69;Lake Oyangen 0.17		Lake Ellasjoen <0.8;Lake Oyangen <0.8
Lake Lovozero, Russia	(AMAP, 2004)	∑PCBs: 2.52	0.87	-	0.02	0.07		CBz:0.15
Chandler, Alaska	(AMAP, 2004)	∑PCBs: 0.06						
Lindeman Lake, N. BC, Canada	(AMAP, 2004)	∑PCBs: 8.3, ∑PCBs10: 1.8	0.9		0.1	Chls=0.3		CBz: 0.5
Fox lake, Southern Yukon	(AMAP, 2004)	∑PCBs:33.5 ∑PCBs10: 12.7	0.7		0.8	0.0		-
Lake Laberge, Southern Yukon	(AMAP, 2004)	∑PCBs 12.7; ∑PCBs10: 3.7	0.8		1.2	Chls=0.4		CBz: 0.4
Lake little Atlin, Canada	(AMAP, 2004)	∑PCBs 28.3; ∑PCBs10: 7.4	3.5		1.1	3.9		CBz: 0.3

Yaya , Lake 6 and 7, Mackenzie River Delta, Canada	(AMAP, 2004)	∑PCBs 6.23, 2.6, 10.8 ∑PCBs10: 2.1,0,0	0.43, 1.3, 0.1	1.57, 0.15, 1.4	CHLs 0.23, -, -	CBz 1.57, -, -
Hanson Lake, Central Yukon 1995	(AMAP, 2004)	∑PCBs 25.9; ∑PCBs10: 5.9	1.3	0.6	0.6	CBz: 1.4
Watson Lake, Southern Yukon 1995	(AMAP, 2004)	∑PCBs 38.6; ∑PCBs10: 5.2	122.6	0.7	0.9	CBz: 1.3
Great Bear, CWT, Canada	(AMAP, 2004)	∑PCBs 27.8; ∑PCBs10: 7.1	0.5	0.2	0.18	CBz: 1.87
Great Slave, Southern NWT, Canada	(AMAP, 2004)	∑PCBs 8.75; ∑PCBs10: 3	0.41	0.31	0.26	CBz: 1.41
Char, Cornwallis Island	(AMAP, 2004)	∑PCBs 0.96; ∑PCBs10: 0.4	0.14	0.01	0.52	CBz: 0.01
Peter Lake, W. Nunavut	(AMAP, 2004)	∑PCBs 4.44; ∑PCBs10: 1	0.11	0.09	0.17	CBz: 0.28

Devon Island, Canada	(AMAP, 2004)	∑PCBs 2.97	0.07	0.23	0.18	-
Ax-Ai, Axel Heiberg Island	(AMAP, 2004)	∑PCBs 2.66; ∑PCBs10: 0.2	0.23	0.14	0.51	CBz: 0.1
Romulus, Ellesmere Island	(AMAP, 2004)	∑PCBs 3.65; ∑PCBs10: 1.2	0.06	0.69	010	CBz: 0.27
Baird Inlet, Ellesmere Island	(AMAP, 2004)	∑PCBs 0.17	0.03	0.08	0.05	CBz: 0.07
Bjornvatnet, NW Spitsbergen	(AMAP, 2004)	∑PCBs10: 6.4**				
Ytertjorna, NW Spitsbergen	(AMAP, 2004)	∑PCBs10: 6.44**				
Ossian, NW Spitsbergen	(AMAP, 2004)	∑PCBs10: 2.74**				
Daltjorna, SW Spitsbergen	(AMAP, 2004)	∑PCBs10: 2.58**				
Tenndammen, Svalbard	(AMAP, 2004)	∑PCBs10: 13.52**				

Latnjajaure, Sweden	(AMAP, 2004)	∑PCBs10: 0.6 ***	0.3	0.06	HCB 0.16
Njalakjaure, Sweden	(AMAP, 2004)	∑PCBs10: 0.6 ***	0.4	0.08	0.15
Louvvajaure, Sweden	(AMAP, 2004)	∑PCBs10: 1.4 ***	1.7	0.14	0.16
Jutsajaure, Sweden	(AMAP, 2004)	∑PCBs10: 1.0 ***	0.6	0.13	0.07
Pahajärvi, Sweden	(AMAP, 2004)	∑PCBs10: 1.4 ***	2.6	0.15	0.12
Abiskojaure, Sweden	(AMAP, 2004)	∑PCBs10: 0.3 ***	0.2	0.02	0.13
Alaska	(Cleemann et al., 2000)	0.04-0.3	0.05-0.6	0.04-0.8	-
Canada		2-39	0.05-5	0.05-3	0.08-1.8
Norway		2-15	0.1-4	<0.1-0.5	0.1-1.4
Finland		1-18	0.2-4	0.1-1.3	1-5
Russia		0.3-3	0.05-1.6	0.03-1.5	0.005-1.5
Russia and Norway	(Skotvold & Savin	0.38-35.4			

	ov, 2003)

ΣPCBs = sum of 15 congeners (28, 31, 52, 99, 101, 105, 118, 128, 138, 153, 156, 170, 180, 183, 187)

ΣPCB10 = sum of 28, 31, 52, 101, 105, 118, 138, 153, 156, 180

* Sum of 7 congeners (101, 105, 118, 138, 153, 156, 180)

** Sum of 7 congeners (28, 52, 101, 118, 138, 153, 180), the exact same congeners analyzed in this study

*** Sum of 7 congeners (28, 52, 101, 105, 138, 153, 180)

ΣCBz = 1,2,3,4-, 1,2,3,5- and 1,2,4,5-tetrachlorobenzene, and hexachlorobenzene; ΣHCH = α-, β-, and γ- HCH; ΣCHLs = sum of heptachlor, heptachlor epoxide, cis- and trans-chlordane, and cis- and trans-nonachlor; ΣDDTs = sum of o,p' and p,p'- DDE, -DDD, and -DDT

Table 7 Output of the models showing a relationship between the sum of concentrations of OHCs in sediments with spatial variables. Independent variables were standardized for a more straightforward interpretation. Congeners were added as random effects in the model. Drins, OCS, Mirex and Methoxychlor were not significant for any variable so not included in the table. None of the random slopes and intercept terms in the models were significant and thus they were excluded from the final structure. Results are from best AIC. R2 is given with lower and upper 95% confidence limits in brackets. Significance codes: *** p<0.001; **p<0.01; *p<0.05

Compounds	Geographical variable	Value	SE	df	*t* value	$R^2_{partial}$
PCBs	Latitude	-0.188*	0.094	94	-2.014	0.053 (0.16-0.002)
	Year	-0.444**	0.146	94	-3.04	0.117 (0.244-0.029)
	Airport	-0.469**	0.12	29	-2.935	0.101 (0.225-0.021)
DDTs	Longitude	0.153**	0.051	65	2.954	0.102 (0.256-0.011)
	Altitude	-0.12*	0.057	65	-2.065	0.073 (0.218-0.003)
HCHs	Latitude	0.2***	0.002	2	95.47	0.542 (0.861-0.127)
	Longitude	-0.355***	0.008	2	-122.97	0.542 (0.861-0.128)
	Altitude	-0.231***	0.0002	2	-112.39	0.518 (0.852-0.1)
	Year	-0.15***	0.0001	2	-115.97	0.602 (0.882-0.206)
PBDEs	Latitude	-0.302***	0.073	118	-3.92	0.08 (0.183-0.015)
	Longitude	-0.262***	0.076	118	-3.15	0.06 (0.16-0.008)
	Year	-0.250***	0.084	118	-2.81	0.04 (0.121-0.008)
	Airport	-0.238***	0.065	118	-3.58	0.06 (0.127-0.002)
Chlordanes + Heptachlors	Latitude	0.311*	0.14	27	-3.78	0.29 (0.532-0.082)
	Altitude	-0.238*	0.123	27	2.514	0.31 (0.548-0.097)
	Year	0.375**	0.118	27	-2.623	0.373 (0.598-0.152)
	Airport	0.372**	0.127	27	2.917	0.353 (0.583-0.134)
HCB	Latitude	0.332*	0.15	19	2.179	0.171 (0.490-0.003)
	Airport	0.56***	0.134	19	4.164	0.429 (0.691-0.153)

Discussion

General Discussion

Concentrations of the analysed Organohalogen Compounds (OHCs) in freshwater-lake sediments from Greenland were low and were in line with other Arctic areas' concentrations, including the Canadian, Norwegian, Swedish, Russian Arctic and Alaska, as compiled in Table 6. However, in some lakes from Kangerlussuaq, Pittufik, Nuuk and Ilulisat, we did find elevated concentrations comparable to other sub-Arctic lakes. These higher concentrations of OHCs, in general, coincided with local anthropogenic presence, mainly airports, military airbases and research stations, and to a lesser extent with population density in the vicinity of the lake. To the best of our knowledge, this is the first instance of analysing a broad spectrum of OHCs along various spatial gradients in Greenlandic freshwater-lake sediments; specifically, the first time of analysing Endosulfans, OCS and Methoxychlor. OHCs have been studied in freshwater lakes sediments of across the Arctic: Norway, Alaska, Russia, and Canada but not much literature was available for Greenland (Table 6). Barring Malmquist et al., (2003), which analysed PCBs (tri- to decachlorinated), BDE-47, Chlordanes (cis- and trans-chlordane) and HxCBz; and Cleemann et al., (2000), which analysed PCBs, HCB, DDTs, Dieldrin and Chlordanes in the freshwater lake sediments of Greenland, no other study to the best of our knowledge has been undertaken.

PCBs is one of the most studied OHCs in the world. Its presence in the Arctic has been long recorded (Adams et al., 2018; AMAP, 2018; Muir & Rose, 2004; Rigét et al., 2016; Sanders et al., 1992). In our study, we recorded <LOD-5.595 ng/g dw which was higher than the ranges reported by other studies in Greenlandic freshwater surface sediments, but comparable with other regions in the Arctic (Table 6). For example, Cleemann et al., (2000) found all the concentrations for PCBs below LOD (0.1 ng/g dw) and Malmquist et al., (2003) detected levels ranging from 0.04 to 0.922 ng/g dw. In other regions of the Arctic, most studies reported concentrations similar or in the low range of our study (Table 6, e.g. (Evenset et al., 2004; Evenset, Christensen, et al., 2007; Skotvold & Savinov, 2003; Stern et al., 2005). However, in Arctic lakes with the presence of migratory birds, concentrations were one order of magnitude higher (up to 72 ng/g dw (Evenset et al., 2004; Evenset, Christensen, et al., 2007)), as a result of marine-derived contaminants transport.

DDTs in our study ranged from 0.023-63.96 ng/g, with two lakes in the Kangerlussuaq area, close to the main Greenlandic airport, exceeding toxicity thresholds (threshold at 5.28 ng/g dw (Environment and Climate Change Canada, 2019; US EPA, 2014). These

concentrations are much higher than the ones found by the other study in Greenland (Table 6, <0.1 ng/g dw (Cleemann et al., 2000)), but, with the exception of the two lakes in Kangerlussuaq region, these concentrations are in the range with other studies in the Arctic (Table 6, in Canadian Arctic (Blais et al., 2005; Muir et al., 1995, 1996; Stern et al., 2005); in Bjørnøya Island, Norway (Evenset et al., 2004; Evenset, Christensen, et al., 2007)). For Kangerlussuaq region, the concentrations are more comparable to the concentrations detected in Yukon lakes in Canadian arctic, located near populated areas and in a region where DDT was heavily applied in the 1950s and 1960s (Rawn et al., 2001).

PBDEs concentrations were much higher in our study, especially in Nuuk (0.43-3.99 ng/g dw; median:0.437 ng/g dw) and Pittufik region (0.943-1.67 ng/g dw; median:1.308 ng/g dw), compared to the other studies in Greenland (Table 6, (Cleemann et al., 2000; Malmquist et al., 2003)) and the majority of other studies in the Arctic (Muir & de Wit, 2010), but similar in range as compiled by de Wit et al., (2006, 2010), Stern et al., (2005) and Evenset, Christensen, et al., (2007) in freshwater lake sediments of Norwegian and Canadian Arctic (Table 6). In particular, in Svalbard and Finnmark area, both in Norway, PBDEs' concentrations ranged from 0.025-9.6 ng/g dw (de Wit et al., 2010; Landers et al., 2008), indicating slightly higher concentrations than our study, and the authors noted that the higher concentrations were comparable to sediments from the industrialized areas.

We observed HCB concentrations in the range of <LOD-1.085 ng/g, with highest concentrations observed in Kangerlussuaq area. These concentrations are higher than other studies in Greenland (Table 6, <0.1 ng/g dw, (Cleemann et al., 2000)) but are in line with other studies done in the Arctic (Table 6, (AMAP, 2004; Evenset et al., 2004; Stern et al., 2005)). The consistent and increasing global use of HCB containing pesticides (as a by-product) (Su et al., 2006), even if HCB itself was banned around the year 1970. Its production as a by-product becomes a source of airborne HCB for the Arctic (Hung et al., 2010), explaining the persistence of HCB in the Arctic.

HCHs were mostly low in most freshwater lake surface sediments analysed (<LOD-0.13 ng/g dw), except for the northern area of Pearyland. These concentrations are higher than other studies in Greenland (Table 6, <0.1 ng/g dw, (Cleemann et al., 2000)) but lower than the ones detected in freshwater lake sediments in other studies in the Arctic (Table 6, (Evenset et al., 2004; Hoferkamp et al., 2010; Stern et al., 2005)).

We detected <LOD-0.74 ng/g dw of Methoxychlor, with the maximum concentrations found in Pittufik and Ilulisat. No study was found about Methoxychlor in freshwater lake sediments of Greenland or anywhere in the Arctic. However, and along with lindane, CUPs

like Methoxychlor are regularly detected in waters, air samples and marine samples (biotic and abiotic) from the Arctic (Hoferkamp et al., 2010; Vorkamp, Rigét, et al., 2004).

We detected Endosulfans in the range of <LOD-0.055 ng/g dw with the maximum and highest median values being detected in Ilulisat. We don't have information for Greenland freshwater lake sediments for Endosulfans, but Endosulfans are proven to enter Arctic lakes in relatively high concentrations: it has been detected in biotic as well as abiotic samples from the Canadian and Greenlandic Arctic (Muir & de Wit, 2010; Stern et al., 2005; Vorkamp et al., 2017; Weber et al., 2010).

Octachlorostyrene (OCS) was not detected in our samples except in Pearyland, Nuuk and Qaanaaq or in other freshwater lake sediments of the Arctic, but it has been detected in air (median concentrations of 0.32 pg/m^3) all over the Arctic (Su et al., 2008). It is also detected in marine fish samples (0.73-1.8 ng/g lw) and marine biota (0.17-9.8 ng/g lw) from Greenland (Vorkamp et al., 2017; Vorkamp, Rigét, et al., 2004; Vorkamp & Rigét, 2014).

The maximum concentrations in Kangerlussuaq area in our study for Chlordanes were in the range of <LOD-0.096 ng/g dw, which is comparable to the concentrations detected by Malmquist et al., (2003) in Kangerlussuaq region of Greenland. These concentrations we detected are much higher than the ones elaborated in the studies done in the other part of the Arctic (Table 5, (Evenset et al., 2004; Muir et al., 1995, 1996)). We detected <LOD-1.24 ng/g dw of Drins, and no other information was found for Drins in Greenland. The concentrations found in our study are in line with all other information found in the Arctic (Table 5, (Stern et al., 2005)).

Local Sources of OHC pollution in Greenland

Presence of big airports (in case of Pittufik which is also a research and US military station) was one of the most important factors determining the concentrations of HCB, Chlordanes and Heptachlors (Table 7). This was not the case for PCBs and PBDEs, which had a negative relationship with the presence of an airport. On the other hand, AMAP, (2004) noted strong local contamination sources in the Nuuk and Thule Air base areas for PCBs and PBDEs but not for chlorinated pesticides, and multiple studies have reported airports, military bases and research stations acting as a local pollution source of OHCs in the Polar regions including Greenland (Ahrens et al., 2015; AMAP, 2004; Cabrerizo, Muir, De Silva, et al., 2018; Cabrerizo, Muir, Köck, et al., 2018; Corsolini et al., 2019; Kjølholt & Hansen, 1986; Vecchiato et al., 2015; Wild et al., 2015).

Population density was another significant factor explaining the presence of PCBs. Indeed, populated areas i.e. villages and towns in Greenland (J. H. Christensen et al., 2002; Vorkamp, Christensen, & Rigét, 2004) and other Arctic areas (Carlsson et al., 2018; Rawn et al., 2001) are known to be sources of OHCs, although no information is available for freshwater surface sediments. Christensen et al., (2002) found high concentrations PCBs in Greenlandic biota in a Southern town of Greenland (Qaqortoq) which they posited that signifies a local emission of PCBs from untreated sewage from the town and wash out from a waste dump site.

Long Range Atmospheric Transport (LRAT)

Latitude was positively correlated with HCHs, HCB, Chlordanes and Heptachlors, indicating LRAT (Wania & Mackay, 1996). However, when local sources of pollution such as lakes in the vicinity of big airports were removed, the influence of latitude disappeared, indicating that stronger sources of contamination than the LRAT dominated the inputs of OHCs to the studied lake sediments. Latitude was also negatively correlated with PCBs and PBDEs, but this is an artifact of the negative relationship among latitude and population density, as explained in the section before.

For altitudinal gradient, DDTs, HCHs, Chlordanes and Heptachlor, all had a negative relationship with the concentration of OHCs (Table 7), indicating higher concentrations close to local pollutant sources. However, when the airport effect was removed, PCBs concentrations did increase with altitude, indicating LRAT (Table 18 SM). DDTs still showed negative trends with altitude, still indicating local pollutant sources in the vicinity of the lake.

Eastern and Western Greenland is affected differently by air masses and sea currents flowing towards and around Greenland, which are related with major pathways for atmospheric contaminant transport from source regions (AMAP, 2004; Kirk & Gleason, 2015). Specifically, both, the East and the West coasts of Greenland are directly affected by atmospheric contaminant transport coming from Eastern North America (Kirk & Gleason, 2015). On the other hand, contaminants arriving by air to the Arctic pole from Europe are transported first to Eastern Greenland by a phenomenon called “Transpolar Drift”. This generated an ocean current called “The Eastern Greenlandic Current” which transports contaminants as it travels along the Eastern coast of Greenland towards the west coast of Greenland (AMAP, 2004). In this study, we used longitude as an indicator of the influence of these air masses. Longitude was positively correlated with DDTs concentrations, and negatively correlated with HCHs and PBDEs concentrations. This longitudinal effect was still strong in the case of DDTs and PBDEs, even after removal of lakes near Airports. For DDTs, this means that the Western part of Greenland

is more polluted than the Eastern part, indicating direct LRAT from Eastern North American continent. The study by Rigét et al., (2004) noted that levels of DDTs in the landlocked populations of Arctic charr in Zackenberg, Northeast Greenland were relatively low compared to the Southeast and Southwest Greenland, similar to what we observe in our study in freshwater lake sediments. For PBDEs and HCHs the negative longitudinal gradient indicates that Eastern Greenland lakes have more of these OHCs than the western part of Greenland, indicating Eurasia and North America influence for these compounds via air masses as well as ocean currents. Cleemann et al., (2000) also posited that the East Greenland Sea Current flowing from the north towards the south of the east coast and up north of Greenland's west coast affected the pollutant concentrations in the lakes situated closer to the sea. The American continent's historically high PBDEs use and its influence on North Atlantic air mass trajectories has already been established in some of the remote high mountain lakes in Europe (Arellano et al., 2014), but Eurasian continent's influence on Greenland weather systems cannot be overlooked (Bindler, Renberg, Appleby, et al., 2001; Bindler, Renberg, John Anderson, et al., 2001; Malmquist et al., 2003; Rose et al., 2004).

Year

The concentrations of most compounds showed to be decreasing with year, which is what is widely reported in the time series studies done in the Arctic, especially in biota (Corsolini et al., 2002; de Wit et al., 2010; Rigét et al., 2019, 2020; Rigét, Vorkamp, et al., 2010; Vorkamp, Rigét, et al., 2004), air samples (Bossi et al., 2008; Hung et al., 2010, 2016) and sediment cores (Nagar et al., 2022). This decrease in concentration with time is also consistent with the past restriction on uses and agreements made in Stockholm Convention (AMAP, 2016; Rigét et al., 2016). For Brominated Flame Retardants (BFRs) like PBDEs, its presence is well known in remote areas even if never being introduced there (Bartrons et al., 2011; Blais et al., 2015; Breivik et al., 2006). Very few studies have been done in Greenland and the Arctic, in general, as it is an emerging contaminant, although, in the studies that were done, an increase in concentrations with the time were observed in the Canadian Arctic and Greenland (de Wit, 2002; de Wit et al., 2006, 2010) and elsewhere (Bartrons et al., 2016).

Conclusions

Generally low levels of OHCs were detected in freshwater lake sediments of Greenland but in some lakes, DDTs, PBDEs and HCB were detected in high concentrations and in case of DDTs, two lakes showed concentrations higher than threshold values. PCBs and DDTs form a part of the major OHCs in Greenland freshwater lake sediments, followed by PBDEs. Other OHCs like Drins, Heptachlors, Mirex, HCB were also detected in low quantities in spite of being banned (Stockholm Convention, 2018). CUPs like Endosulfans, HCHs, Methoxychlor were also detected, albeit, in low concentrations. These CUPs have been also identified in various Arctic Media by several studies (Hoferkamp et al., 2010), but not much information was found on Greenland. Octachlorostyrene, which is known to bioaccumulate in Greenland wildlife (Vorkamp et al., 2017), was also detected in a few freshwater sediment samples in our study. Local sources of pollution were the principal factor determining the OHC concentrations. Airports, airbases and populated areas were found to be significant sources of pollution. Year as a variable was also a key factor and it was negatively related to the OHC concentrations, a phenomenon also observed by other marine and freshwater studies.

Greenland is not as pristine as has always been imagined; it has pockets of contamination from local sources as well as pollutants arriving via LRAT from the Eurasian and American continents. Although multiple studies have tried to study the OHCs in Greenland, usually, the focus was mostly to understand how OHCs are accumulated in large marine animals like polar bears, seals, and birds, since they are keystone Arctic species. In this study, we try to elucidate OHCs distribution in freshwater lake sediments, which will add on the data available about Greenland freshwater food web components and give us a richer illustration of OHCs accumulation in the Arctic. The concentrations found are not negligible and thus, they are concerning. On top of this, climate change may additionally exacerbate the reemission of OHCs from ice, sediments, and soils, increasing the mobilization of these pollutants in the Arctic.

Chapter 3: Long range transport and local effects enhance OHCs accumulation in Arctic Charr (*Salvelinus alpinus*) from Greenland freshwater lakes

Abstract

The Arctic is currently exposed to multiple environmental stressors such as contamination or extreme climate events that affect the whole arctic ecosystem equilibrium. In particular, the Greenlandic population has relatively high values of organohalogen compounds (OHCs). The aim of this study was to determine the range of concentrations of polychlorinated biphenyls (PCBs), dichloro-diphenyl-trichloroethanes (DDTs) and polybrominated diphenyl ethers (PBDEs) and understand OHCs accumulation and distribution patterns in the top predator Arctic charr across Greenland freshwater lakes. We found that PCBs and DDTs concentrations in some Arctic charr crossed the toxicity thresholds, which may be of concern since it is an important component in the diet of the local population. The most important factors determining PCBs, PBDEs and DDTs accumulation in Arctic charr were mean annual air temperature (indicating Long-Range Atmospheric Transport, LRAT) and anthropogenic impact e.g., presence of airports. The Arctic charr from lakes with higher anthropogenic impact also accumulated higher level of heavier molecular weight PCBs. Fish length was also an important factor determining PBDEs bioaccumulation, indicating growth dilution of PBDEs in Arctic charr. Some Layman metrics were significant predictors for DDTs and PBDEs bioaccumulation in fish, giving insight into the relevance of biomagnification, trophic diversity and niche overlap effects for the cycling of these organic compounds across the freshwater food webs. OHCs concentrations in Greenlandic Arctic charr cannot be ignored. Besides, climate change may enhance revolatilisation and re-emission of these legacy compounds high enough to be considered a "secondary source" of pollution. Due to Arctic ecosystems sensitivity, this simultaneously impact by multiple stressors can seriously endanger their ecological balance.

Introduction

The Arctic ecosystems are under threat by extensive anthropogenic environmental stress, such as contamination or extreme climate events, which is thought to be exacerbated by rapidly deteriorating Earth's climate (Steindal et al., 2021). Due to the Arctic's unique location and low temperatures, the Arctic has become a repository for the semi-volatile contaminants that have the capability of transboundary movement (Fernández & Grimalt, 2003). Arctic wildlife, including some fish species, can be highly contaminated with mixtures of compounds such as Persistent Organic Pollutants (POPs) (AMAP, 2004). Exposure of these contaminants through diet remains one of the major risks for the delicate balance of the Arctic ecosystem health, including humans (Kosek & Ruman, 2021). The Greenlandic population, for example, have some of the highest levels of POPs globally (AMAP, 2015; Long et al., 2012), jeopardising child development, immune function and reproductive abilities (Hjermitslev et al., 2020).

Some organohalogen compounds (OHCs) are classified as POPs, for e.g., polychlorinated biphenyls (PCBs), dichloro-diphenyl-trichloroethanes (DDTs), hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB) and polybrominated diphenyl ethers (PBDEs), due to their persistence, combined with high lipophilicity as well as resistance to biological degradation and tendency to bioaccumulate and biomagnify in food webs (AMAP, 2004; Vorkamp et al., 2008). As a result of the high concentration they can achieve in the top trophic positions of the food web, they cause a high health concern in exposed Arctic wildlife including birds and fish, both marine and freshwater, and, ultimately, humans (AMAP, 2016; Rigét et al., 2016). One of the primary input routes for OHCs to the remote Arctic environment, including Greenland, is through Long-Range Atmospheric Transport (LRAT) (Hung et al, 2010). Due to the nature of global atmospheric circulation patterns, the OHCs get transported to the higher latitudes via a unique phenomenon called "grass-hopping", which is defined as multiple cycles of deposition and evaporation, driven by seasonal, frontal and diurnal changes in temperature (Kirk & Gleason, 2015; Wania, 2003). In particular, the semi-volatile components of contaminant mixtures have been documented to volatilize at warmer temperature and travel towards the poles efficiently due to their tendency "to condense" at colder temperatures (Simonich & Hites, 1995; Wania, 2003; Wania & Mackay, 1993, 1996; Wania & Westgate, 2008). In particular, the Arctic environment is therefore considered an important reservoir for these compounds because the cold regions retain OHCs as a result of this temperature-dependent partition between gas, water and particles during long-range

transport (Fernández & Grimalt, 2003). The cycling of OHCs across ecosystems is driven not only by physicochemical properties of the chemicals and environmental factors (e.g. temperature), but also, by biogeochemical cycles (e.g. snow melt or degradation in soils and sediments) (Blais, 2005; Lohmann et al., 2007; Ma et al., 2016). This is more important in the case of legacy OHCs, such as PCBs, DDTs, HCHs and HCB, whose net re-emission from the environmental mediums is triggered by declining atmospheric concentrations and controlled mainly by temperature and biogeochemical processes, especially in an OHCs reservoir environment like the Arctic (Nizzetto et al., 2010).

Greenland is an ideal region to study the fate of OHCs in the environment because, despite their remoteness and low population density, it is located in the Arctic where OHCs accumulate due to lower temperatures and LRAT (Barrie et al., 1992; Burkow & Kallenborn, 2000; Hung et al., 2016). In addition, local sources of pollution are also occurring in Greenland but may not be accurately represented in the global emission scenarios. Waste dumps, industrial, research and military installations, airbases/airports, increasing urbanization, settlements and so on can all be considered as local sources of OHCs present in the Arctic/Greenland (Malmquist et al. 2003; Kjølholt and Hansen 1986; Hoferkamp, Hermanson, and Muir 2010; Vorkamp and Rigét 2014; Christensen et al. 2002; Nagar et al. in prep.).

Arctic charr is the top predator fish in Greenlandic freshwater food webs (Jeppesen et al., 2001, 2017) and forms an important component in the diet of the local population from this region (Kozak et al., 2021). OHCs bioaccumulation in Arctic charr have been studied in the polar environments of Norway (Evenset et al., 2004, 2005; Gauthier et al., 2018), Canada (Cabrerizo, Muir, Köck, et al., 2018; Kidd et al., 1998; Muir et al., 2013), Sweden (Nyberg et al., 2015), as well as Greenland (Cleemann et al., 2000; Rigét et al., 2004, 2016, 2020; Vorkamp, Christensen, & Rigét, 2004), due to its importance as sentinel freshwater lake species. In particular, non-anadromous charr or landlocked Arctic charr are specially suitable for analyses for OHCs bioaccumulation because they are the only fish species in many lakes and isolated from the ocean (Cabrerizo, Muir, Köck, et al., 2018; Vincent & Hobbie, 2000; Vincent & Laybourn-Parry, 2009). Thus, all pollutants bioaccumulated in fish come from the lake or its catchment and do not have ocean currents influential sources (Letcher et al., 2010; Rigét et al., 2019). While much information on levels and trends of OHCs in marine animals, birds and fish in the Arctic, is available, less information is available for freshwater fish, like Arctic charr for the same. Most of these studies have focused on temporal trends of the studied compounds with the exception of Cleemann et al. (2000), who attempted to examine the

concentrations of PCBs, DDTs, HCHs, dieldrin, HCB and Chlordanes in Arctic charr from four different Greenlandic locations. The concentrations found were low for most compounds analysed and they did not find any indication of LRAT. Despite it being generally agreed that the trends of OHCs compounds are decreasing in Greenland, the local Greenlandic population is still showing concerning levels of POPs (AMAP, 2015; Long et al., 2012), with serious health consequences (Hjermitslev et al., 2020). Therefore, there is the urgent need of an extensive study covering the full extension of Greenland to determine precise OHCs concentration ranges and elucidate the main drivers of OCHs bioaccumulation in Arctic charr.

Objectives

The primary objective of this chapter was to understand the accumulation patterns of PCBs, DDTs and PBDEs of landlocked Arctic charr in Greenlandic freshwater lakes, which form a main source for human and wildlife diet. In particular, we aimed to determine concentration ranges of these compounds in Greenlandic freshwater landlocked Arctic charr. Secondly, we wanted to understand how lake environmental factors, such as mean annual air temperature, longitude, local sources of pollution (presence of airports or population density), conductivity, total nitrogen, total phosphorous, chlorophyll-a, and year affect the bioaccumulation and distribution patterns of OHCs in Greenlandic Arctic charr. Thirdly, we wanted to understand how Arctic charr niche space in Greenlandic freshwater lakes further plays a part in the bioaccumulation of these OHCs in Arctic charr. To the best of our knowledge, this study is the first instance of such comprehensive spatial study with multiple stressors (environmental and biological) affecting the OHCs accumulation, which has never been attempted in the Arctic charr within Greenland before.

Materials and Methods

Study site

Twenty-five lakes were studied along the coast of Greenland, between 64º-82ºN and 20º-69ºE (Figure 6), in late summer during 1998-2016. The study covered multiple demarcations of Greenland (regions), namely, Ilullisat, Kangerlussuaq, Nuuk, Pearyland, Pittufik, Qaanaaq, Zackenberg. All lakes were considered oligotrophic (chlorophyll a < 2 µg/L) and water surface temperature at the day of the sampling ranged from 0.64 to 8.35 ºC. Lake area and depth ranged from 0.5 to 72 ha (17 ± 16 ha) and 0.7 to 50 m (12 ± 11 m), respectively. Lakes were either isolated or had an indirect hydrologic connection with the sea through streams. In the Ilulissat region (i.e., Northern part), Arctic charr was the only fish species present, whereas charr and sticklebacks mostly co-occurred in the Nuuk region (i.e., the Southern study area) (Figure 6). Sampling was conducted when the anadromous specimens typically were in the sea, to maximize the catchability of non-anadromous charr to limit the exposure of the fish to the OHCs from the marine sources.

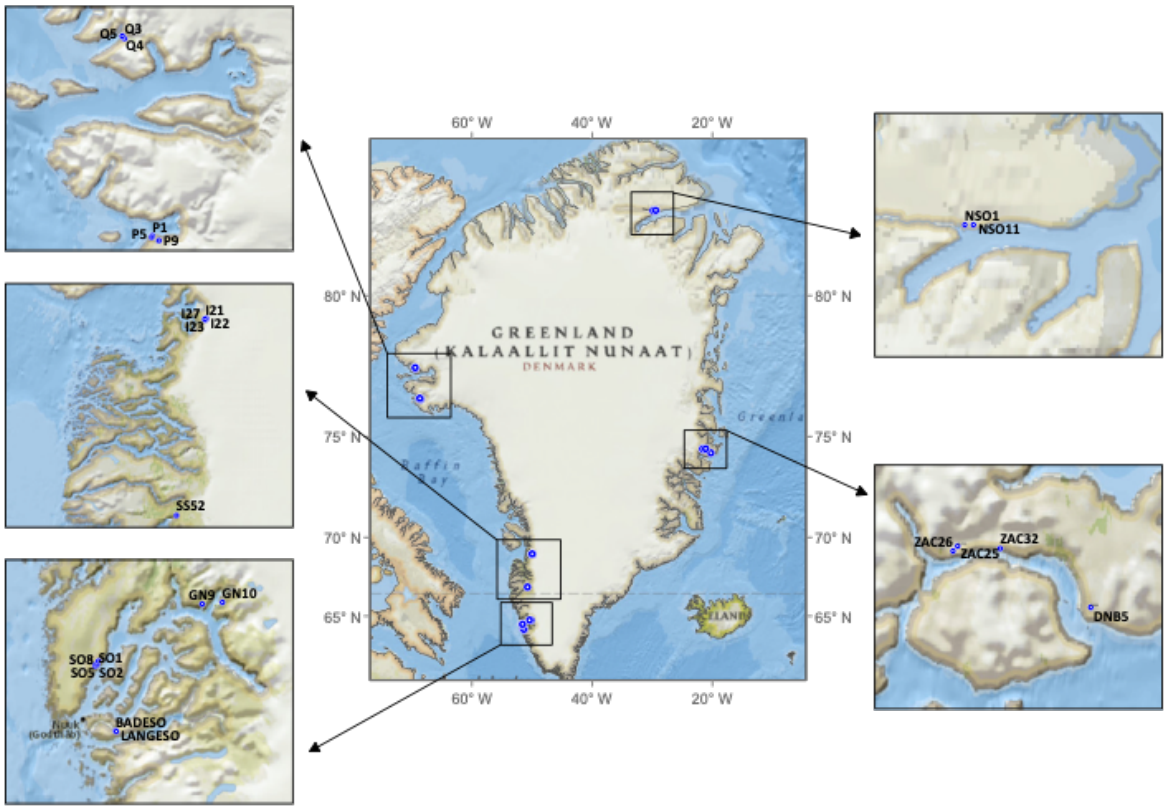


Figure 6 Map showing the locations of the freshwater lakes in Greenland where freshwater Arctic charr was studied.

Environmental variables

A composite sample was collected with a 5 L Heart valve sampler at 0.5-3 m intervals (depending on the depth of the lakes) from the surface to 1 m above the bottom in the deepest part of the lakes and mixed. For chlorophyll a, a duplicate 1 litre sample was sub-sampled from the pooled sample, filtered on a GF/C filter (Whatman) and frozen until analysis. Lake water chlorophyll a was determined spectrophotometrically after ethanol extraction (Jespersen & Christoffersen, 1987), lake water total phosphorus was determined as molybdate reactive phosphorus (Murphy & Riley, 1962) following persulphate digestion (Koroleff, 1970) and total nitrogen as nitrite + nitrate after potassium persulphate digestion (Solórzano & Sharp, 1980). In situ measurements of water temperature and conductivity were done with an YSI multiparameter sonde (model 6600 V2). Lake area was determined based on satellite images, and maximum depth was measured in situ for each lake.

Fish sampling

Arctic charr were caught by monofilament survey gillnets. Each gillnet was 42 m wide and 1.5 m deep and divided into 14 sections with a mesh size ranging from 6 to 75 mm (knot to knot following a geometric series: 6.25, 8, 10, 12.5, 16.5, 22, 25, 30, 33, 38, 43, 50, 60 and 75 mm). The gillnets were placed randomly in the near-shore zone, in the profundal zone in shallow lakes, and in the pelagic zone at half the depth in deep lakes. Depending on the size of the lake, the number of nets used varied from one to eight and were set in the afternoon and were left overnight (~8 hours fishing time) to maximise fish catchability, because gillnet catching is highly dependent on fish activity (Prchalová et al., 2009). Each charr individual was counted and measured (fork length in mm and weight in g). A clean piece of a white muscle tissue was removed from the total sample of the fish and frozen at -20ºC.

Stable isotope analysis (SIA)

In the laboratory, fish muscle samples were oven-dried at 60^0C for 24 h, homogenized by grinding into a fine powder, and weighed (0.5 – 1.5 mg animal tissue) prior to further preparation for SIA. The samples were packed into tin capsules and analysed for stable isotopes at the UC Davis Stable Isotope Facility, U.S.A. The analyses were performed on a PDZ Europa ANCA-GSL elemental analyzer interfaced with a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK).

Layman's community-wide metrics based on δ^{13}C and δ^{15}N stable isotope signatures (Layman et al. 2007) were calculated using fish data only and niche width areas were measured

using a Bayesian approach based on multivariate-based metrics (A. L. Jackson et al., 2011; Layman et al., 2012). The metrics analysed were $\delta^{15}N$ range (NR), $\delta^{13}C$ range (CR), total area (TA) representing convex hull area encompassed by all fish individuals in $\delta^{13}C$– $\delta^{15}N$ bi-plot space, mean distance to centroid (CD), mean nearest neighbour distance (NND), standard deviation of nearest neighbour distance (SDNND), standard ellipse area (SEA), and standard ellipse area corrected by sample size (SEAs).

PCBs, DDTs, and PBDEs Analysis

The length of the fish for PCBs, DDTs, and PBDEs analysis was fixed, when possible, between 150-200 cm to reduce the effect of cannibalistic tendencies of Arctic char and to reduce the variation emerging from differences in fish size/biomass within and across lakes. Indeed, no differences appeared among fish length and concentrations of PCBs, DDTs and PBDEs analysis within most lakes (Table SM 20-22, Figures SM 15-17).

Chemicals for fish muscle Analysis

Residue analysis n-hexane, dichloromethane, iso- octane, methanol, acetone and anhydrous sodium sulphate for analysis were from Merck (Darmstadt, Germany). Aluminium foil was rinsed with acetone and let dry at ambient temperature prior to use. Neutral Aluminium oxide type 507C was from Fluka AG (Switzerland). Cellulose extraction cartridges of 20 mm I.D. and 80 mm long were from Whatman (UK). Aluminium oxide, sodium sulphate, and cartridges were cleaned by Soxhlet extraction with dichlorome- thane–methanol (2:1, v / v) for 24 h before use. Sodium sulphate and aluminium oxide were activated overnight at 400 8C and 120 8C, respectively. Standards of 1,2,4,5-tetrabromobenzene (TBB), PCB 209 and the solution mixture of organochlorines were purchased from Dr Ehrenstoffer (Augsburg, Germany). A solution mixture of BDEs, BDE 118 and BDE C_3^* 209 was acquired from Cambridge Isotope Laboratories (Andover, MA, USA).

Fish extraction and analyses

Muscle tissue was ground with activated anhydrous sodium sulphate (0.5–2 g) and was introduced into a previously cleaned cellulose cartridge. TBB, PCB [209] were used as internal standards. These compounds used as internal standard mixtures were added for the study of the recoveries for the organochlorine compounds and PBDEs. The cartridge was then Soxhlet extracted with n-hexane–dichloromethane (4:1, v / v) for 4 h. Then, the extract was vacuum evaporated until 1 ml and further concentrated to 50 ml in isooctane under a gentle nitrogen flow.

Organochlorine compound analysis

Before chromatographic analysis, an internal standard of PCB-142 was added to each of the samples. Samples were identified and quantified for OCs using a GC (Agilent Technologies 7890N) coupled to a mass spectrometer (MS, Agilent Technologies 5975C) operating in negative chemical ionisation mode (GC-NICI-MS) with a HP-5MS capillary column (60 m length, 0.25 mm internal diameter, 0.25 μm film thickness; JW Scientific) protected with a retention gap. The injection was performed in splitless mode. Injector and detector temperatures were 280 ^{o}C and 325 ^{o}C, respectively. The oven temperature was held at 90 ^{o}C for 2 min, increased to 130 ^{o}C at 15 ^{o}C/min and 4 ^{o}C/min to 310 ^{o}C with a final holding time of 10 min. Ultrapure Helium and Ammonia were used as carrier and reagent gasses, respectively. The OCs analysed were PCB congeners 28, 52, 101, 118, 138, 153, 180, DDT metabolites 2,4-DDD, 4,4-DDD, 2,4-DDE, 4,4-DDE, 2,4-DDT and 4,4-DDT.

Polybromodiphenyl ether analysis

Before chromatographic analysis, internal standards of BDE-118 and BDE C_3^* 209 were added to all the samples. A GC (Agilent Technologies 7890N) coupled to a mass spectrometer (MS, Agilent Technologies 5975C) operating in negative chemical ionisation mode (GC-NICI-MS) was used for identification and quantification of the PBDE congeners (17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190 and 209). The instrument was equipped with a low bleed fused silica capillary column (15m length, 0.25 mm ID, 0.10 μm film thicknesses; DB-5MS) protected with a retention gap. The oven temperature was programmed from an initial temperature of 90 ^{o}C which was kept for 1.5 min followed by heating to 200 ^{o}C at 40 ^{o}C/min, a second increase up to 275 ^{o}C at 5 ^{o}C/min and a third increase to 300 ^{o}C at 40 ^{o}C/min. This temperature was held for 10 min and then increased to 310 ^{o}C at 10 ^{o}C/min with a final holding time of 2 min. Ammonia was used as the reagent gas. Identification and quantification were performed by injection of PBDEs standard solutions (Vizcaíno et al., 2009; Bravo et al., 2017).

Quality Assurance and Quality Control

Three procedural blanks were analysed with each batch of samples. Identification and quantification of OCs and PBDEs were performed by injection of external standards at different concentrations, and all the samples were blank corrected. Method detection limits were calculated from the average signals of the procedural blank levels plus three times the standard deviation. They ranged between 0.001 and 1.146 ng/g for the OCs and 0.012 and 0.337 ng/g for the brominated compounds. The limits of quantification were calculated from the averages

of the procedural blanks plus five times the standard deviation. They ranged between 0.002 and 1.829 ng/g for the OCs and between 0.019 and 0.537 ng/g for PBDEs. One-half of the limits of detection and limits of quantification were assigned to non-detected and non-quantified values, respectively.

Airport activity, number of inhabitants per Greenland demarcation and temperature data

Airport data was obtained from Greenland Airport Authority (Mittarfeqarfiit, 2012). Airport as a variable was scaled from 0 to 3 depending on the number of passengers using each airport and the size of the runway at the airport (Table 15 SM). Pittufik (Thule Air Base) and Kangerlussuaq (formerly Søndre Strømfjord Air Base) were given the highest weightage because of their size, current use, and historical military use; Nuuk, Zackenberg and Ilulisat were given medium weightage; and Qaanaaq, Pearyland and Daneborg were given minimum weightage.

The number of people living in each Greenlandic demarcation (region) was obtained from Statistics Greenland (Statistics Greenland, 2020) and rounded off to the closest higher value (for example, if the population was 18757, it was rounded off to 19000) (Table 16 SM).

Mean annual air temperature data was obtained from CRU TS monthly high-resolution gridded multivariate climate dataset (Harris et al., 2020). Many studies have observed correlation between air temperature and lake water temperature, including the Arctic areas (Harvey et al., 2011; Huang et al., 2017). Therefore, air temperatures were considered to be a suitable proxy for the lake water temperatures.

Statistical Analyses

To both simultaneously quantify the distribution patterns of PCBs, DDTs and PBDEs in addition to the abundance of the constituent congeners on the sites, we used multilevel linear regression models (MLMs) (Jackson et al., 2012), which offer the possibility for integrating group of compounds trends (PCBs, DDTs and PBDEs) and specific congener analysis per each group of compounds (Bartrons et al., 2016) . We used these multilevel models because they can separate the effects of collinearity among environmental drivers and factor out the effect in overall congener concentrations that do not involve changes in composition; in addition to

provide information about congener composition by simultaneously identify the responses of individual congeners to the environmental variables.

The data was divided into groups of compounds (PCBs, DDTs, PBDEs) and the models can be interpreted as several linear regressions in which differences in slopes and intercept among different congeners are random variables (mixed effect linear regression models). Using predictor (independent) variables enables this approach to assess the effects of environmental drivers on overall PCBs, DDTs and PBDEs concentrations and congener compositions, while considering spatial correlations in the residuals. Spatial autocorrelation term was added in the model by adding a covariance matrix that depends on the Euclidean distance between sites in the residual variation equation (corExp/corGaus function in the *nlme* package, Pinheiro et al. 2019). Without using predictor variables, this approach tests for spatial correlations in OHC concentrations and congener composition. The response (dependent) variables we tested in each model were the concentrations of PCBs (PCB28, 52, 101, 118, 153, 138 and 180 congeners), DDTs (DDDs, DDEs and DDTs metabolites), PBDEs (BDE17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183 and 190 congeners), respectively. The predictor (independent) variables we tested in each model included environmental and biotic variables such as mean annual air temperature, year, longitude, airport, chlorophyll-a (chl-a), conductivity, total nitrogen (TN), total phosphorus (TP) and median fish length per lake (Table 8). We could not include population density in the model because it was highly correlated with the mean annual air temperature ($r = 0.87$) and with the latitude ($r = -0.86$) (Table 23 SM). Variables were transformed when needed to account for the assumptions of normality and heteroscedasticity in each model residuals with the R package *bestNormalize* (Peterson & Cavanaugh, 2019). Afterwards, all independent variables were centred and scaled to determine what predictors had the largest effect on the dependent variable. We used Random Forest (Feld et al., 2016; Liaw & Wiener, 2002) to select the optimal variables to be included in the linear mixed effects models and we used backward model selection (Venables & Ripley, 2002) to select the 'best' putative model, according to the Akaike Information Criterion (AIC).

Table 8 Selected Lake physico-chemical variables and fish length (cm) for the different lakes. Chl-a (chlorophyll a), Cond. (conductivity), TN (total nitrogen), TP (total phosphorus). Levels of Airport activity come from Table SI-4: weightage was scaled from 0 to 3 depending on the number of passengers using it and the size of the runway at the airport. Airport data was obtained from Mittarfeqarfiit (2012) and number of inhabitants was obtained from Statistics Greenland (2020).

Lakes	Region	Latitude	Longitude	Year of fish sampling	Mean Annual air temp. (°C)	Population (number of individuals)	Airport activity	Chla- (ug/L)	Cond. (ms/ cm^2)	TN (mg/L)	TP (mg/L)	Fish length (cm)
BADESO	Nuuk	64.13	-51.35	2013	-2.69	19k	2	0.68	19	0.05	0.004	17.7
DNB5	Zackenberg	74.32	-20.13	1999	-9.33	13	0	0.62	19	0.19	0.004	14.5
GN10	Nuuk	64.77	-50.12	2011	-2.68	19k	2	0.96	25	0.47	0.01	20
GN09	Nuuk	64.76	-50.35	2011	-2.68	19k	2	0.8	22	0.3	0.004	15.6
I21	Ilullisat	69.06	-49.92	2012	-7.36	5k	1	0.4	104	0.2	0.008	16.4
I22	Ilullisat	69.06	-49.91	2012	-7.36	5k	1	0.5	178	0.16	0.006	18.3
I23	Ilullisat	69.07	-49.89	2012	-7.36	5k	1	1.2	40	0.1	0.016	11.5
I27	Ilullisat	69.06	-49.93	2012	-6.39	5k	1	0.9	101	0.56	0.008	19.4
LANGESO	Nuuk	64.13	-51.34	2013	-2.69	19k	2	0.56	19	0.12	0.004	17.5
NSO1	Pearyland	82.18	-29.78	2006	-17.80	13	0	0.41	242	0.11	0.003	30.5
NSO11	Pearyland	82.18	-29.34	2006	-17.58	13	0	0.48	199	0.16	0.003	19.75
P1	Pittufik	76.58	-68.66	2001	-12.36	100	3	0.43	133	0.004	0.004	16.25
P5	Pittufik	76.57	-68.67	2001	-12.36	100	3	0.61	64	0.004	0.004	13.75
P9	Pittufik	76.55	-68.49	2001	-12.82	100	3	0.61	101	0.004	0.004	11.75
Q3	Qaanaaq	77.70	-69.36	2016	-10.89	700	0	0.2	31	0.203	0.178	13.5
Q4	Qaanaaq	77.71	-69.41	2016	-10.89	700	0	0.8	18	0.272	0.008	32
Q5	Qaanaaq	77.71	-69.42	2016	-10.89	700	0	1.6	32	0.212	0.007	20
SO1	Nuuk	64.46	-51.59	2006	-0.35	19k	2	1.1	46	0.37	0.007	15.5
SO2	Nuuk	64.46	-51.58	2007	-0.35	19k	2	1.6	40	0.21	0.005	17.9
SO5	Nuuk	64.46	-51.56	2006	-0.35	19k	2	1.4	54	0.24	0.005	16.25
SO8	Nuuk	64.48	-51.55	2006	-0.35	19k	2	1.1	43	0.17	0.004	16.9
SS52	Kangerlussuaq	67.02	-50.72	1998	-4.98	500	3	0.79	7	0.08	0.009	15
ZAC25	Zackenberg	74.49	-21.48	1998	-10.81	100	1	0.55	14	0.22	0.009	19
ZAC26	Zackenberg	74.47	-21.52	1998	-9.94	100	1	0.47	8	0.14	0.002	14.5
ZAC32	Zackenberg	74.48	-21.04	1998	-10.81	100	1	0.7	5	0.07	0.002	13

To account for fish community characteristics in the bioaccumulation and biomagnification of OHCs, we used Layman metrics. To avoid over-parametrisation of the former models and because we didn't have Layman metrics for all the lakes with OHCs information, we built another set of multilevel linear regression models with the same structure as explained in the paragraph before but with only Layman metrics as unique independent variables. These models were performed individually per each metric as a result of the high intercorrelation among all Layman metrics (Table 24 SM).

Data were analysed and plotted using R, v. 4.1.1 (R Core Team, 2021)

Results

Lake-wise fish median concentrations of PCBs ranged from <LOD- 51.04 ng/g ww (7 congeners), DDTs ranged from <LOD-15.27 ng/g ww (6 metabolites), PBDEs ranged from <LOD-7.8 ng/g ww (14 congeners) (Table 9, Table 25 SM). PCBs, DDTs and PBDEs concentrations exceed the toxicity thresholds set by Environmental Canada (7.6 ng/g PCBs, 6.3 ng/g of DDTs and 1 ng/g of PBDEs, Environment Canada, 1999). PCBs and DDTs exceeded the concentration in on lake in Zackenberg area and in all three lakes in Pittufik area, whereas PBDEs exceeded toxicity thresholds in all the lakes sampled in Pittufik, Zackenberg and Illulisat.

Overall, mean annual air temperature and anthropogenic activity were the best predictors of PCBs, DDTs and PBDEs bioaccumulation in fish (Table 10). Fish length was only selected in the best AIC model for PBDEs as an additional predictor variable. Mean annual air temperature was selected in all best models and had always a negative relationship with the concentrations of PCBs, DDTs and PBDEs, indicating LRAT (Table 10, Figure 7-9). Random effects were not significant in these models in relation to mean annual air temperature, indicating similar trends for all the congeners studied. The presence of big airports and military bases was selected in all best models and was always positively related with the concentrations of PCBs, DDTs and PBDEs (Table 10, Figure 7-9). Airport as random effect was significant only for PCBs, with the higher molecular weight PCBs (PCB138 and 180) with the stronger positive relationship with the anthropogenic impact in the lake (presence of big airports and military bases in the region) (Table 11). Median Arctic charr length per lake was also selected in the best model for PBDEs, in addition to the mean annual air temperature and anthropogenic local effect (Table 10, Figure 9).

Table 9 Concentrations of the organohalogen compounds found in the fish from the lakes studied in Greenland (ng/g ww).

	HCB	HCHs	endosulfans	drins	DDTs	PCBs	PBDEs
Pearyland	0.022[a]-0.12	0.050-0.25	0.11-0.43	0.36-0.46	0.18-0.57	0.35-1.4	0.31-0.32
2[b], 7[c]	0.072	0.15	0.27, 0.27	0.41	0.38	0.90	0.32
Zackenberg	0.076-0.98	0.18-3.3	0.37-4.1	0.42-3.2	1.6-14	2.1-17	1.4-8.6
4, 14	0.33[d], 0.13[e]	1.3, 0.89	1.8, 1.3	1.2, 0.61	6.4, 4.8	9.4, 9.1	3.7, 2.4
Nuuk	0.04-0.75	0.35-2.6	0.066-0.77	0.035-1.2	0.97-5.8	1.6-9.6	0.31-4.8
8, 36	0.23, 0.17	1.4, 1.1	0.31, 0.26	0.38, 0.27	3.0, 2.6	4.6, 3.9	1.6, 1.3
Ilullisat	0.18-1.0	0.061-2.2	0-0.51	0-0.25	0.74-1.8	1.1-3.3	0.62-6.6
4, 15	0.49, 0.38	0.76, 0.41	0.23, 0.20	0.13, 0.14	1.3, 1.4	2.4, 2.7	3.0, 2.4
Pittufik	0.45-1.2	0.39-2.3	2.8-5.9	0.14-0.93	4.4-17	34-48	4.6-7.2
3, 12	0.77, 0.68	1.1, 0.76	4.1, 3.6	0.54	10, 9.0	39, 34	5.5, 4.6
Qaanaaq	0.14-0.31	0.21-0.81	0.026-0.54	0.054-0.30	0.16-1.4	0.68-2.1	0.16-1.4
3, 12	0.23, 0.24	0.55, 0.62	0.24, 0.14	0.14, 0.071	0.59, 0.26	1.6, 2.0	1.0, 1.4
Kangerlussuaq	0.10	1.3	1.4	0.85	7.8	8.4	7.1
1, 3	0.10	1.3	1.4	0.85	7.8	8.4	7.1

[a]Lake interval calculated from the mean of each lake. [b]Number of lakes. [c]Number of fish. [d]Mean. [e]Median (when mean and median are the same only one value is included).

Table 10 Output of the best multilevel linear regression models (MLMs) relating concentration of OHC congeners in fish (dependent variable) with environmental variables (independent variables), according to the Akaike information criterion (lowest-AIC model). The full model included the following environmental and biotic variables: mean annual air temperature, year, longitude, airport activity (Table SI-4), chlorophyll-a (chl-a), conductivity, total nitrogen (TN), total phosphorus (TP) and fish length. Fish median concentrations per lake and environmental variables were transformed when needed to control for normality and heteroscedasticity. Spatial autocorrelation structure was significant (*p-value < 0.05*) and added to the model. All independent variables were centred and scaled to determine what predictors had the largest effect on the dependent variable. Significance of environmental variables for determining fixed and random effects in the best multilevel model: **** p-value<0.001; ** p-value< 0.01; * p-value<0.05;* - means random effects not significant. SE (standard error), df (degrees of freedom). PCBs (PCB28, 52, 101, 118, 153, 138 and 180 congeners), DDTs (DDDs, DDEs and DDTs metabolites) and PBDEs (BDE17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183 and 190 congeners).

Compounds	Environmental variable	Fixed effects coefficient (slope)	SE	df	*t* value	Random effects coefficient
PCBs	Temperature	-0. 194 **	0.073	166	-2.673	-
	Airport activity	0. 257 *	0. 108	166	2.386	0.240**
DDTs	Temperature	- 0.188 ***	0.050	141	-3.699	-
	Airport activity	0.252 ***	0.049	141	5.167	-
	pH	0.117 **	0.036	141	3.182	-
PBDEs	Temperature	-0.201 ***	0.046	330	-4.589	-
	Airport activity	0.172 ***	0.042	330	4.007	-
	Fish Length	-0.149 ***	0.030	330	-5.006	-

Table 11 Multilevel linear regression model (MLM) random effect coefficients giving congener-specific responses to airport activity (significant random effect coefficient in Table 3). Coefficients are the random effect plus the estimate for fixed effects in order to account for the mean slope. The most important predictor variable (largest effect) for each species is bold.

PCBs	Random effects for airport activity
PCB 28	0.187
PCB 52	0.107
PCB 101	0.267
PCB 118	-0.063
PCB 153	0.279
PCB 138	**0.467**
PCB 180	**0.547**

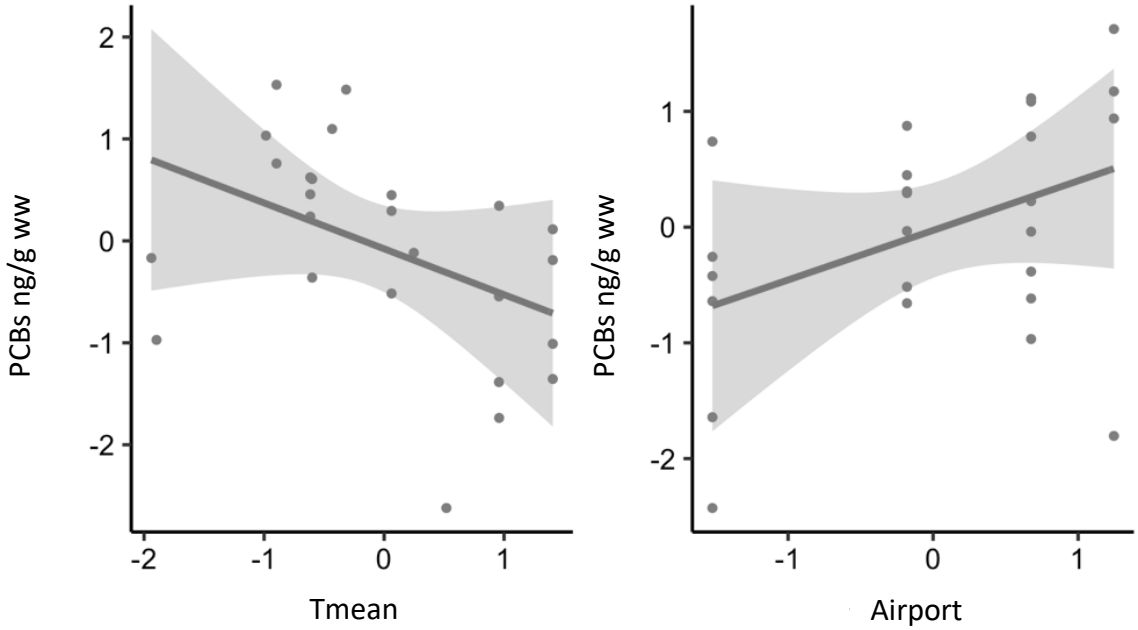


Figure 7 Residual plots showing the relationship between normalised sum of PCBs (28 + 52 + 101 + 118 + 153 + 138 + 180 congeners) concentration in Arctic charr from Greenland versus each significant normalised and centred predictor variable in the best (lowest-AIC model) multilevel linear regression models (model outputs are shown in Table 3): mean annual temperature (Tmean) and airport activity (Airport, Table SI-4). The lines depict the least-squares regression lines and the grey area depicts 95% confidence interval.

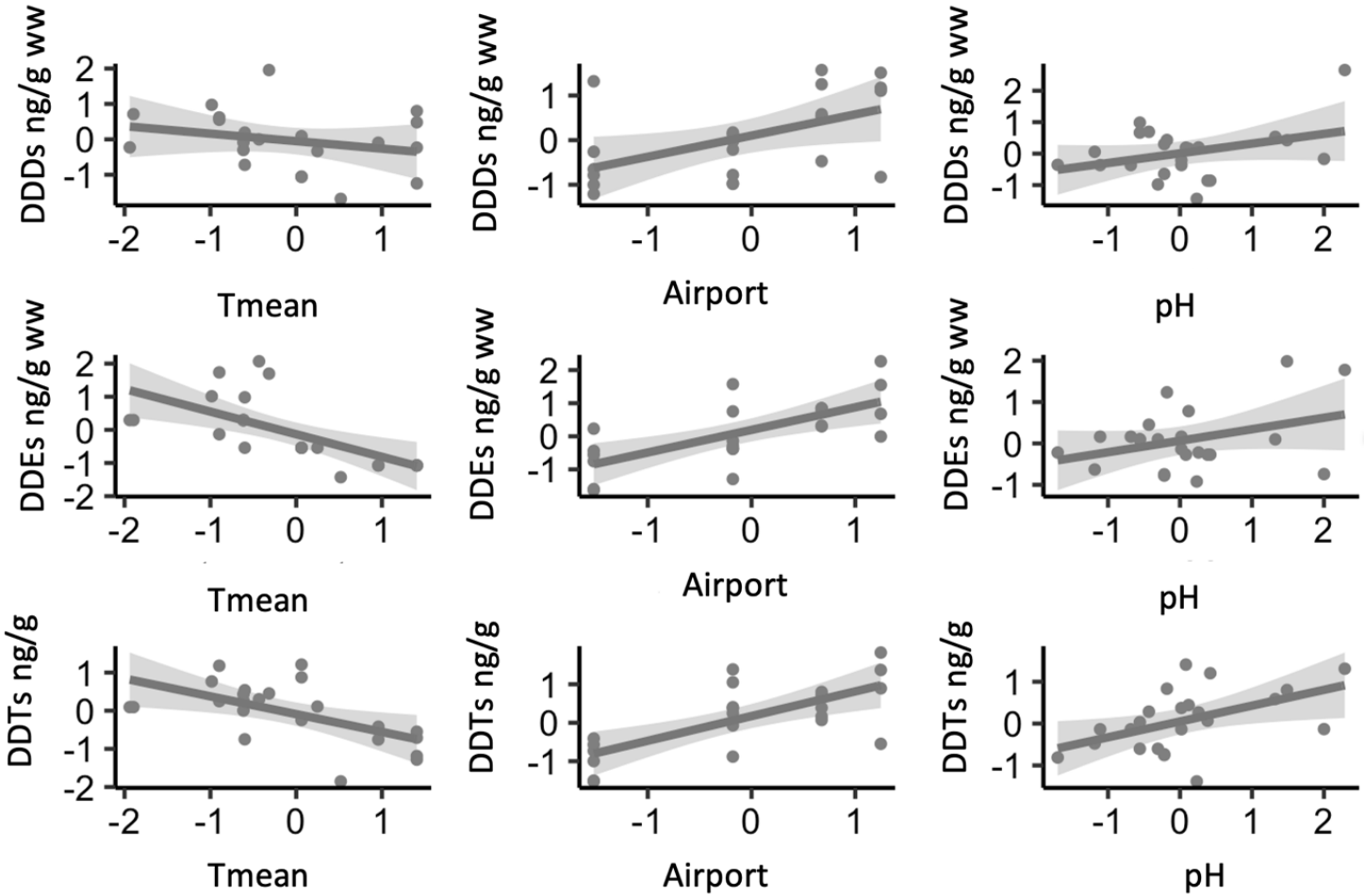


Figure 8 Residual plots showing the relationship between normalised DDDs, DDEs and DDTs concentration in Arctic charr from Greenland versus each of the normalised and centred predictor variable in the best (lowest-AIC model) multilevel linear regression models (model outputs are shown in Table 3): mean annual temperature (Tmean) and airport activity (Airport, Table SI-4). The lines depict the least-squares regression lines and the grey area depict 95% confidence interval.

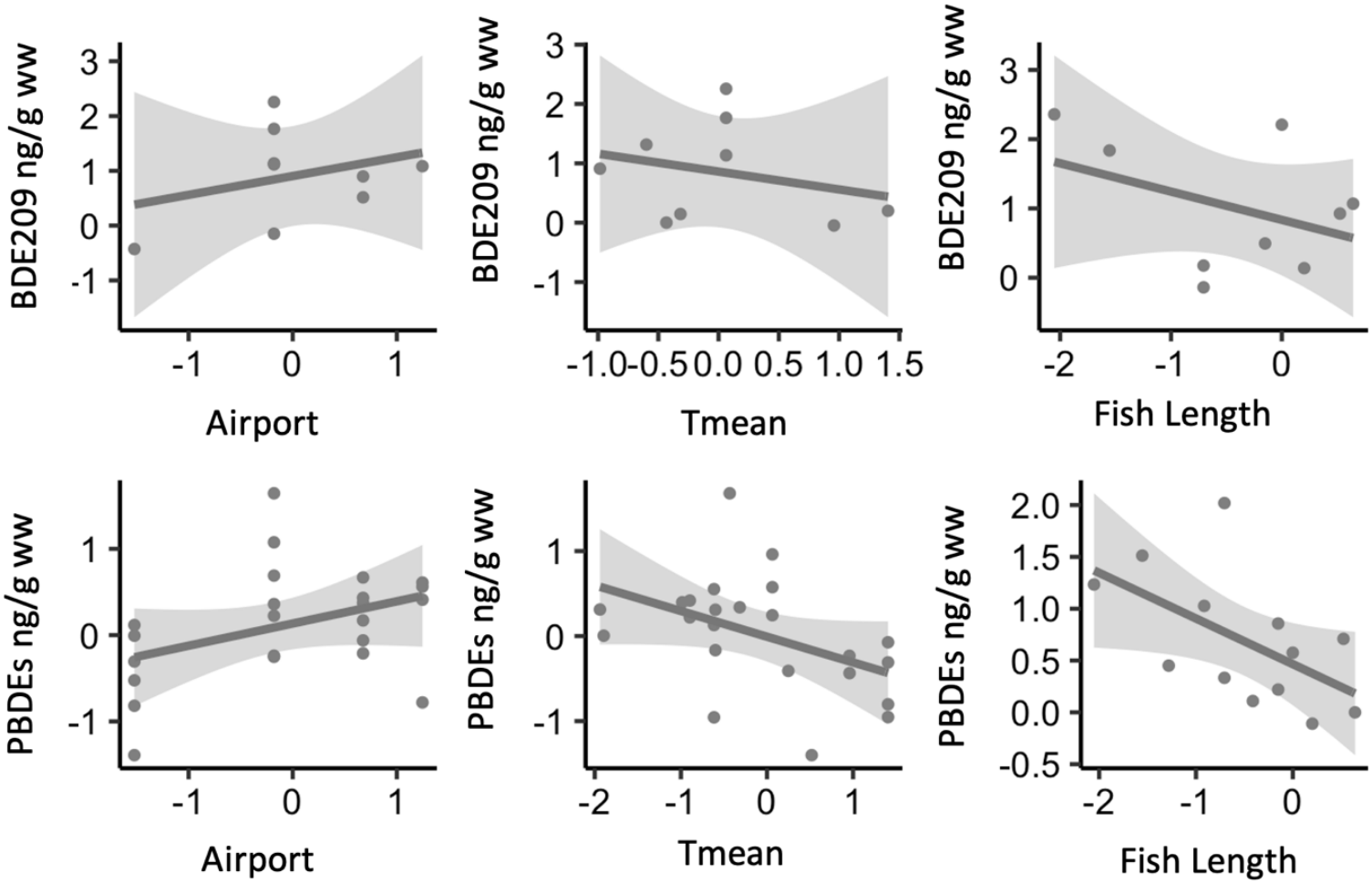


Figure 9 Residual plots showing the relationship between normalised BDE209 and sum of PBDEs (17 + 28 + 47 + 66 + 71 + 85 + 99 + 100 + 138 + 153 + 154 + 183 + 190 congeners) concentration in Arctic charr from Greenland versus each of the normalised and centred predictor variable in the best (lowest-AIC model) multilevel linear regression models (model outputs are shown in Table 3): mean annual temperature (Tmean), airport activity (Airport, Table SI-4) and fish length. The lines depict the least-squares regression lines and the grey area depicts the 95% confidence interval.

The Layman metrics models (Table 12, Figures 10-11) showed that the total nitrogen range exploited by the fish population (NR, $\delta^{15}N$ range) was positively related to DDTs (ß=0.101); mean nearest neighbour distance (NND), which is a measure of the overall density of the fish population packing, was positively related to DDTs and PBDEs; mean distance to centroid (CD), which implies fish population trophic diversity, was positively related to PBDEs; and standard ellipse area (SEA), which describes the mean core fish population isotopic niche (which is robustness to variation in sample size) and SEAs (Standard ellipse area corrected by sample size) were positively related to PBDEs. No Layman Metrics were significant for PCBs.

Table 12 Output of the best multilevel linear regression models (MLMs) relating concentration of OHC congeners in fish (dependent variable) with Layman's fish community-wide metrics, based on Arctic char $\delta^{13}C$ and $\delta^{15}N$ stable isotope signatures (independent variable), according to the Akaike information criterion (lowest-AIC model). Fish median concentrations per lake and environmental variables were transformed when needed to control for normality and heteroscedasticity. Spatial autocorrelation structure was significant (p-value < 0.05) and added to the model. Significance of environmental variables for determining fixed and random effects in the best multilevel model: *** p-value<0.001; ** p-value< 0.01; * p-value<0.05. DDTs (DDDs, DDEs and DDTs metabolites) and PBDEs (BDE17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183 and 190 congeners). δ15N range (NR), mean nearest neighbour distance (NND), mean distance to centroid (CD), standard ellipse area (SEA), and standard ellipse area corrected by sample size (SEAs).

Compounds	Layman metrics	Fixed effects coefficient (slope)	SE	df	*t* value
DDTs	NR	0.101*	0.050	107	1.994
	NND	0.132 **	0.043	107	3.058
PBDEs	CD	0.103 **	0.033	251	3.108
	NND	0.091 **	0.032	251	2.791
	SEA	0.082 *	0.035	251	2.326
	SEAs	0.082 *	0.035	251	2.326

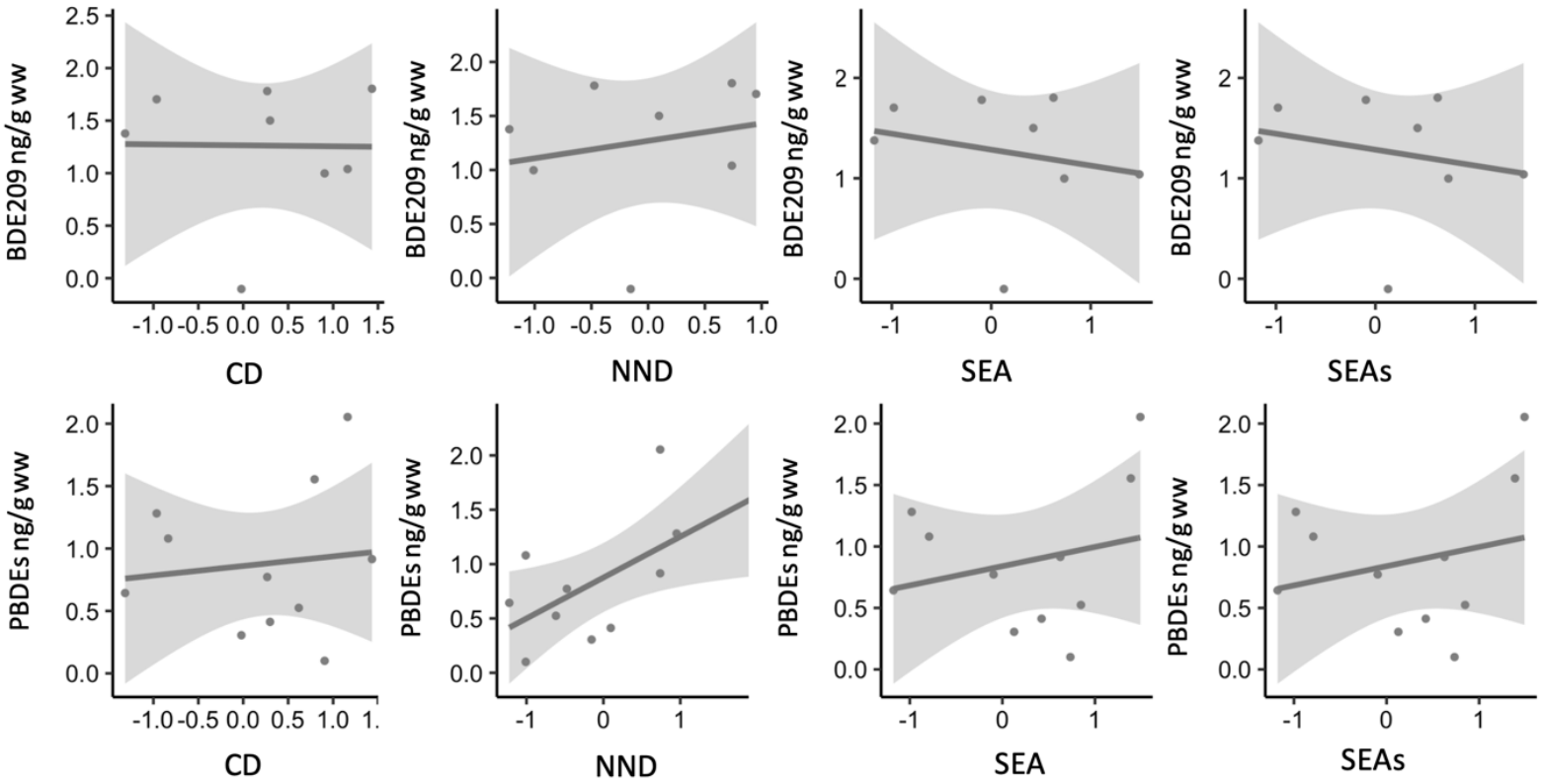


Figure 10 Linear relationship plot between normalised BDE209 and sum of PBDEs (17 + 28 + 47 + 66 + 71 + 85 + 99 + 100 + 138 + 153 + 154 + 183 + 190 congeners) in Arctic charr from Greenland versus each of the normalised Layman metrics (model outputs are shown in Table 4): mean annual temperature (NR), airport activity (Airport) and fish length. δ15N range (NR), mean nearest neighbour distance (NND), mean distance to centroid (CD), standard ellipse area (SEA), and standard ellipse area corrected by sample size (SEAs). The lines depict the least-squares regression lines and the grey area depicts the 95% confidence interval.

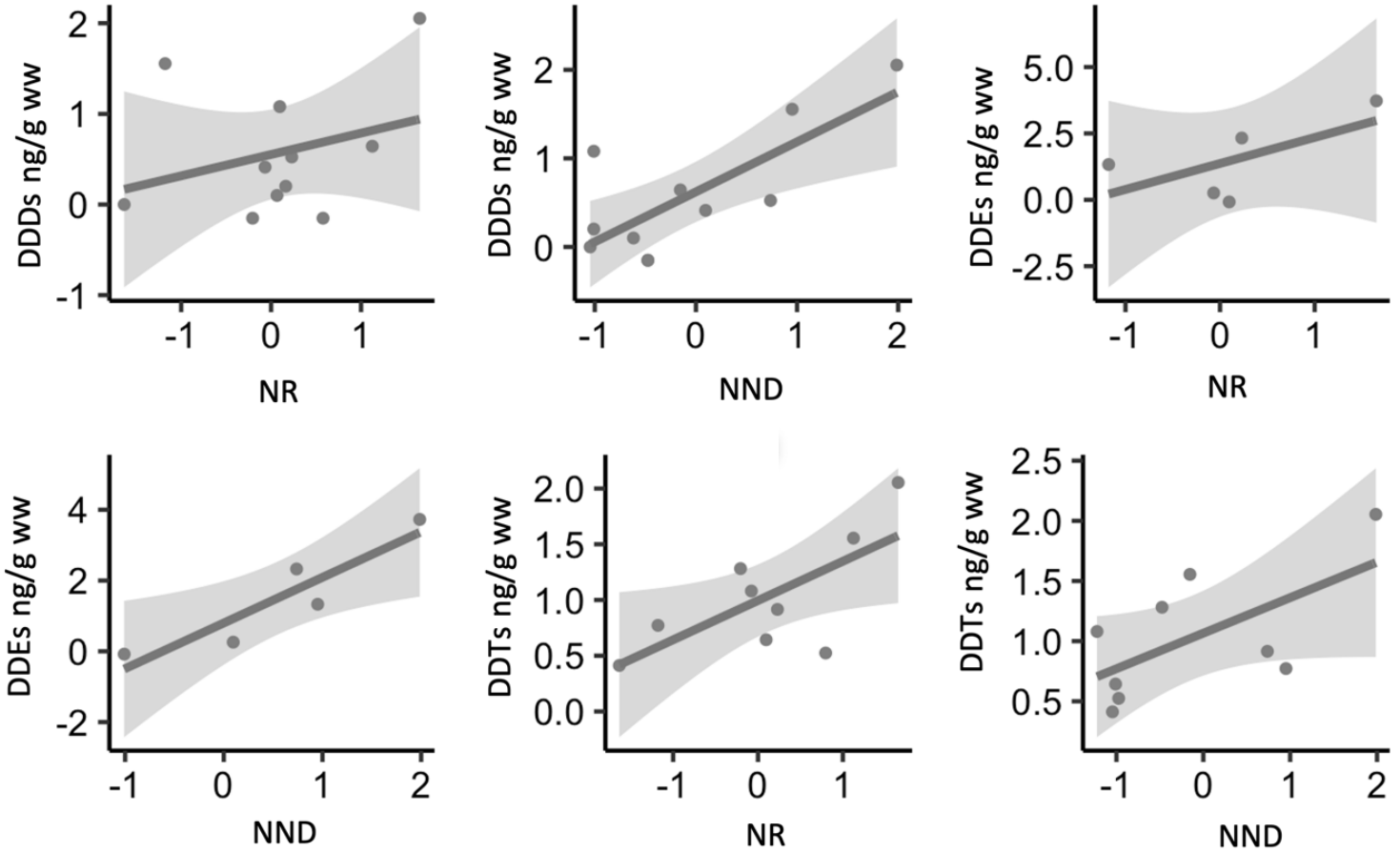


Figure 11 Linear relationship plot between normalised DDD, DDE and DDT concentration in Arctic charr from Greenland versus each of the normalised Layman metrics (model outputs are shown in Table 4): mean annual temperature (NR), airport activity (Airport) and fish length. δ15N range (NR), mean nearest neighbour distance (NND), mean distance to centroid (CD), standard ellipse area (SEA), and standard ellipse area corrected by sample size (SEAs). The lines depict the least-squares regression lines and the grey area depicts 95% confidence interval.

Discussion

General ranges of concentrations

The values reported in our study fall within the ranges of <LOD-51.04 ng/g ww for PCBs (7 congeners), <LOD-15.27 ng/g ww for DDTs (6 metabolites) and <LOD-7.8 ng/g ww for PBDEs (14 congeners), with the highest concentrations in Pittufik and Zackenberg areas, all in the vicinity of anthropogenic source of OHCs, i.e., airport and research station. Our results fall in the top range of two previous studies performed for organochlorines in Greenlandic Arctic charr (Table 13). Cleemann et al., (2000) evaluated Arctic charr PCBs and DDTs concentrations in four different Greenlandic locations (11 congeners of PCBs, range: 8.2-36 ng/g ww and 3 metabolites of DDTs, range: 2.5-12 ng/g ww). Rigét et al., (2010) evaluated Arctic charr PCBs from a small lake from southwest Greenland (10 congeners, range:1.53-16.32 ng/g ww). For PBDEs, we also found much higher values than those in Lake Fergusson (Southwest Greenland) (6 congeners, 0.90 ng/g ww) (Vives, Grimalt, Lacorte, et al., 2004). Specifically, both our study and Cleemann et al., (2000) found some charr individuals exceeding the toxicity threshold for PCBs and DDTs; and half of our charr samples also exceeded the toxicity thresholds set for PBDEs (Environment Canada, 1999). These results are concerning given the importance of Arctic charr as a food source for the Greenlandic population diet (Kozak et al., 2021) and the high levels of POPs found in them (AMAP, 2015; Long et al., 2012).

When comparing our values with those from other regions in the Arctic, such as the Norwegian Arctic (Table 13), Arctic charr from lakes of the remote Bjørnoya Island had higher levels of PCBs (7 congeners, mean concentrations: 694 ng/g ww) and ppDDE (mean concentrations: 58 ng/g ww) than in our study when bird colonies were present close to the lake, but lower levels of PCBs (7 congeners, mean concentrations: 49 ng/g ww) and ppDDE (mean concentrations: 3.4 ng/g ww) than in our study in lakes without bird colonies (Evenset et al., 2004). The role of birds as biovectors of organic pollutants is remarkable, as also studied in other Greenlandic lakes (Chapter 1, this thesis). In Svalbard (Norway), PCBs concentrations in Arctic charr were also higher than the ones in our study (7 congeners, range: 30.8-114 ng/g ww (Christensen et al., 2008). In the case of PBDEs, concentrations, remote lakes in Norway, such as the ones in Bjørnoya and Svalbard Islands, regularly showed low concentrations in Arctic charr (Christensen et al., 2008; de Wit et al., 2006, 2010). However, some remote lakes, such as lake Ellasjøen in Bjørnoya, achieved PBDE concentrations in Arctic charr up to 17

ng/g ww (7 congeners), values that are often compared with those in other industrialized areas in the Arctic (de Wit et al., 2010).

The Canadian Arctic is well represented area in terms of OHCs studies in general and when referring to Arctic charr, and consistently reports high level of OHCs contamination. Indeed, in Cornwallis and Ellesmere Islands, PCBs and DDTs were found to have greater levels of OHCs in Arctic charr than our study (87 PCB congeners, range: 4.7-127 ng/g ww and 6 DDTs congeners: 0.54-61.12 ng/g ww, (Cabrerizo et al., 2018)). In Nunavut, PCBs in Arctic charr from three remote lakes were also high (5 congeners, range: 7.3 - 289 ng/g ww (Muir & Lockhart, 1993)). However, in the Northwest Territories from the Canadian Arctic, PCBs and DDTs concentrations were lower (102 PCB congeners, range: 6.69-13.07 ng/g ww, 6 DDTs congeners, range: 2.9-6.33 ng/g ww, (Kidd et al., 1998)).

Table 13 Median (unless mentioned otherwise) concentrations and ranges (in brackets) reported in fish Arctic charr (*Salvelinus alpinus*). All values are in ng/g ww unless mentioned otherwise. When the number of congeners was available, the number was indicated below the concentrations. 10 PCBs: CB28, CB31, CB52, CB101, CB105, CB118, CB138, CB153, CB156, CB180; 7 congeners PCBs: CB 28, 52, 101, 118, 138, 153 and 180; 8 congeners PCBs: CB28, PCB52, PCB101, PCB105, PCB118, PCB123, PCB153, PCB128

Area	PCBs	DDTs	PBDEs	Reference
Greenland	0.5 (<LOD-51.04) 7 congeners	0.965 (<LOD-15.27) 6 metabolites	0.32 (<LOD-7.8) 14 congeners	This study
Greenland (north-west). Avanersuaq	(3.5-12.9) 10 congeners	(1.3-4.5) 3 metabolites	-	(Cleemann et al., 2000)
Greenland (mid-west). Nuuk	(4.1-13.7)	(0.8-4.2)	-	
Greenland (south). Qaqortoq	(0-32)	(0.8-14.2)	-	
Greenland (mid-east). Tasiilaq	<LOD-80	(3.2-20.8)	-	
Greenland (east). Ittoqqortoormiit	120 (47-2630) ng/g lw 10 congeners	160 (76-2020) ng/g lw 5 metabolites	9.8 (3.7-210) ng/g lw 11 congeners	(Vorkamp, Christensen, & Rigét, 2004)
Greenland (east). Ittoqqortoormiit	110 (37-3160) ng/g lw 10 congeners	120 (57-2580) ng/g lw 5 metabolites	7.4 (3.3-270) ng/g lw 11 congeners	
Greenland (south). Lake Fergusson	-	-	Mean: 0.90 6 congeners	(Vives, Grimalt, Catalan, et al., 2004)
Norway. Lake Ellasjøen, Bjørnøya,			Small arctic char:15.1 Big Arctic char: 17	(Evenset et al., 2005)
Norway. Lake Ellasjøen, Bjørnøya	694 7 congeners	ppDDE: 58 (mean)		(Evenset et al., 2004)
Norway. Lake Oyangen, Bjørnøya	49 7 congeners	ppDDE: 3.4		
Norway. Lake Ellasjøen, Bjørnøya	118 7 congeners	1.18	1.92	(Christensen et al., 2008)
Norway. Lake Oyangen, Bjørnøya	26.85	2.2	0.28	

Norway. Lakes in Svalbard	(17.7-114) 7 congeners	(5.29-4.55)	(0.42-1.17)	
Russia (Arctic). Nenets Autonomous Okrug	(0.56-2.25) 8 congeners	(0.33-1.11) 4 metabolites	-	Lakhmanov et al., 2020)
Canada. Resolute Lake	(33-120) 87 congeners	(2-8.7)	-	(Cabrerizo, Muir, Köck, et al., 2018)
Canada. Char Lake	(18-127) 87 congeners	(4.8-52)	-	
Canada. Amituk Lake	(12-125) 87 congeners	(1.06-61.12)	-	
Canada. Lake Hazen	(4.78-37) 87 congeners	(0.54-11.61)	-	
Canada. Nunavut	(7.9-289) 5 congeners	-	-	(Muir & Lockhart, 1993)
Canada. North-western territories	(6.69-13.07) 102 congeners	(2.9-6.33) 6 metabolites	-	(Kidd et al., 1998)

Temperature effect

Mean annual air temperature had a negative relationship with the concentrations of PCBs, DDTs and PBDEs, indicating long-range air transport (LRAT), as also observed in other abiotic and biotic compartments in other regions of the Arctic (Carlsson et al., 2018;. Christensen et al., 2002; Czub et al., 2008; de Wit et al., 2010; Evenset, Christensen, et al., 2007; Gregor & Gummer, 1989; Oehme & Manø, 1984; Rawn et al., 2001; Rose et al., 2004). So far, other studies have tried to understand the levels and trends in Arctic charr for OHCs, but no LRAT studies were available related to the temperature gradients in the Arctic for charr, and specifically no other studies have examined the distribution of OHCs in freshwater lakes in Greenland over temperature gradients.

The experimental phase change pseudo enthalpies calculated from the slopes of the regression straight lines for the compounds exhibiting significant temperature dependencies were much lower than the theoretical enthalpies (Table 14), with larger differences for PBDEs. Theoretical enthalpies being ΔH 75.7 kJ/mol for DDTs ppDDT), ΔH 121-144 kJ/mol for PCBs and ΔH 154-168 kJ/mol for PBDEs, indicating strong local pollution influence in these lakes. Indeed, we did find a strong local pollution signal as well in our models defined by the presence of big airports in the vicinity of the lakes, in addition to a strong positive relationship between mean annual air temperature and population density in the area (r=0.87), which did not allow us to include population density in the models, but it was certainly diluting the LRAT effect. In addition, for compounds such as PBDEs whose emission started very recently and are yet to be completely banned, differences in theoretical enthalpies are so large because the LRAT effect may show up more consistently in upcoming decades.

Table 14 Correlation Coefficients (r^2), Slopes, and Enthalpies from the transformed concentrations for PCBs, DDTs and PBDEs. [a] Calculated enthalpies (kJ,mol-1) following the equation: ΔH = SR ln(10), where S = slope of the regression straight lines, R = 8.314 $J \cdot K^{-1}$ and ln(10) = 2.303.
Significance codes: * *p<0.001; ** p< 0.01; * p<0.05***

Compounds	r^2	Slope (S)	ΔH kJ/mol [a]
PCBs	0.09**	2730	52.3
DDTs	0.16***	2640	50.6
PBDEs	0.12*	1311	25.1

Local pollution

Anthropogenic impact was found to be another important factor in Greenland PCBs, DDTs and PBDEs fate, with the higher molecular weight PCBs more bioaccumulated in fish from lakes in the vicinity of airports or military bases with higher activity. Current and former military bases throughout the Arctic, especially those with the older RADAR equipment, have been identified by several studies as significant contributors to the contamination of the Arctic (Scrudato et al., 2012). For example, significant PCB contamination at formerly used defence site in Alaska was found in fish and mussels from both freshwater and marine waters (Adams et al., 2019), or Thule air base has been already described as a local source of PCB pollution in biological matrix of Scallops, in North West Greenland (Kjølholt & Hansen, 1986). DDTs are also known to have been used at military bases and various communities in the Arctic to reduce the population of the biting-insects (AMAP, 2004; Rawn et al., 2001). However, no significant distinction in the DDT/DEE ratio has been found in relation to airport activity. Additionally to the local sources of contamination studied here, other local pollution sources such as research stations (Vecchiato et al., 2015; Wild et al., 2015), as the one in Zackenberg in our study; mineral exploration, coal mining, and heavy industry (AMAP, 2004); untreated sewage and waste dumps (Christensen et al., 2002); seabird as biovectors for OHCs (Blais et al., 2005; Evenset et al., 2004; Evenset, Carroll, et al., 2007; Evenset, Christensen, et al., 2007); and revolatilisation of OHCs from their Arctic sinks (Ma et al., 2011, 2016), have also been identified as local sources of OHCs in the Polar environment. More government action is needed here to minimize the risks of these local sinks of pollution in such fragile ecosystems.

Fish length

We found that median Arctic charr length per lake was a significant factor explaining PBDEs concentrations in Arctic charr. In particular, PBDEs concentrations decreased when fish was larger, indicating a “dilution” of the accumulated PBDEs in fish as a result of a rapid increase of muscle tissue (Arnot & Gobas, 2004; Fisk et al., 1998). Unfortunately, we don’t have age information for these fish to calculate the growth rate of each fish (the ratio between weight and age) in each lake, which could more easily help elucidate the direct cause of the effects found. What we usually found, though, was a slight positive relationship of fish length in each lake with total nitrogen, and a negative relationship with airport presence in the vicinity of the lake (Table 27 SM). It is indeed well known how pollutant bioaccumulation and chemical toxicokinetics in organisms are strongly influenced by biological and ecological processes including growth dynamics (individual and population growth rates and seasonal weight loss),

diet shifts and foraging ecology (McLeod et al., 2016). For example, lakes with higher nitrogen concentrations are usually more productive (Elser et al., 2007; Prater et al., 2021); and productivity of the lake is often related to biodilution of organic pollutants in organisms. Indeed, the second-best model for PBDEs selected TN (in addition to temperature and airport activity) as a negative predictor variable of PBDE concentrations. Increased productivity results in longer and more complex food webs with increased biomass at each trophic level, which spreads the OHCs fate across the different trophic levels biomass and decreases the OHCs biomagnification across the food web (Kozak et al., 2021). However, no statistical support for this mechanism was found in other studies in Arctic lakes (Gantner et al., 2010). Finally, the reason why in our study fish in the vicinity of airports are shorter may be potentially related with the direct effects of PBDE toxicity on growth (Schell et al., 2006), since some of these individuals have very high concentrations of PBDEs, overreaching the toxicity thresholds defined by the policy agencies (Environment Canada, 1999).

Layman metrics

Layman metrics are an analytical approach to calculate "community-wide" measures of trophic structure using stable isotopes ratios (Layman & Post, 2007), which have not been used so far to understand the OHCs dynamics in freshwater food webs. We found that higher fish trophic diversity (i.e., higher total nitrogen range exploited by the fish population – NR, $\delta^{15}N$ range; higher average degree of fish trophic diversity – mean distance to centroid, CD; and higher divergence in fish trophic niche – fish population trophic evenness, NND) was positively related to the concentrations of DDTs (NR and NND) and PBDEs (NND and CD) in Greenlandic Arctic charr. These results indicate higher DDTs and PBDEs biomagnification when Arctic charr was feeding on multiple trophic positions, according to the food-web biomagnification of persistent organic pollutants theory (Kelly et al., 2007). This biomagnification effect could in some cases be produced by the presence of three-spined stickleback (*Gasterosteus aculeatus* L.) in the lake, which would increase and diversify the trophic position of the Arctic charr community, as observed by the positive relationship among NR and the presence of sticklebacks in 10 lakes out of 25 lakes studied (*p-value <0.0001,* $r^2=0.094$, Table 28), only in Kangerlussuaq and Nuuk regions. This relationship among trophic position of Arctic charr and the presence of sticklebacks in the lakes was also described by Arranz et al (in prep.) in some of the studied lakes from Nuuk and Ilulissat. Arranz et al (in prep) also found how the presence of three-spined stickleback in the lake had higher influence on the trophic position of the fish than the lake-habitat structure. The metrics related to the

degree of isotopic niche overlap (standard ellipse area, SEA, and SEAs, which is the same metric but corrected by sample size) were highly correlated between each other (Table 24 SM) and positively related to PBDEs, which may reinforce the idea that when both pelagic and profundal habitats are important, the biomagnification of pollutants in these lakes is enhanced as a result of higher fish trophic diversity and longer food webs. With these results and the lack of influence of the fish carbon range (CR) Layman metric on the concentrations of the OCHs analysed, we cannot speculate about the potential littoral habitat influence on the OCHs bioaccumulation by Arctic charr, which (if present) could affect fish biomagnification due to the higher pollution dilution when feeding on more productive benthic habitats (Guildford et al., 2008). No available information has been found in the literature comparing Layman metrics and OHCs bioaccumulation in fish but this line of research points to very promising results for the interpretation of pollutants dynamics in freshwater food webs.

Conclusions

Regrettably, the Arctic cannot be considered a pristine environment any longer. Due to the Arctic's unique climate, its flora and fauna is highly vulnerable to the transboundary pollutants, including OHCs, which get deposited in its cold environments, acting as a sink. Some studies focus on the levels and trends of OHCs in the Arctic/Greenland and denote LRAT as the reason for the high concentrations of POPs. However, the expanding human footprint on these pristine areas has also led to the formation of local sources of OHCs in Arctic, as well as in Greenland, which creates added pressure on the already vulnerable Arctic ecosystems. This is extremely detrimental especially for freshwater ecosystems as a result of their low temperatures, low nutrients, long periods of darkness and high sediment load when they are glacier-fed (Kosek & Ruman, 2021). In this study, we have tried to distinguish between the effects of LRAT vs. local pollutant sources using freshwater biota (e.g., Arctic charr) as sentinel species, which have been less frequently studied than Arctic marine biota. Results are concerning because some of the concentrations detected face the toxicity threshold and Arctic charr is an important food source especially for the Inuit population inhabiting Greenland.

The Arctic is thus currently facing multiple stressors: historical cold war military installations, increasing exploration for oil and minerals, long range transport of pollutants and on top of it all: climate change-induced rapid warming (Macdonald et al., 2003; Vincent & Hobbie, 2000). With increasing temperatures in the Arctic, revolatilisation and re-emission of OHCs increases from their sinks in abiotic compartments and concentrations released can be high enough to be considered a "secondary source" even if the "primary" source emissions of OHCs are going down (Nizzetto et al., 2010). Simultaneously, range shifts of cold water species has been observed and is expected from climate change (Jeppesen et al., 2017; Patra et al., 2015), in addition to the exposure to infectious diseases and zoonoses (AMAP, 2018), which might make the biota more vulnerable to the contaminants. Thus, it is crucial to keep tracking these compounds in the Arctic environments as the Arctic may go from being a receptor to an emitter of OHCs bringing its ill effects to the local biota, including humans.

GENERAL DISCUSSION AND CONCLUSIONS

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General Discussion

The concentrations levels of OHCs in Greenlandic freshwater surface sediments, sediment cores and Arctic charr were found to be in accordance with the studies in Greenland (Cleemann et al., 2000; Malmquist et al., 2003; Rigét, Vorkamp, et al., 2010). Except for samples from a few regions like Pittufik, Zackenberg and Kangerlussuaq, where the recorded concentrations were higher. The concentrations in these regions also exceeded the toxicity thresholds set for the sediment and freshwater fish (Cleemann et al., 2000; Environment and Climate Change Canada, 2019; US EPA, 2013). However, comparing to the other areas of Arctic areas, namely, from Canada, Norway, Sweden, Russia and Alaska (AMAP, 2004, 2016; Blais & Muir, 2005; Cabrerizo, Muir, Köck, et al., 2018; Christensen et al., 2008; Evenset et al., 2004; Muir et al., 1995, 1996; Rawn et al., 2001; Stern et al., 2005) the concentration ranges were similar. Temporal trends for the compounds did not have a homogenous response: some compounds showed a decreasing trend, the other showed an increasing trend and some didn't show any trend at all in the sediment cores and surface sediment. This non-homogenous response was also observed in other sediment core study from Greenland (Malmquist et al., 2003). Seabirds were found to be an important carrier of OHCs to the remote Greenlandic freshwater lakes as was found in Norwegian Arctic (Evenset, Carroll, et al., 2007) and Canadian Arctic (Blais et al., 2005) creating "hotspots" of OHCs contamination. Latitudinal gradient was significant for the presence of OHCs in surface sediment. On the other hand, temperature, which is inversely related to the latitudinal gradient was found to be significant factor for the OHCs found in Arctic charr. Both these gradients indicate long-range atmospheric transport (LRAT) (Wania & Mackay, 1993). These results will be discussed in detail in the following paragraphs. Many studies have tried to understand the presence and bioaccumulation of OHCs in the Arctic mostly using contaminant levels and their spatial/ temporal trends which together gives a complete picture of the contaminant pattern in Greenland (Cleemann et al., 2000; Malmquist et al., 2003) and the Arctic (AMAP, 2004, 2016; Muir et al., 1995). Not many studies, though, have done this with a greater spatial resolution than this study.

Temporal Patterns

According to the trends in sediment cores (Chapter 1), OHCs like PCBs, DDTs, HCB, HCHs, Drins and Heptachlors temporally decreased after peaking in 1970s due to the effects of the bans placed on these compounds (AMAP, 2004). In contrast, Methoxychlor, Octachlorostyrene and Chlordanes, the former two still in current production and rarely studied

in the Arctic, show an increasing temporal trend. Finally, PBDEs temporal trends were consistent in the cores towards the surface, neither increasing nor decreasing. Essentially, despite the bans of some of OHCs, they were still found to persist in the Arctic freshwater sediments. These results are agreement with other studies in sediment core matrix. For instance, in Greenland Malmquist et al., (2003) observed decreasing trends for PCBs, BDE47, but no trends were observed for Chlordanes and HCB. In Canadian Arctic (Stern et al., 2005) observed maximum concentrations near the top of the core for PCBs, PBDEs, HCHs, and Endosulfans. For DDT and its metabolites maximum had high flux around 1970s. In the Norwegian Arctic observed that PCBs and DDTs contamination peaked around 1970s but started declining afterwards similar to what was observed in this study, however they observed PBDEs to be increasing till the maximum year in their study that was 2001 (Chapter1) (Evenset, Christensen, et al., 2007).

Comparing temporal trends from sediment core (Chapter 1) with surface sediment ones (Chapter 2), intriguingly, it was observed that for surface sediments, the OHCs such as PCBs, HCHs and PBDEs, showed a decreasing trend with the year from which the lakes were sampled across the Greenlandic spatial gradient (Chapter 2).

The two studies (Chapter 1 and 2) indicate that even if the concentrations of the OHCs are decreasing or expected to decrease at the lower latitudes due to ban or reduction in their production (AMAP, 2014; Ritter et al., 1995), for the Arctic it is a different story altogether due to it being a sink to the OHCs pertaining to its low temperatures.

Spatial Patterns

Chapter 2 and 3 dealt with understanding spatial patterns of OHCs in sediments and fish. Spatial patterns of OHCs gives us important tools to understand the concentrations across to mitigate the OHCs ill-effects in the biota as well as to assess the effects of global regulations on OHCs. Although LRAT is considered a primary contaminant pathway to the Arctic, biovectors such a seabirds also play a significant role in transporting and distributing OHCs in remote regions causing heavy amplification of concentrations in those areas (Blais et al., 2007). Migratory species travel thousands of miles towards the Arctic, and many are known to carry pollutants to the remote areas. Seabirds are considered probably the most relevant biovectors for OHCs transport to the Arctic/Greenland. Their population may reach tens of millions in individuals along the Greenland coast in the North Water Polynya (González-Bergonzoni et al., 2017). Spatial patterns are elaborated further in the following points.

Long Range Atmospheric Transport

The concentrations of PCBs, DDTs and PBDEs in Arctic charr had a negative relationship with mean annual temperature (Chapter 3), indicating long-range air transport of OHCs, which has also been observed in other biotic compartments in other regions of the Arctic (Carlsson et al., 2018; Christensen et al., 2002; Czub et al., 2008; de Wit et al., 2010; Evenset, Christensen, et al., 2007; Gregor & Gummer, 1989; Oehme & Manø, 1984; Rose et al., 2004). Moreover, the calculated the experimental phase change pseudo enthalpies for PCBs, DDTs and PBDEs were lower than the theoretical enthalpies for the compounds indicating that the local pollution effects were significant in the lakes in addition to the LRAT (Chapter 3).

The LRAT effect with mean annual temperature was less pronounced in sediment probably because of >50% of our surface sediment samples had values <LOD (very homogeneous among them, then) and the temperature also correlated positively with population (>0.85). Indeed, HCHs, HCB, Chlordanes and Heptachlor had a positive relationship with latitude although this relationship vanished when local sources of OHCs were considered in the models (Chapter 2).

Another interesting result observed is the presence of low molecular weight PCBs (PCB28, 52, 101) in the top layers of the sediment core NOW5 while higher molecular weight PCBs were in lower layers of the sediment core (Chapter 1). This was also observed by and was attributed to delayed deposition of low-chlorinated PCBs owing to the hypothesis of "cold condensation" (Malmquist et al., 2003). Indicating, that these results are generally in agreement with the Global Distillation theory of persistent organic compounds that predicts a temperature-dependent partitioning of semi- volatile compounds (Wania & Mackay 1993; 1996).

Bird Effects: Biovectors

In the present study, the role of seabirds for the transport of organochlorine compounds to very remote sites, e.g., western Greenland, was evaluated (chapter 1). The concentrations of all organohalogen compounds were much higher in the lake under the influence of seabirds than in the other lakes showing the strong influence of these seabird populations in the transport and deposition of these hydrophobic compounds to remote sites. Concentrations of heavier PCBs, whose concentrations were higher in NOW5 as compared to the other lakes, indicated an increase of higher molecular weight contaminants into food webs, which are difficult to metabolize and further accumulates in the food web of the lake creating "hot-spots" of contaminants in the Arctic lakes (Evenset, Carroll, et al., 2007). Seabirds occupy high trophic

positions in the marine food web, and as a results, often accumulate elevated levels of contaminants due to biomagnification (Michelutti, Liu, et al., 2009). When they congregate on shore, often in dense nesting colonies, they funnel a portion of their bioaccumulated contaminants to the land via guano (and mortality). Only a handful of studies have studied the phenomenon of seabirds bringing in OHCs to the Arctic, specifically, in Canadian arctic (Blais et al., 2005; Michelutti, Keatley, et al., 2009; Michelutti, Liu, et al., 2009) and Norwegian Arctic (Evenset et al., 2004; Evenset, Carroll, et al., 2007; Evenset, Christensen, et al., 2007).

Local effect: compare sediments vs. fish

Anthropogenic effects were apparent and significant in both Chapter 2 and Chapter 3. Current and former military bases, research stations, populated sites are strewn throughout Greenland and across the Arctic as well. The fish and sediment samples around these local sources show a higher contamination level, even exceeding the toxicity levels (Chapter 2 and 3). These military bases have been found to be source of OHCs equipment, PCBs in old RADAR equipment, PBDEs in current electronic equipment and pesticides like DDTs to reduce the populations of biting insects (AMAP, 2004; Scrudato et al., 2012).

Studies have reported airports, military bases and research stations acting as a local pollution source of OHCs in the Polar regions including Greenland (Ahrens et al., 2015; AMAP, 2004; Cabrerizo, Muir, De Silva, et al., 2018; Cabrerizo, Muir, Köck, et al., 2018; Corsolini et al., 2019; Kjølholt & Hansen, 1986; Vecchiato et al., 2015; Wild et al., 2015).

Population density of the towns and settlements were also a significant factor (Chapter 2 and 3). We could not include population in the models with Arctic charr for Chapter 3 because the correlation between temperature and population surpassed the threshold for having reliable results in the models ($r=>0.65$). Therefore, the negative trend of temperature with the OHCs concentrations “masks” the effect of population. Hence, the LRAT without the local effect would probably show a stronger signal.

Arctic is not pristine

Greenland is not as pristine as has always been imagined; it has OHCs arriving via LRAT from the Eurasian and American continents, pockets of OHCs contamination from the local sources, as well as biovector mediated transport of OHCs. It is clear that the anthropogenic production of harmful POPs has colonised the whole globe, even the remote environments like the Arctic. In detail, LRAT is one of the main mechanism for OHCs to travel from lower latitudes to the Arctic (Burkow & Kallenborn, 2000) . Local sources within the Arctic have also proven to be important to the OHCs levels in sediments and fish. Airports, military installations, research stations and sometimes population can be the local source of pollution (Kjølholt & Hansen, 1986; Malmquist et al., 2003; Rose et al., 2004; Vecchiato et al., 2015).To their own detriment, the migratory species have fallen in the crosshairs of this pollution and through no fault of their own have aided in accumulating POPs in their nesting areas, in turn negatively affecting the other food web components of the freshwater lakes of the Arctic where these migratory birds nest.

Multiple studies have tried to study the OHCs in Greenland, however, the focus has been to understand how OHCs are accumulated in large marine animals like polar bears, seals, and birds, since they are keystone marine arctic species. Considering that freshwater species like Arctic charr forms an important part of the diet of indigenous people, and high levels of POPs were found in the indigenous populations, it is imperative to study these fish as well (AMAP, 2015; Carlsson et al., 2018; Lakhmanov et al., 2020). In this thesis, we try to elucidate OHCs distribution in freshwater lake sediments and Arctic fish, which will supplement the data in Greenland freshwater food web components and give us a richer illustration of OHCs accumulation in the Arctic. Worryingly enough, the concentrations in sediment and fish are concerning in Greenland as they are not negligible. On top of this, climate change may additionally exacerbate the reemission of OHCs from ice, sediments, and soils, increasing the mobilization of these pollutants in the Arctic abiotic compartments and might concentrate into the freshwater organisms (Ma et al., 2011).

The future: Climate change effects

The presence of these OHCs in the Arctic is extremely concerning considering it is also one of the places to be most impacted by increased warming due to climate change (Ma et al., 2016), especially because both of the stressors (climate change and OHCs) are dependent on temperatures (Macdonald, 2005; Macdonald et al., 2003). Additionally, the Arctic is currently

also facing the following stressors: increasing military installations, exploration in the Arctic for oil and minerals, long range transport of pollutants (Macdonald et al., 2003; Vincent & Hobbie, 2000). Climate change may also intensify the re-emission of POPs which were deposited long back in the various environmental compartments (sediments, soil, glaciers) in the cold climate of the Arctic. Then, multiple new sources of POPs might emerge, leading to changes in the rates of transport as well as deposition in the lakes. In this way, the concentrations released will be high enough to be more considered an "emitter" than a "receptor", even if the primary source emissions of OHCs are going down (Nizzetto et al., 2010).

Climate change processes can influence every step along the transport and climate change and climate variability also increase the risk from contaminants by changing exposure to chemicals, either through the alteration of bioaccumulation pathways or through alteration of POPs concentrating mechanisms in abiotic media (Macdonald et al., 2003).

Arctic is considered a sentinel of the upcoming global changes due to its sensitivity to climate change and the region being a barometer for global contamination of POPs (Kallenborn et al., 2012). Thus, it is imperative to study OHCs in the Arctic/Greenland. Moving forward, it will be important to understand the whole encompassing threats to the Arctic as a whole. Especially, not just the legacy compounds but also there are new/novel compounds that are being discovered to have reached the Arctic (e.g., Endosulfans, Octachlorostyrene, Pentachlorobenzene, PFOS, PFOA, novel flame retardants and so on) even if never produced or used there. The future studies on OHCs must focus on both severe stressors simultaneously; adding climate variables might explain the "confounding factors" and give us a complete picture of POPs in the Arctic. Specifically, we can expand upon this thesis/study by comparing climate indicators (e.g., NAO, AO, PNA)[2], and long temporal studies (as in chapter 1) as well as spatial gradient studies (as in chapter 2 and 3) in sediment cores as well as in Arctic biota.

[2] NAO = North Atlantic Oscillation, AO = Arctic Oscillation, and PNA = Pacific North American Pattern

General Conclusions

Chapter 1

- This study shows that levels of contamination in the lake NOW5 is positively correlated to the presence of birds in the lake catchment and the other two lakes are contaminated but to a lesser extent due to atmospheric deposition. The most volatile, hexachlorobenzene and the hexachlorocyclohexanes, were about 20 time higher in NOW5 whereas the enrichment of the Chlordanes, PBDEs and PCBs was between 4 and 6 times and DDTs three times. These differences evidence a selective effect in the seabird accumulation and transport of organohalogen to remote sites.
- This study also indicates that, evidently, the global regulations on POPs have resulted decrease in the concentrations but contaminants like HCB, PCBs, DDTs, HCHs, PBDEs, still persist in the Arctic environment (Stockholm Convention, 2018).
- Seabirds play a significant role in the transport of organohalogen compounds to remote sites but their effect is selective depending on the chemical composition of these pollutants.

Chapter 2

- Generally low levels of OHCs were detected in freshwater lake sediments of Greenland but in some lakes, DDTs, PBDEs and HCB were detected in high concentrations and in case of DDTs, two lakes showed concentrations higher than threshold values.
- PCBs and DDTs form a part of the major OHCs in Greenland freshwater lake sediments, followed by PBDEs. Other OHCs like Drins, Heptachlors, Mirex, HCB were also detected in low quantities in spite of being banned (Stockholm Convention, 2018).
- CUPs like Endosulfans, HCHs, Methoxychlor were also detected, albeit, in low concentrations. These CUPs have been also identified in various Arctic Media by several studies (Hoferkamp et al., 2010), but not much information was found on Greenland. Octachlorostyrene, which is known to bioaccumulate in Greenland wildlife (Vorkamp et al., 2017), was also detected in a few freshwater sediment samples in our study.
- Local sources of pollution were the principal factor determining the OHC concentrations. Airports, airbases and populated areas were found to be significant sources of pollution.

- Year the lake was sampled in as a variable was also a key factor, and it was negatively related to the OHC concentrations, a phenomenon also observed by other marine and freshwater studies (Nyberg et al., 2015; Rigét et al., 2016; Rigét, Bignert, et al., 2010).

Chapter 3

- Temperature and local effects best explained the patterns of PCBs, DDTs and PBDEs accumulation in the Arctic charr which indicate the long-range transport of the OHCs to the remote environments of Greenland.
- Total Nitrogen (TN), as nutrient content in the lake, was significant in explaining the concentrations of PBDEs in Arctic charr indicating the biodilution effects on PBDEs bioaccumulation in Arctic charr.
- These concentrations of PCBs, DDTs as well as PBDEs detected are higher than the toxicity threshold for Arctic charr, this is concerning because Arctic charr is an appreciated food especially by the Indigenous Inuit population inhabiting Greenland.
- Food web metrics were also an important determining factor for DDTs and PBDEs concentrations.
    - The total Nitrogen range exploited by the fish population (NR) indicated higher biomagnification with longer food webs.
    - The models indicated that Population trophic evenness (NND) were positively related to DDTs and PBDEs.
    - Population trophic diversity (CD) was positively related to PBDEs indicating that the lakes with a similar degree of fish trophic diversity experienced higher DDTs and PBDEs bioaccumulation.
    - The degree of isotopic niche overlap (SEA and SEAs) indicated that the populations with similar diet, in this study, pelagic diets, experienced higher biomagnification of PBDEs.
- This is one of the first studies to compare Layman Metrics and OHCs bioaccumulation in fish.

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ANNEX

Chapter 2 Supporting Material

Table 15 Airport data obtained from Greenland Airport Authority (Mittarfeqarfiit, 2012) used to classify the Greenland areas in this study.

Airport location	Number of Passengers	Runway length (meters)	Military Or Research Station	Levels awarded
Pituffik/Thule Air Base	NA	3,047	Big Research and Military Station	3
Kangerlussuaq	~136,000	2,810	No	3
Nuuk	~69,000	950	No	2
Ilulisat	~40,000	845	No	1
Zackenberg	-	-	Medium Research Station	1
Daneborg	Aerodrome	-	Small Military Station	0
Pearyland (Station Nord)	Aerodrome	-	Small Research and Military Station	0
Qaanaaq	-	-	-	0

Table 16 Population data obtained from Statistics Greenland (Statistics Greenland, 2020) to classify the Greenland regions in this study.

Region	Population (number of individuals)
Pittufik/Thule Air Base	100
Kangerlussuaq	700
Nuuk	19000
Ilulisat	5000
Zackenberg	100
Daneborg	13
Pearyland (Station Nord)	0
Qaanaaq	700

Table 17 Concentrations of OHCs in Greenland freshwater lakes in our study. The values represent the sum of the concentrations of the congeners analyzed per each group of compounds. The units are in ng/g dw.

Region		Ilulisat	Kangerlussuaq	Nuuk	Pearyland	Pittufik	Qaanaaq	Zackenberg
ΣPCBs	Max	1.20	3.77	5.59	1.54	0.37	0.06	<LD
	Min	<LD[3]	0.40	0.04	0.05	0.21	<LD	<LD
	Med[4]	0.35	0.96	0.48	0.79	0.29	<LD	<LD
	SD	0.56	0.93	1.86	1.05	0.11	0.03	-
ΣDDTs	Max	1.50	63.96	1.89	1.97	0.58	0.29	0.31
	Min	0.15	0.06	0.21	0.22	0.14	0.02	0.20
	Med	0.34	1.02	0.66	1.09	0.36	0.15	0.26
	SD	0.62	16.82	0.55	1.24	0.31	0.13	0.08
ΣHCHs	Max	<LD	<LD	0.08	0.004	0.02	0.13	0.008
	Min	<LD	<LD	<LD	<LD	0.06	<LD	<LD
	Med	<LD	<LD	<LD	0.02	0.01	<LD	0.004
	SD	-	-	0.03	0.003	0.007	0.08	0.006
ΣPBDEs	Max	1.09	4.31	3.99	0.05	1.67	1.23	0.63
	Min	0.23	<LD	0.44	0.05	0.94	<LD	0.58
	Med	0.77	<LD	1.17	0.05	1.31	0.57	0.61
	SD	0.37	1.15	1.34	0.003	0.52	0.62	0.04
ΣChlordanes	Max	1.42	0.10	3.08	1.75	1.96	0.32	0.06
	Min	0.01	<LD	0.28	0.34	0.21	<LD	0.02
	Med	0.18	<LD	1.23	1.05	1.08	<LD	0.04
	SD	0.66	0.03	1.17	0.10	1.24	0.18	0.03
ΣHeptachlors	Max	<LD	<LD	0.55	<LD	0.02	<LD	<LD
	Min	<LD	<LD	<LD	<LD	<LD	<LD	<LD
	Med	<LD	<LD	<LD	<LD	0.09	<LD	<LD
	SD	-	-	0.19	-	0.14	-	-
ΣDrins	Max	0.21	0.37	0.57	1.24	0.23	0.15	0.05
	Min	<LD	<LD	0.173	<LD	0.0078	<LD	<LD
	Med	0.004	<LD	0.33	0.62	0.12	0.11	0.02
	SD	0.10	0.10	0.13	0.87	0.15	0.08	0.04

[3] <LD = < Limits of Detection

[4] Med = Median values

ΣEndosulfans	Max	0.05	<LD	0.05	0.02	0.02	0.02	0.01
	Min	0.005	<LD	0.0009	0.003	0.009	<LD	0.0008
	Med	0.02	<LD	0.009	0.01	0.01	0.01	0.007
	SD	0.02	-	0.02	0.10	0.006	0.009	0.008
HCB	Max	0.02	1.08	0.02	0.06	<LOD	0.04	0.03
	Min	<LD	<LD	<LD	0.03	<LD	<LD	0.02
	Med	0.01	0.13	<LD	0.05	<LD	0.01	0.02
	SD	0.01	0.27	0.009	-	0	0.02	0.004
Mirex	Max	<LD	0.01	0.11	<LD	<LD	<LD	<LD
	Min	<LD	<LD	<LD	<LD	<LD	<LD	<LD
	Med	<LD	<LD	<LD	<LD	<LD	<LD	<LD
	SD	-	0.003	0.04	-	-	-	-
Methoxychlor	Max	0.67	<LD	0.47	0.05	0.74	<LD	<LD
	Min	<LD	<LD	<LD	<LD	<LD	<LD	<LD
	Med	0.07	<LD	<LD	0.03	0.37	<LD	<LD
	SD	0.32	-	0.18	0.04	0.52	-	-
Octachlorostyrene	Max	<LD	<LD	0.04	0.11	<LD	0.03	<LD
	Min	<LD	<LD	<LD	<LD	<LD	<LD	<LD
	Med	<LD	<LD	<LD	0.0536	<LD	<LD	<LD
	SD	-	-	0.17	0.07	-	0.02	-

Table 18 Output of the models relating concentration of OHCs with spatial variables in sediment removing Airport samples. Independent variables were standardized for a more straightforward interpretation. None of the random values were significant and thus were excluded from the final models. Results are from best AIC model. Spatial autocorrelation was significant and was added to the model structure. R2 is given with lower and upper 95% confidence limits in brackets. Significance codes: ***p<0.001; **p<0.01; *p<0.05; +p<0.1

	Independent variable	Value	SE	df	*t* value	R2 *partial*
PCBs	Altitude	0.25**	0.11	23	2.29	0.106 (0.379-0.001)
	Year	-0.669**	0.187	23	-3.57	0.23 (0.509-0.028)
DDTs	Longitude	0.145**	0.053	46	2.738	0.14 (0.334-0.016)
	Altitude	-0.145*	0.065	46	-2.232	0.11 (0.299-0.007)
PBDEs	Longitude	-0.288**	0.075	92	-4.04	0.08 (0.183-0.015)
	Year	-0.209**	0.074	92	-2.99	0.06 (0.16-0.008)

Table 19 Output of the models showing a relationship between the sum of concentrations of OHCs in sediments with spatial variables. Independent variables were standardized for a more straightforward interpretation. Congeners were added as random effects in the model. Drins were not significant for any variable so not included in the table. None of the random slopes and intercept terms in the models were significant and thus they were excluded from the final structure. Results are from best AIC. R2 is given with lower and upper 95% confidence limits in brackets. Significance codes: *** p<0.001; **p<0.01; *p<0.05

	Independent variable	**Value**	**SE**	**df**	***t* value**	**R2** $_{partial}$
PCBs	Population	0.291*	0.086	98	3.364	0.093 (0.214-0.016)
	Year	-0.493**	0.155	98	-3.183	0.097 (0.221-0.019)
	Airport	-0.471***	0.129	98	-3.628	0.132 (0.262-0.038)
DDTs	Longitude	0.155**	0.052	65	3.003	0.102 (0.256-0.011)
	Altitude	-0.135*	0.057	65	-2.357	0.073 (0.218-0.003)
HCHs	Population	-0.276***	0.0199	3	-13.871	0.397 (0.804-0.020)
	Altitude	-0.785*	0.235	3	-3.334	0.307 (0.763-0.004)
	Airport	0.156**	0.0122	3	12.846	0.236 (0.724-0.002)
PBDEs	Longitude	-0.064*	0.030	121	-2.083	0.022 (0.094-0)
HCB	Airport	0.296***	0.067	18	4.396	0.112 (0.426-0.001)

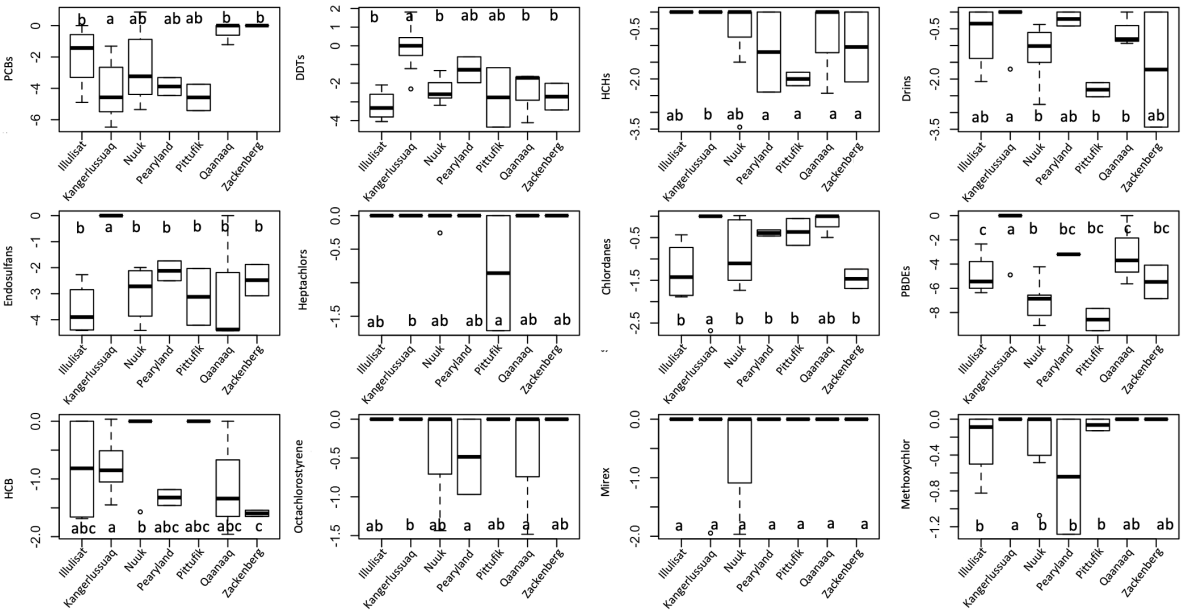

Figure 12 Variability of OHCs concentrations (ng/g dry weight) in Greenland based on the areas where the samples were taken. Boxplots represent the logarithm of the concentration of each family of compounds. Small letters refer to significant differences in concentration among areas (Pairwise Wilcox test, $p<0.05$). Different letters indicate significant differences.

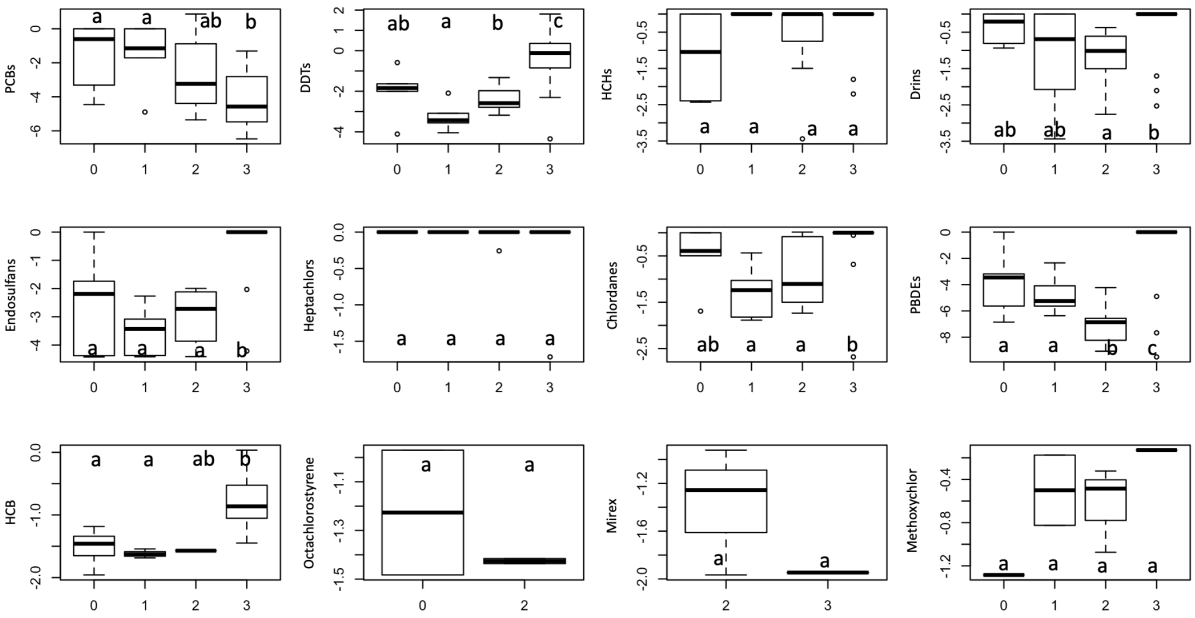

Figure 13 Variability of OHCs concentrations (ng/g dry weight) in Greenland based on the airport presence (0 indicates no airport and 3 indicates the biggest possible airport/airbase located in the study area). Boxplots represent the logarithm of the concentration of each family of compounds. Small letters refer to significant differences among airport levels (Pairwise Wilcox test, $p<0.05$). Different letters indicate significant differences. Airport was scaled from 0-3 depending on the size and use of the airport; 0 being no airport present, 1- airport with one runway (< 900 m) and small number of passengers, 2- airport with runway (> 900 m) and higher number of passengers than 1, 3- with the biggest airport (longer runways, > 2500 m) and highest number of passengers.

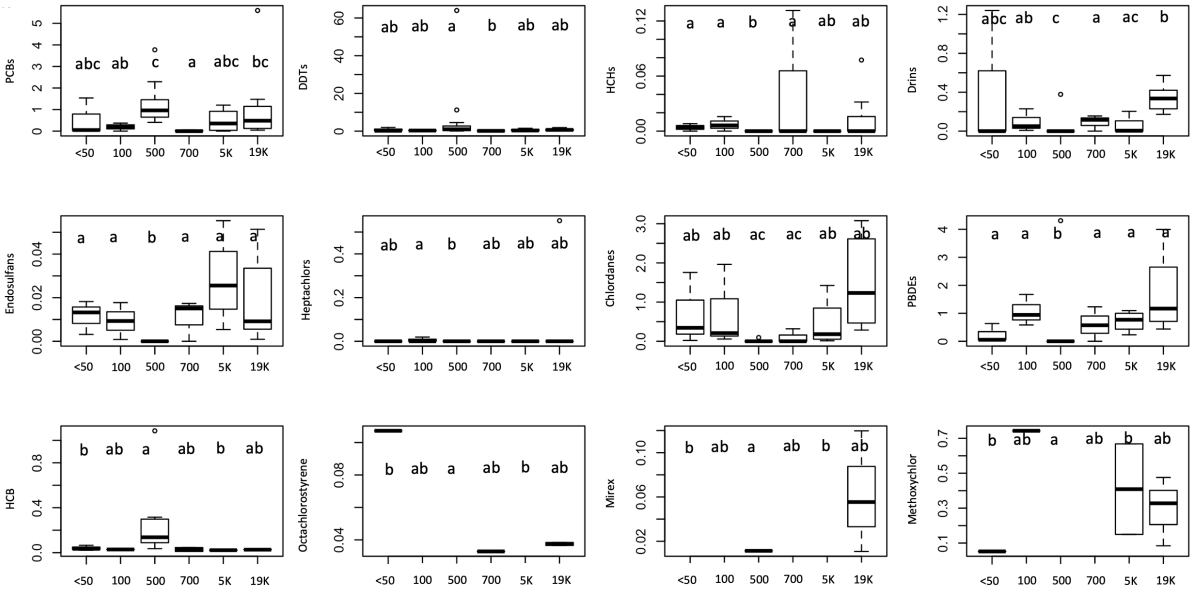

Figure 14 Variability of OHCs concentrations (ng/g dry weight) in Greenland based on the population presence. Boxplots represent the logarithm of the concentration of each family of compounds. Small letters refer to significant differences among population levels (Pairwise Wilcox test, $p<0.05$). Different letters indicate significant differences.

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Table 20 Adjusted R-Squared (Adj R^2) and *p-value* from the multilevel linear regression models (MLMs) relating concentration of PCBs (PCB28, 52, 101, 118, 153, 138 and 180 congeners) in Arctic charr (dependent variable) with fish length (independent variable). Fish median concentrations and length per lake were transformed to control heteroscedasticity. Spatial autocorrelation structure was significant (p-value < 0.05) and added to the model. Adj R^2 is the measure of goodness of fit of the linear regression model.

Lake	*p-value*	Adj R^2
BADESO	p>0.05	0.65
LANGESO	p>0.05	-0.21
DNB5	p>0.05	-0.37
GN10	p>0.05	-0.34
GN09	p>0.05	-0.35
I21	p>0.05	0.15
I22	p>0.05	-0.44
I23	p>0.05	0.93
I27	p>0.05	-0.46
NSO1	p>0.05	0.88
NSO11	p>0.05	-0.24
P1	p>0.05	-0.38
P5	p>0.05	-0.19
P9	p>0.05	-0.49
Q3	p>0.05	0.64
Q4	p>0.05	0.62
Q5	p>0.05	-0.23
SO1	p>0.05	0.68
SO2	p>0.05	-0.29
SO5	p>0.05	0.50
SO8	p>0.05	-0.32
SS52	p>0.05	-0.99
ZAC25	p>0.05	0.02
ZAC26	p>0.05	0.07
ZAC32	p>0.05	0.79

Table 21 Adjusted R-Squared (Adj R^2) and p-value from the multilevel linear regression models (MLMs) relating concentration of DDTs (DDDs, DDEs and DDTs metabolites) in Arctic charr (dependent variable) with fish length (independent variable). Fish median concentrations and length per lake were transformed to control heteroscedasticity. Spatial autocorrelation structure was significant (p-value < 0.05) and added to the model. Adj R^2 is the measure of goodness of fit of the linear regression model.

Lake	*p-value*	Adj R^2
BADESO	p<0.05	0.69
LANGESO	p>0.05	-0.26
DNB5	p>0.05	-0.13
GN10	p>0.05	-0.58
GN09	p>0.05	0.90
I21	p>0.05	-0.75
I22	p>0.05	-0.49
I23	p>0.05	0.45
I27	p>0.05	-0.74
NSO1	p>0.05	0.91
NSO11	p>0.05	-0.49
P1	p>0.05	-0.46
P5	p>0.05	-0.37
P9	p>0.05	0.024
Q3	p>0.05	-0.24
Q4	p>0.05	-0.46
Q5	p>0.05	-0.78
SO1	p>0.05	0.72
SO2	p>0.05	-0.33
SO5	p<0.01	0.97
SO8	p>0.05	0.64
SS52	p>0.05	-0.99
ZAC25	p>0.05	-0.88
ZAC26	p>0.05	-0.41
ZAC32	p>0.05	0.83

Table 22 Adjusted R-Squared (Adj R^2) and p-value from the multilevel linear regression models (MLMs) relating concentration of PBDEs (BDE17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183 and 190 congeners) in Arctic charr (dependent variable) with fish length (independent variable). Fish median concentrations and length per lake were transformed to control heteroscedasticity. Spatial autocorrelation structure was significant (p-value < 0.05) and added to the model. Adj R^2 is the measure of goodness of fit of the linear regression model. – indicates that R^2 was not calculable/did not exist for the lake.

Lake	*p-value*	Adj R^2
BADESO	p>0.05	-0.33
LANGESO	p>0.05	-0.29
DNB5	p>0.05	0.65
GN10	p>0.05	-0.37
GN09	p>0.05	0.88
I21	p>0.05	0.72
I22	p>0.05	-0.26
I23	p>0.05	-0.31
I27	p>0.05	-0.99
NSO1	p>0.05	-0.90
NSO11	p>0.05	–
P1	p>0.05	-0.07
P5	p>0.05	0.36
P9	p>0.05	0.05
Q3	p>0.05	-0.12
Q4	p>0.05	0.13
Q5	p>0.05	–
SO1	p<0.0001	0.98
SO2	p>0.05	-0.24
SO5	p<0.01	-0.14
SO8	p>0.05	-0.33
SS52	p>0.05	-0.99
ZAC25	p>0.05	0.12
ZAC26	p>0.05	0.37
ZAC32	p>0.05	0.61

Table 23 Correlation table for all environmental variables considered to be included in the models. Temp: Mean Annual Air Temperature, Chl-a: Chlorophyl-a, TN: Total Nitrogen, TP: Total Phosphorus, Lat: Latitude, Long: Longitude

Independent variables	Temp	Airport	Chl-a	Cond.	EVI	TN	TP	Population	Year	Fish Length	Lat	Long
Temp	1	0.43	0.55	-0.52	0.31	0.38	-0.12	0.87	0.22	-0.24	-0.97	-0.15
Airport	0.43	1	0.13	-0.18	0.53	-0.26	-0.28	0.38	-0.34	-0.44	-0.49	-0.36
Chl-a	0.55	0.12	1	-0.32	-0.04	0.32	-0.29	0.47	0.19	-0.008	-0.45	-0.21
Conductivity	-0.52	-0.18	-0.33	1	0.17	-0.12	-0.12	-0.27	0.04	0.35	0.44	0.03
EVI	0.31	0.53	-0.04	0.17	1	-0.06	-0.55	0.38	-0.45	-0.31	-0.47	0.44
TN	0.38	-0.26	0.32	-0.12	-0.06	1	0.06	0.35	0.39	0.27	0.3	0.04
TP	-0.12	-0.28	-0.29	-0.12	-0.55	0.06	1	-0.15	0.32	-0.17	0.19	-0.28
Population	0.87	0.38	0.48	-0.27	0.38	0.35	-0.15	1	0.33	-0.06	-0.86	-0.13
Year	0.22	-0.34	0.19	0.04	-0.45	0.32	0.39	0.33	1	0.35	-0.19	-0.51
Fish Length	-0.24	-0.44	-0.008	0.35	-0.31	0.27	-0.17	-0.06	0.35	1	0.28	0.001
Lat	-0.97	-0.49	-0.45	0.44	-0.47	-0.3	0.19	-0.86	-0.19	0.28	1	0.08
Long	-0.15	-0.36	-0.21	0.03	0.44	0.04	-0.28	-0.13	-0.51	0.001	0.08	1

Table 24 Correlation table for all the Layman Metrics. Total area representing convex hull area encompassed by all species in $d^{13}C–d^{15}N$ bi-plot space (TA), $\delta^{13}C$ range (CR), $\delta^{15}N$ range (NR), mean distance to centroid (CD), mean nearest neighbour distance (NND), standard deviation of nearest neighbour distance (SDNND), standard ellipse area, (SEA), and standard ellipse area corrected by sample size (SEAs).

Layman Metrics	TA	CR	NR	CD	NND	SDNND	SEA	SEAs	Lake Area	Lake Depth
TA	1	0.845	0.789	0.809	-0.107	0.280	0.743	0.694	0.3	0.31
CR	0.845	1	0.516	0.839	0.007	0.288	0.677	0.638	0.15	0.46
NR	0.788	0.516	1	0.653	0.070	0.455	0.711	0.690	0.08	-0.1
CD	0.809	0.839	0.653	1	0.314	0.458	0.942	0.926	0.03	0.23
NND	-0.107	0.006	0.070	0.314	1	0.715	0.383	0.447	-0.43	-0.2
SDNND	0.280	0.288	0.455	0.458	0.715	1	0.552	0.585	-0.45	-0.11
SEA	0.743	0.677	0.711	0.942	0.383	0.552	1	0.996	-0.03	0.04
SEAs	0.694	0.638	0.690	0.942	0.447	0.585	0.996	1	-0.08	0.0006
Lake Area	0.30	0.15	0.08	0.03	-0.43	-0.45	-0.03	-0.08	1	0.58
Lake Depth	0.31	0.46	-0.1	0.23	-0.2	-0.11	0.04	0.0006	0.58	1

Table 25 Statistical parameters of the concentrations of the organohalogen compounds (in ng/g wet weight) found in the studied lakes Arctic charr per lake in Greenland. PCBs (sum of PCB28, 52, 101, 118, 153, 138 and 180 congeners), DDTs (sum DDDs, DDEs and DDTs metabolites) and PBDEs sum of (BDE17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183 and 190 congeners). Min: minimum; Max: maximum; SD: standard deviation; <dl: concentration below the limit of detection.

PCBs					
Lake	**Mean**	**Median**	**Min**	**Max**	**SD**
DNB5	16.92	11.46	0.32	44.4	20.6
GN10	9.29	0.32	0.07	27.5	15.75
GN9	2.91	3.13	1.56	4.04	1.25
I21	3.73	1.38	1.08	8.74	4.34
I22	1.7	1.57	<dl	3.67	1.98
I23	3.01	1.98	1.23	5.82	2.46
I27	0.59	0.31	0.26	1.21	0.53
LANGESO	1.74	0.39	0.1	6.07	2.89
NSO1	1.11	0.12	<dl	3.22	1.83
NSO11	0.12	0.1	<dl	0.28	0.14
P1	33.75	33.33	24.82	43.5	7.75
P5	48.03	51.04	24.22	65.8	17.8
P9	33.6	33.6	22.29	44.9	9.49
Q3	0.91	0.5	<dl	2.61	1.04
Q4	0.3	0.29	0.11	0.51	0.2
Q5	0.28	0.22	0.03	0.58	0.28
SO1	1.74	0.22	0.07	8.05	3.53
SO2	5.18	0.93	<dl	22.8	9.91
SO5	4.83	2.79	<dl	13.7	6.1
SO8	2.09	0.3	0.12	7.24	3.04
SS52	8.33	3.34	<dl	24.9	14.4
ZAC25	4.05	4.35	1.52	6.27	2.39
ZAC26	13.71	13.82	6.33	20.8	6.08
ZAC32	1.31	0.2	0.08	3.64	2.03
DDDs					
Lake	**Mean**	**Median**	**Min**	**Max**	**SD**
DNB5	7.13	6.34	0.06	15.8	7.44
GN10	3.78	1.08	0.02	10.3	5.63
GN9	0.38	0.23	<dl	0.92	0.48
I21	0.87	0.7	<dl	1.92	0.97
I22	0.35	0.35	<dl	<dl	<dl
I23	0.97	0.35	<dl	2.92	1.68
I27	0.03	0.03	<dl	0.06	0.03
LANGESO	0.46	0.04	<dl	1.77	0.87
NSO1	0.02	0.35	<dl	0.07	0.04
NSO11	0.05	0.05	<dl	0.09	0.04

P1	1.47	1.82	<dl	2.23	1.02
P5	3.49	3.64	1.52	5.16	1.66
P9	3.11	3.68	0	5.08	2.25
Q3	0.26	0.35	<dl	1.27	0.57
Q4	0.01	0.35	<dl	0.03	0.02
Q5	0.02	0.35	<dl	0.05	0.03
SO1	0.53	0.35	<dl	1.54	0.74
SO2	3.95	1.92	<dl	14.9	6.19
SO5	2.14	1.37	<dl	5.8	2.76
SO8	2.85	1.58	1.07	6.22	2.29
SS52	3.84	0.35	<dl	11.5	6.64
ZAC25	0.7	1.02	<dl	1.09	0.61
ZAC26	1.43	1.28	<dl	3.16	1.36
ZAC32	0.22	0.04	0.01	0.6	0.33

DDEs

Lake	**Mean**	**Median**	**Min**	**Max**	**SD**
DNB5	3.33	1.5	<dl	10.3	4.86
GN10	1.07	0.62	<dl	3.22	1.86
GN9	0.62	0.62	<dl	<dl	<dl
I21	0.62	0.62	<dl	<dl	<dl
I22	0.62	0.62	<dl	<dl	<dl
I23	0.62	0.62	<dl	<dl	<dl
I27	0.62	0.62	<dl	<dl	<dl
LANGESO	0.65	0.62	<dl	2.59	1.29
NSO1	0.62	0.62	<dl	<dl	<dl
NSO11	0.62	0.62	<dl	<dl	<dl
P1	1.54	1.35	<dl	3.46	1.43
P5	8.15	7.39	2.91	14.9	5.87
P9	3.1	3.95	<dl	4.5	2.09
Q3	0.37	0.62	<dl	1.28	0.57
Q4	0.62	0.62	<dl	<dl	<dl
Q5	0.62	0.62	<dl	<dl	<dl
SO1	0.25	0.62	<dl	1.23	0.55
SO2	0.62	0.62	<dl	<dl	<dl
SO5	0.62	0.62	<dl	<dl	<dl
SO8	1.4	0.62	<dl	7.01	3.14
SS52	1.48	0.62	<dl	4.43	2.56
ZAC25	1.64	1.69	<dl	3.22	1.61
ZAC26	4.47	4.57	1.88	6.87	2.06
ZAC32	0.62	0.62	<dl	<dl	<dl

DDTs

Lake	**Mean**	**Median**	**Min**	**Max**	**SD**
DNB5	3.73	0.46	0.27	13.75	6.68
GN10	0.87	0.42	<dl	2.19	1.17

GN9	0.45	0.35	<dl	0.99	0.5
I21	1.09	1.26	<dl	2	1.01
I22	0.76	0.97	<dl	1.12	0.52
I23	0.44	0.29	<dl	1.04	0.54
I27	0.24	0.33	<dl	0.4	0.21
LANGESO	0.24	0.21	<dl	0.95	0.48
NSO1	0.31	0.21	<dl	0.92	0.53
NSO11	0.21	0.21	<dl	<dl	<dl
P1	1.2	0.56	<dl	3.69	1.69
P5	5.75	4.24	1.43	13.1	5.2
P9	2.72	2.23	<dl	6.41	3.24
Q3	0.27	0.21	<dl	0.96	0.42
Q4	0.21	0.21	<dl	<dl	<dl
Q5	0.1	0.21	<dl	0.3	0.17
SO1	0.17	0.21	<dl	0.55	0.25
SO2	0.12	0.21	<dl	0.6	0.27
SO5	0.5	0.44	<dl	1.13	0.47
SO8	0.79	0.23	<dl	2.29	0.97
SS52	2.36	0.21	<dl	7.08	4.09
ZAC25	0.39	0.49	<dl	0.68	0.35
ZAC26	0.82	0.77	0.34	1.37	0.46
ZAC32	0.57	0.31	<dl	1.4	0.73

BDE209

Lake	**Mean**	**Median**	**Min**	**Max**	**SD**
DNB5	0.26	0.2	<dl	0.64	0.31
GN10	0.14	0.15	<dl	0.43	0.25
GN9	0.19	0.15	<dl	0.57	0.33
I21	2.11	1.32	0.32	4.7	2.3
I22	0.76	0.64	<dl	1.75	0.76
I23	1.54	1.42	0.58	2.62	1.02
I27	<dl	0.15	<dl	<dl	<dl
LANGESO	0.36	0.3	<dl	0.84	0.43
NSO1	<dl	0.15	<dl	<dl	<dl
NSO11	<dl	0.15	<dl	<dl	<dl
P1	0.13	0.15	<dl	0.52	0.26
P5	0.13	0.15	<dl	0.53	0.27
P9	1.21	1.1	<dl	2.66	1.27
Q3	0.93	0.15	<dl	3.13	1.4
Q4	<dl	0.15	<dl	<dl	<dl
Q5	<dl	0.15	<dl	<dl	<dl
SO1	0.27	0.15	<dl	0.94	0.41
SO2	0.13	0.15	<dl	0.34	0.18
SO5	0.59	0.45	<dl	1.47	0.62
SO8	0.42	0.15	<dl	1.08	0.57

SS52	0.87	0.15	<dl	2.6	1.5
ZAC25	0.58	0.7	<dl	1.04	0.53
ZAC26	1.26	0.32	<dl	4.39	2.11
ZAC32	0.28	0.15	<dl	0.85	0.49
		PBDEs			
Lake	**Mean**	**Median**	**Min**	**Max**	**SD**
DNB5	1.25	0.99	0.49	2.54	0.93
GN10	<dl	1.5	<dl	<dl	<dl
GN9	0.01	1.5	<dl	0.03	0.02
I21	3.13	2.03	1.93	5.44	2
I22	3.1	2.08	<dl	8.25	3.62
I23	3.52	3.62	1.64	5.3	1.83
I27	0.21	1.5	<dl	0.64	0.37
LANGESO	0.05	1.5	<dl	0.17	0.08
NSO1	0.07	1.5	<dl	0.22	0.13
NSO11	<dl	1.5	<dl	<dl	<dl
P1	2.84	2.86	2.21	3.42	0.51
P5	5.33	3.08	<dl	15.2	6.77
P9	4.44	3.75	0.88	9.39	3.64
Q3	0.46	1.5	<dl	2.28	1.02
Q4	1.5	1.5	<dl	<dl	<dl
Q5	1.5	1.5	<dl	<dl	<dl
SO1	0.21	0.29	<dl	0.41	0.19
SO2	0.01	1.5	<dl	0.05	0.02
SO5	0.51	0.34	<dl	1.35	0.65
SO8	0.42	1.5	<dl	1.73	0.75
SS52	6.1	1.5	<dl	18.3	10.6
ZAC25	0.16	0.11	<dl	0.37	0.19
ZAC26	6.86	7.48	0.58	11.9	5.02
ZAC32	1.64	1.95	<dl	2.97	1.51

Table 26 Lake-wise biological parameters of length and weight for Arctic charr. The table also include lake altitude, lake depth (m) and lake area (m^2) as well as presence/absence data about three-spined stickleback occurring in the lake along with Arctic charr.

Lakes	Region	Median Fish Length (cm)	Median Fish Weight (gm)	Presence of Stickleback in the lake[5]	Altitude	Lake Depth (m)	Lake Area (m^2)
BADESO	Nuuk	17.7	45	1	54	34	72.45
DNB5	Zackenberg	14.5	33	0	84	3	26
GN10	Nuuk	20	77	1	120	10.5	10
GN09	Nuuk	15.6	38.5	1	177	9.5	15.6
I21	Ilullisat	16.4	40.9	0	297	29.4	24
I22	Ilullisat	18.3	51.1	0	293	20.4	13.8
I23	Ilullisat	11.5	16.5	0	283	49.7	28.7
I27	Ilullisat	19.4	81.4	0	291	5.3	0.8
LANGESO	Nuuk	17.5	47.5	1	80	13	29.72
NSO1	Pearyland	30.5	328	0	102	0.7	2.47
NSO11	Pearyland	19.75	87.5	0	192	8	19.48
P1	Pittufik	16.25	36.5	0	252	2.4	26.31
P5	Pittufik	13.75	22	1	184	1.5	4.67
P9	Pittufik	11.75	13.5	0	131	2.4	6.74
Q3	Qaanaaq	13.5	23	0	16	10.7	1.65
Q4	Qaanaaq	32	342	1	47	11.2	0.46
Q5	Qaanaaq	20	71	0	43	17.2	41.9
SO1	Nuuk	15.5	46	1	12	12.6	4.7
SO2	Nuuk	17.9	46	1	44	3.6	3.2
SO5	Nuuk	16.25	26.5	1	27	8.9	2.2
SO8	Nuuk	16.9	31	1	70	13.4	25
SS52	Kangerlussuaq	15	24	1	285	3.3	14.5
ZAC25	Zackenberg	19	44	1	270	4.2	5.9
ZAC26	Zackenberg	14.5	19	1	300	2.5	4
ZAC32	Zackenberg	13	18	1	282	12	28.5

[5] Presence of stickleback in the lake. 1 indicates that the stickleback fish is present in the lake and 0 indicates that the stickleback fish is not present in that particular lake

Table 27 Output of the best multilevel linear regression models (MLMs) relating fish length (dependent variable) with environmental variables (independent variables. Environmental variables were transformed when needed to control for normality and heteroscedasticity. Spatial autocorrelation structure was significant (p-value < 0.05) and added to the model. Significance of environmental variables for determining fixed and random effects in the best multilevel model: *** p-value<0.001; ** p-value< 0.01; * p-value<0.05. SE (standard error), df (degrees of freedom).

Dependent variable	Independent variable	Slope	SE	df	*t* value	Random effects coefficient
Fish length	Temperature	-0.067	0.073	167	-0.886	-
Fish length	Total Nitrogen	0.478***	0.069	167	6.964	-
Fish length	Airport	-0.358***	0.07	167	-5.085	

Table 28 Output of the linear regression models (MLMs) relating δ15N range (NR) and standard ellipse area corrected by sample size (SEAs) (dependent variables) versus the presence/absence of three-spined stickleback in the lake (independent variable). Spatial autocorrelation structure was significant (p-value < 0.05) and added to the model. Significance of environmental variables for determining fixed in the best multilevel model: *** p-value<0.001; ** p-value< 0.01; * p-value<0.05*; - means random effects not significant. δ15N range (NR), mean nearest neighbour distance (NND), mean distance to centroid (CD), standard ellipse area (SEA), and standard ellipse area corrected by sample size (SEAs).

Layman Metrics	Variable	Value	SE	df	*t* value	Random effects coefficient
SEA/s	Stickleback	0.787 ***	0.155	125	5.057	-
NR	Stickleback	0.4893 ***	0.071	125	6.814	-

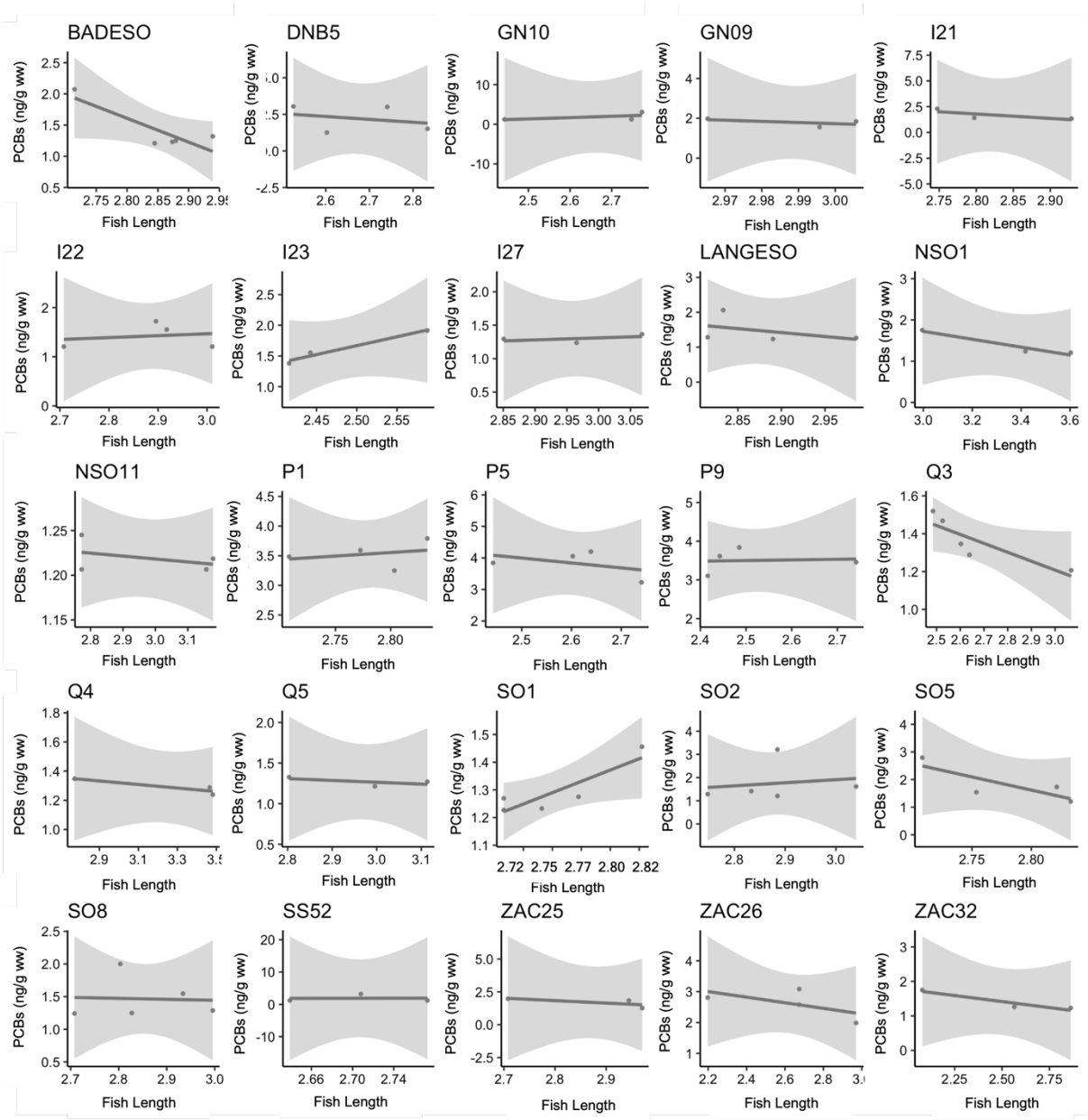

Figure 15 Linear relationship plot between normalised sum of PCBs (28 + 52 + 101 + 118 + 153 + 138 + 180 congeners) concentration in Arctic charr from Greenland versus log-normalised fish length (cm) (model outputs are shown in Table SI-1). The lines depict the least-squares regression lines and the grey area depicts the 95% confidence interval.

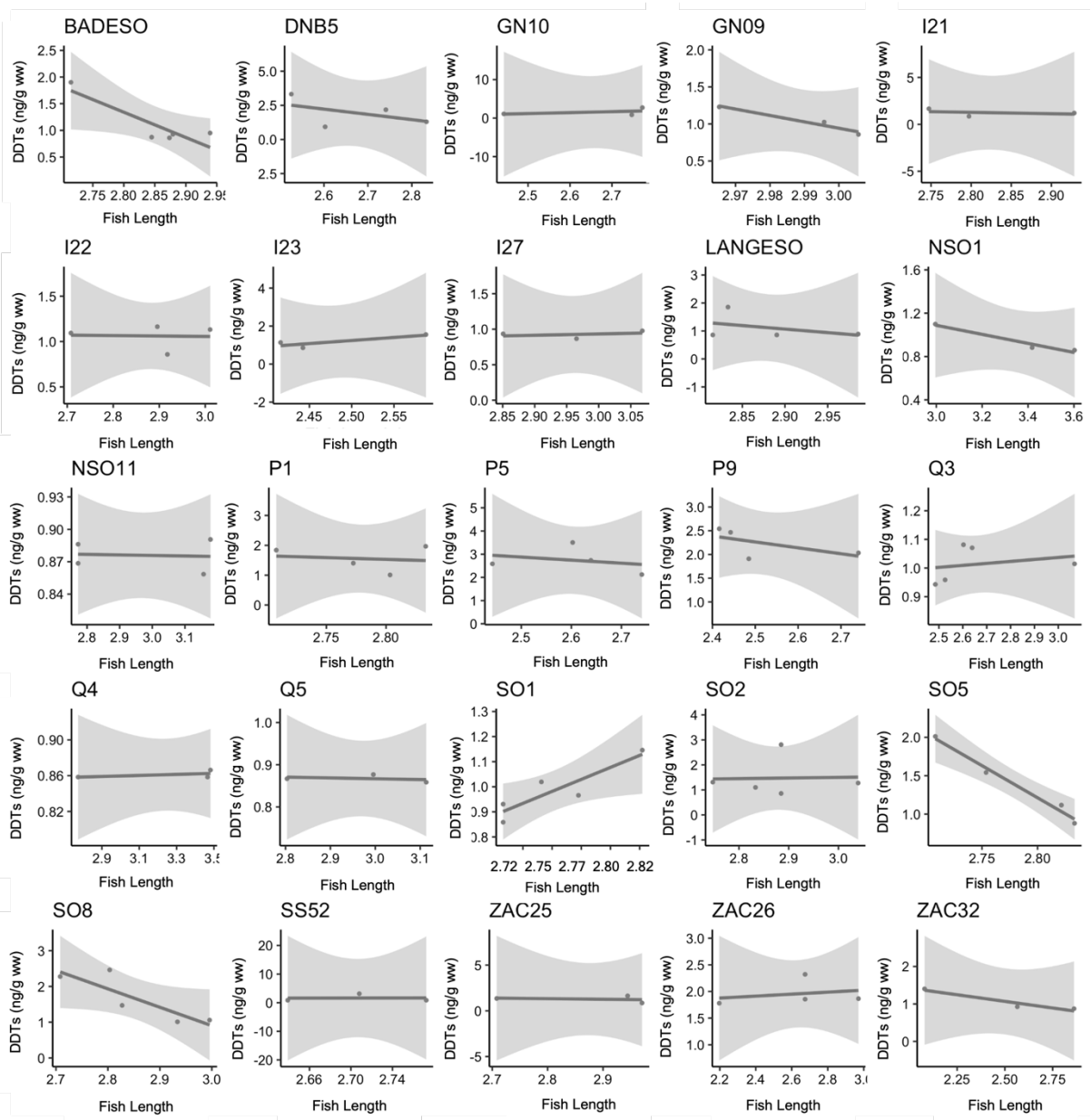

Figure 16 Linear relationship plot between normalised sum of DDTs (DDDs, DDEs and DDTs metabolites) concentration in Arctic charr from Greenland versus log-normalised fish length (cm) (model outputs are shown in Table SI-2). The lines depict the least-squares regression lines and the grey area depicts the 95% confidence interval.

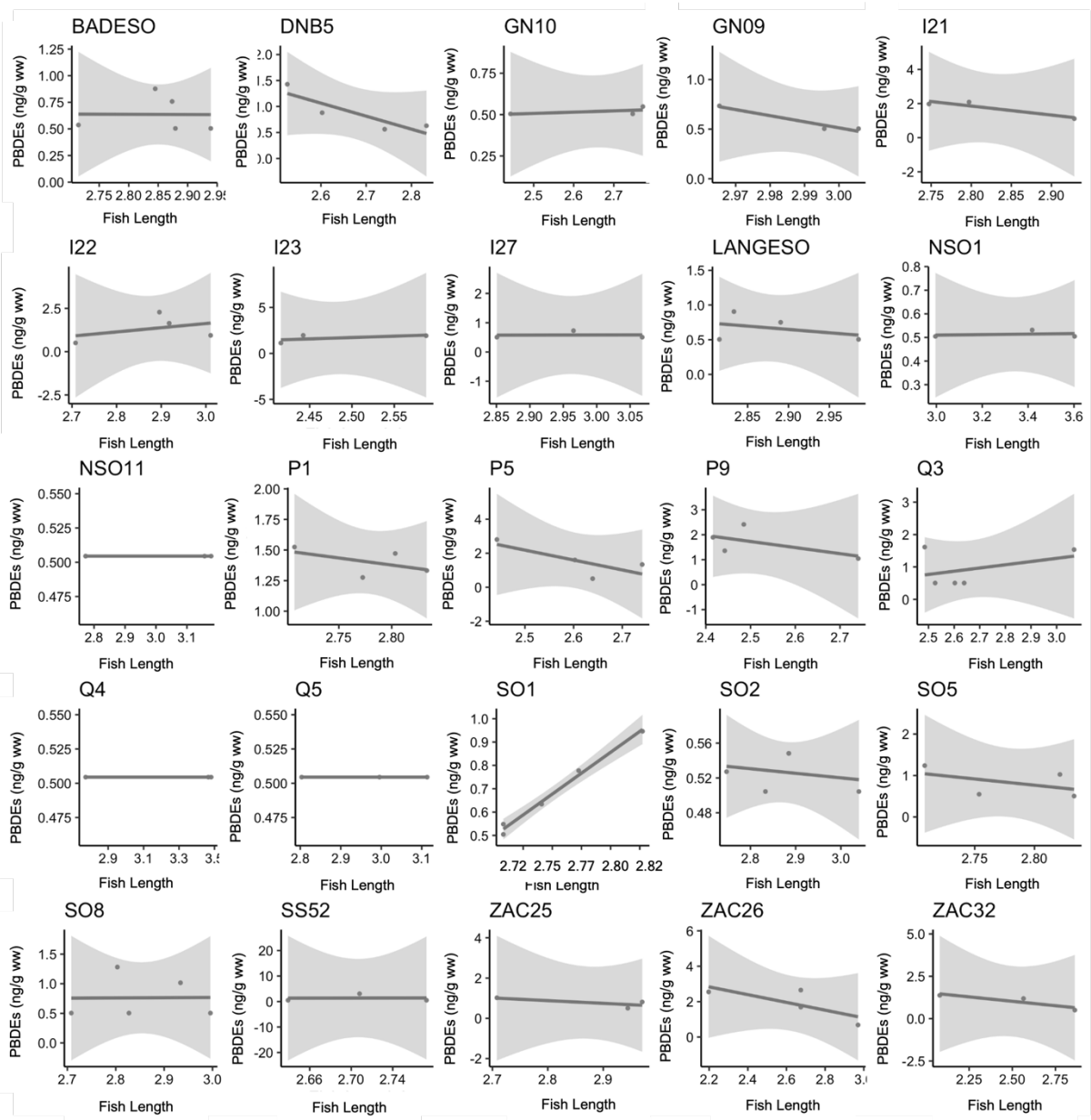

Figure 17 Linear relationship plot between normalised sum of PBDEs (BDE17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183 and 190 congeners) concentration in Arctic charr from Greenland versus log-normalised fish length (cm) (model outputs are shown in Table SI-3). The lines depict the least-squares regression lines and the grey area depicts the 95% confidence interval.

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Seabird-mediated transport of organohalogen compounds to remote sites (North West Greenland polynya)

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HIGHLIGHTS

- The lake with bird droppings was acidic (pH = 3.4), the others close to neutral (pH = 8).
- Seabirds efficiently transport organohalogen compounds to Arctic sites.
- The bird-mediated deposition preserves the less stable and more volatile compounds.
- Organohalogen deposition was highest in the upper sediments of the polynya lake.
- Birds are introducing important organohalogen amounts in Arctic sites, except DDTs.

GRAPHICAL ABSTRACT

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ABSTRACT

The role of sea birds as carriers of pollutants over long distances was evaluated by analyzing organochlorine and organobromine compounds in lake sediment cores from three remote sites around the North Water polynya (North West Greenland). One lake, NOW5, was in the vicinity of a little auk (*Alle alle* L.) bird colony, whereas the other two lakes, NOW14 and Q5, were undisturbed by seabirds. The former was strongly acidic (pH = 3.4) but the latter had a pH close to 8. Due to the guano loading, NOW5 exhibited higher chlorophyll concentrations (74 μg/L) than the other two lakes (1.6–3.4 μg/L), higher content of total phosphorous (0.34 mg/L vs. 0.007–0.01 mg/L) and total nitrogen (3.75 mg/L vs. 0.21–0.75 mg/L).

The concentrations of all organohalogen compounds were substantially greater in NOW5 than in the other lakes, indicating the strong influence of these seabirds in the transport and deposition of these compounds to remote sites. However, not all compounds showed the same increases. Hexachlorocyclohexanes and endosulfans were more than 18 times higher in NOW5, the drin pesticides and hexachlorobenzene (HCB), between 9.5 and 18 times and DDTs, polybromodiphenyl ethers (PBDEs), polychlorobiphenyls (PCBs) and chlordanes about 2.7–6 times. These differences demonstrated that the bird-mediated deposition has preservation effects of the less stable and more volatile compounds, e.g. those with log Kaw < −2.4, log Koa < 9 and/or log Kow < 6.8.

The sedimentary fluxes of PCBs, HCHs, drins, chlordanes, PBDEs, HCB and endosulfans were highest in the upper sediment layer of the polynya lake (year 2014). In contrast, the highest DDT fluxes were found in 1980. These trends

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indicate that despite restrictions and regulations, bird transport continues to introduce considerable amounts of organohalogen pollutants to the Arctic regions with the exception of DDTs, which show successful decline, even when mediated by bird metabolism.

1. Introduction

Organic molecules with high degrees of halogen substitution, e.g. organochlorine and organobromine compounds, were produced and used due to their high chemical stability, fire and thermal resistance, and, in some cases, pesticide activity. Unfortunately, these properties caused environmental pollution problems and human health deleterious effects. First, their high stability to environmental degradation and semi-volatility boosted their spread over long distances through the atmosphere. Second, their hydrophopic properties favoured their accumulation in flora and fauna, which led to biomagnification along the aquatic and continental trophic chains.

A substantial number of compounds with these properties have been phased out of use and production. Most organochlorine compounds such as polychlorobiphenyls (PCBs), aldrin, dieldrin, endrin, heptachlor, and other legacy pollutants listed in the Stockholm Convention's "dirty dozen" (Korosi et al., 2017) have been banned worldwide in the last decades. For instance, among the banned compounds, aldrin, dieldrin and endrin were used as insecticides from the 1950s to the early 1970s (Blais and Muir, 2005). Aldrin is readily metabolised to dieldrin in plants and animals which is more resistant to biodegradation making it more toxic (Vorkamp et al., 2004). Giving another example, among hexachlorocyclohexanes (HCHs), γ-HCH was widely used around the globe but the overall usage significantly decreased in the 1980s and 1990s (Hung et al., 2010) despite the fact that it is still in use in some countries. Endosulfan and methoxychlor belong to a new group of less persistent chlorinated pesticides and are still used in Europe, USA and, most likely, in other world areas.

Despite of these restrictions, many of these compounds called persistent organic pollutants (POPs) are still known to linger in the various environmental compartments from close and distant sites of human activity, reaching the most remote places of the planet, such as high mountains (Grimalt et al., 2001, 2004a; Grimalt et al., 2004b) and Arctic areas, where they were never produced or used (Ma et al., 2011, 2016; Rigét et al., 2010b). In the absence of significant local anthropogenic inputs, the regional and global distributions of these compounds is increasingly reflecting phase partitioning between the environmental reservoirs such as air, water, soil, vegetation and ice, where POPs get accumulated. In general, the concentrations of phased-out or heavily restricted contaminants like PCBs, DDTs, hexachlorobenzene (HCB), chlordanes, dieldrin and their metabolites are now stabilizing or decreasing (Muir and de Wit, 2010). In contrast, many brominated flame retardants, for example, the polybromodiphenyl ethers (PBDEs), which have the same bioaccumulative properties such as PCBs, are still in production and use and their concentrations are in fact, increasing in the Arctic (de Wit et al., 2010).

Knowledge on contamination trends and origins is critical for determining the extent of POP transport and accumulation to the Arctic (Rigét et al., 2020; Rigét et al., 2016; Rigét et al., 2019). In addition to atmospheric transport, some studies indicate that migratory species may also play a critical role in translocating POPs between ecosystems, increasing productivity in otherwise unproductive systems (Blais et al., 2007; Evenset et al., 2004; Michelutti et al., 2009a, 2010). This is especially true for sea birds which feed at sea and come to land to breed, bringing nutrients as well as contaminants into freshwater systems (Blais, 2005; Davidson et al., 2018; Evenset et al., 2007a; González-Bergonzoni et al., 2017; Polis et al., 1997). Many avian species are migratory, travelling thousands of kilometers from breeding sites to wintering grounds, spending majority of their life in both areas (Wang et al., 2019). In recent decades, a number of surveys have indicated large accumulations of various POPs in birds all across the world, suggesting that pollutant levels in these organisms are related to their surrounding environments (Blais et al., 2007; Bustnes et al., 2012; Mehlum and Daelemans, 1995; Roosens et al., 2007; Huertas et al., 2016; Wang et al., 2019). Seabirds may be the most globally relevant bio-vectors since they are keystone species that represent the dominant form of wildlife along coastlines worldwide and form dense nesting colonies that can number in the millions of individuals (Michelutti et al., 2009a).

Local nutrient enrichment from guano has been documented, but the possibility of POP contamination in areas near seabird nesting sites has only been probed by a handful of studies (Blais, 2005; Choy et al., 2010; Evenset et al., 2007a, 2007b; Michelutti et al., 2009a, 2009b). Most of these studies have been conducted at Cape Vera on Devon Island (Nunavut, Canada; 76°15′N, 89°15′W) where a colony of northern fulmars (*Fulmarus glacialis*, L.) was observed to release POPs and metals to the environment through their guano (Blais, 2005; Choy et al., 2010; Michelutti et al., 2009a, 2009b). Another study was conducted in Lake Ellasjøen (Bjørnøya; Barents Sea; 74°30′N, 19°00′E) where colonies of little auk (*Alle alle*), kittiwake (*Rissa tridactyla*, L.) and glaucous gull (*Larus hyperboreus*, Gunnerus) are present (Evenset et al., 2007a, 2007b). These studies have been focussed on the transport of PCBs and DDTs, and, in the case of Lake Ellasjøen, also hexabromocyclododecanes.

In the present study, we are exploring the efficiency of transport of POPs by guano deposits in one Greenland site, at the southern end of the North Water Polynya, Northern Baffin Bay, which lies between Greenland and Canada (Fig. 1). This site allocates the largest polynya in the Arctic which covers around 85,000 km^2 with little auk. Our study focusses not only with the most hydrophobic POPs, e.g. PCBs, and DDTs, but also on more hydrophilic compounds such as aldrin, dieldrin, endrin, heptachlor, HCHs, chlordanes, endosulfans and HCB. PBDEs have also been considered. North Water Polynya (NOW) is one of the most productive marine environments in the Arctic owing to the combination of year-round nutrient rich, open waters and constant light in the summer, making it an ideal study location (González-Bergonzoni et al., 2017; Ribeiro et al., 2021). Three freshwater lakes located along the coast of NOW were selected based on their ecological conditions: one with a large migratory colony of little auk in the catchment (North Water; NOW5), one with no birds and historical human presence (Hunter gatherer Inuit-Thule people) from around 1400 CE (NOW14) and one without any interference from birds or humans (Q5).

Sediment cores were collected in each of these lakes to provide time-trend information on whether increased restrictions in the use of some products at lower latitudes may have resulted in decreasing levels in the Arctic and/or whether banned compounds are still transported to this remote environment due to possible time lags (Malmquist et al., 2003). In this regard, paleolimnological studies in remote sites provide useful information on the fate and transport processes of these pollutants (Fernandez et al., 2000; Korosi et al., 2017). By using lake sediments, past atmospheric deposition rates can indirectly be estimated and compared with current contamination levels. Unfortunately, there is a dearth of information on depositional chronology of concentrations or fluxes of contaminants in freshwater lake sediments from the Arctic compared to the high altitude freshwater lakes (Grimalt et al., 2001; Grimalt et al., 2004a, 2004b). Only a few studies have provided information on concentrations and fluxes of contaminants in freshwater lakes in the European Arctic (Evenset et al., 2007a) and Canadian Arctic (Muir et al., 1995, 1996; Stern et al., 2005), making the present study an important contribution to the available literature.

Here, we seek to understand what has been the transfer of POPs to these reference Arctic freshwater lakes in Greenland at present and in the past, and how the presence of bird colonies may have affected their deposition pattern. Specifically, a chronological comparison of the POPs accumulation

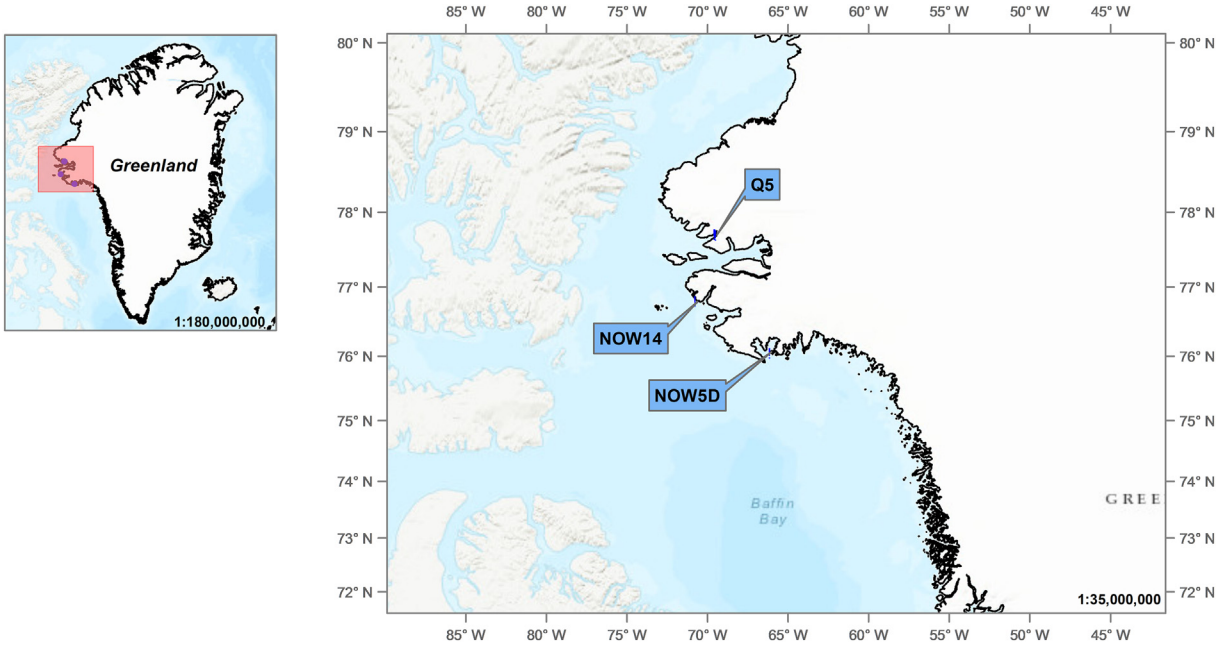

Fig. 1. Maps showing the location of the studied lakes. NOW5 is the lake hosting a polynya.

in sediment cores from the three selected lakes, starting from the industrialisation period to the present, is reported.

2. Materials and methods

2.1. Sampling

Samples were collected from the three freshwater lakes on the coast of NOW polynya in the summers of 2014 (NOW5), 2015 (NOW14), and 2016 (Q5; Fig. 1). Lake coring was carried out using an HTH gravity corer with an internal diameter of 8.5 cm. The cores were sliced and stored frozen until analysis. Further details of sampling and dating of the sediment cores have been described elsewhere (Davidson et al., 2018).

2.2. Chemicals and reagents

Acetone, ethyl acetate, cyclohexane, isooctane and copper (particle size <63 μm) were from Merck (Darmstadt, Germany). The Florisil cartridges (20CC; 5 g) were acquired from Waters (Milford, MA, USA). Standards of 1,2,4,5-tetrabromobenzene (TBB), PCB 209 and the solution mixture of OCs were purchased from Dr. Ehrenstoffer (Augsburg, Germany). Solution mixtures of BDEs, BDE 118 and [3-^{13}C] BDE-209 were acquired from Cambridge Isotope Laboratories (Andover, MA, USA).

2.3. Analytical method

The frozen sediment core slices were freeze-dried overnight. Sediments (0.1–1.0 g) were placed in a glass centrifuge tube (10 mL), spiked with surrogate standards (TBB and PCB 209) and kept in contact overnight. After that period, the samples were extracted with 10 mL ethyl acetate/cyclohexane (5:2, v/v) by vortex mixing for 1 min and ultrasonic stirring (10 min). The extract was centrifuged (10 min; 3000 rpm) and transferred to 40 mL flasks. This procedure was repeated twice. The total extracts were then concentrated to 1 mL by vacuum rotary evaporation. About 200 mg of activated copper was added to the extracts and left overnight to eliminate sulphur. Clean-up was performed using 5 g florisil cartridges after conditioning that were eluted with 20 ml of ethyl acetate/cyclohexane (5:2, v/v). This extract was finally concentrated to 0.5 mL.

Copper was activated by ultrasound stirring in a suspension of hydrochloric acid (25%; v/v) for 15 min. This procedure was followed by several Milli-Q washes for acid elimination until pH 7. Two rinses with acetone removed the water, and lastly, the activated copper was stored in hexane at −20 °C.

2.3.1. Organochlorine compound analysis

Before chromatographic analysis, an internal standard of PCB-142 was added to each sample. The OCs were identified and quantified by gas chromatography (GC; Agilent Technologies 7890 N) coupled to mass spectrometry (MS, Agilent Technologies 5975C) operating in negative chemical ionisation mode (GC-NICI-MS). This instrument was provided with a HP-5MS capillary column (60 m length, 0.25 mm internal diameter, 0.25 μm film thickness; JW Scientific) protected with a retention gap. The injection was performed in splitless mode. Injector and detector temperatures were 280 °C and 325 °C, respectively. The oven temperature was held at 90 °C for 2 min, increased to 130 °C at 15 °C/min and to 310 °C at 4 °C/min with a final holding time of 10 min. Ultrapure helium and ammonia were used as carrier and reagent gasses, respectively.

2.3.2. Polybromodiphenyl ether analysis

Before chromatographic analysis, internal standards of BDE-118 and [3-^{13}C]BDE-209 were added to all the samples. A GC (Agilent Technologies 7890N) coupled to a MS (Agilent Technologies 5975C) operating in negative chemical ionisation mode (GC-NICI-MS) was used for identification and quantification of the PBDE congeners (17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190 and 209). The instrument was equipped with a low bleed fused silica capillary column (15 m length, 0.25 mm ID, 0.10 μm film thicknesses; DB-5MS) protected with a retention gap. The oven temperature was programmed from an initial temperature of 90 °C which was kept for 1.5 min followed by heating to 200 °C at 40 °C/min, a second increase up to 275 °C at 5 °C/min and a third increase to 300 °C at 40 °C/min. This temperature was held for 10 min and then increased to 310 °C at 10 °C/min with a final holding time of 2 min. Ammonia was used as reagent gas. Identification and quantification were performed by injection of PBDEs standard solutions (Vizcaino et al., 2009; Bravo et al., 2017).

2.4. Quality assurance

Three procedural blanks were analysed with each batch of samples. Identification and quantification of OCs and PBDEs were performed by

injection of external standards at different concentrations, and all the samples were blank corrected. Method detection limits were calculated from the average signals of the procedural blank levels plus three times the standard deviation. They ranged between 0 and 0.0020 ng/g for the individual OCs and 0.001 and 0.0030 ng/g for the brominated compounds. The limits of quantification were calculated from the averages of the procedural blanks plus five times the standard deviation. They ranged between 0 and 0.0050 ng/g for the individual OCs and between 0.001 and 0.10 ng/g for PBDEs. One-half of the limits of detection and limits of quantification were assigned to non-detected and non-quantified values, respectively. Pentachlorobenzene was below the LOD in most sediment sections and therefore not included in further analysis.

3. Results and discussion

The lakes had a strong difference in terms of depositional setting. The waters of NOW5 were highly acidic with a pH of 3.4, whereas the pH values of NOW14 and Q5 were close to 8 (Table 1). This difference can be attributed to the influence of *A. ale* guano depositions (Davidson et al., 2018). In Spitzbergen, guano depositions of these birds also resulted in acidic lake water (Zwolicki et al., 2013). These highly acidic values have not been reported in other lakes receiving high amounts of guano depositions from other bird species.

These guano depositions are also responsible for the other observed differences between the lake waters. Thus, NOW5 has higher total phosphorous and nitrogen, 0.34 mg/L and 3.75 mg/L, respectively, than the other two lakes, 0.007–0.01 mg/L and 0.21–0.75 mg/L, respectively. Obviously, these differences led to strong contrasts in lake productivity, e.g. NOW5 show high chlorophyll concentrations (74 μg/L vs. 1.6–3.4 μg/L, respectively).

3.1. Concentrations

The concentrations of all organochlorine and organobromine compounds studied were higher in NOW5 lake than in the other two reference lakes (NOW14 and Q5; Table 2). The median concentrations of DDTs, PBDEs, PCBs, and chlordanes in the NOW5 core, 1.9 ng/g, 1.3 ng/g, 1.2 ng/g, and 0.040 ng/g, respectively, are about 2.7–6 times higher than the medians in NOW14 and Q5 lake cores, 0. 43–0. 64 ng/g, 0.22–0.37 ng/g, 0.26–0.44 ng/g, and 0–0.010 ng/g, respectively. In the case of the drin pesticides and HCB, the NOW5 medians of 0.74 ng/g and 0.36 ng/g, respectively, are about 9.5–18 times higher than in NOW14-Q5, 0.050–0.078 ng/g and 0.020–0.023 ng/g, respectively. HCHs' and endosulfans' medians in NOW5, 0.18 ng/g and 0.020 ng/g, respectively, are more than 18 times higher than in NOW14-Q5, 0–0.010 ng/g and below detection limit, respectively.

Table 1
Characteristics of the studied lakes.

	NOW5 (Salve Ø)	NOW14 (Nuuliit)	Q5 (Qaanaaq)
Latitude	76.04386	76.800518	77.70713
Longitude	−65.99149	−70.60262	−69.41987
Core length to 1900 (cm)	0–12.5	0–5.5	0–12.5
Year of sampling	2014	2015	2016
Depth (m)	18	1	17
pH	3.4	8.3	7.98
Chla (μg/cm^2) or μg/L	74	3.4	1.6
T (°C)	2.4	11.90	8.1
TP (mgP/L)	0.37	0.01	0.007
TN (mg/L)	3.75	0.75	0.212
Living organisms in the catchment	Birds (little auk, thick-billed murre, common eider)	Inconsistent presence of Humans (Thule people)	None

The concentrations of all POPs tested in lakes with no bird influence (NOW14 and Q5; Table 2) are lower than those reported in the lacustrine cores from high mountain European lakes (Grimalt et al., 2004a), Yukon lakes (Rawn et al., 2001) and Lake Ellasjøen (Bear Island; Norway; Evenset et al., 2007b) (Table 3). The concentrations of HCB, HCHs, endrins, and endosulfans in NOW14 and Q5 (Table 2) are also lower than those reported in cores from other Arctic lakes, including the Canadian Arctic, Alaska and Bear Island (Table 3).

However, the concentrations of DDTs in these lakes with no bird influence (max. 0.8–1.7 ng/g; Table 2) are higher than those observed in lake cores from Alaska and Devon Island (max 0.15–0.20 ng/g; Stern et al., 2005; Allen-Gil et al., 1997) and similar to those from some Canadian Arctic lakes (Muir et al., 1995, 1996). The concentrations of PCBs (max. 0.48–0.90 ng/g; NOW14 and Q5; Table 2) are also lower than those reported in lacustrine cores from Svalbard and the Canadian Arctic (max 2.5–59 ng/g; Muir et al., 1995, 1996; Rose et al., 2004), similar to those from Kangerlussuaq (Greenland; max 0.60–1.3 ng/g; Malmquist et al., 2003) and higher than in lake cores from Alaska (0.12 ng/g; Allen-Gil et al., 1997). The concentrations of PBDEs (max. 0.27–0.37 ng/g; Table 2) are comparable to those reported in lake cores from Devon Island (Nunavut, Canada; max. 0.25 ng/g; Stern et al., 2005) and higher than those reported in Kangerlussuaq (Greenland; max. 0.001–0.02 ng/g; Malmquist et al., 2003).

Except for DDT in Lake Redon, which has comparable values (max. 15–16 ng/g; Tables 2–3), the concentrations of all POPs from the core of the lake of strong bird influence, NOW5, are lower than those reported in the lake cores from remote high mountains of Europe (Grimalt et al., 2004a). In contrast, the higher concentrations caused by guano deposition mean that these POP concentrations in the core from this lake (NOW5) which is situated very close to NOW14 and Q5 has now higher values than in many of the Arctic sites discussed above.

Similarly, the maximum concentrations of DDTs, drins, PBDEs, PCBs, HCHs, HCB, chlordanes and endosulfans, in NOW5, which are 16 ng/g, 7.9 ng/g, 6.2 ng/g, 3.8 ng/g, 1.2 ng/g, 0.65 ng/g, 0.47 ng/g, and 0.25 ng/g, respectively, are higher than those in Kangerlussuaq lakes (Greenland), where PCBs, PBDEs, chlordanes and HCB concentrations, were 0.60–1.3 ng/g, 0.001–0.02 ng/g, 0.03–0.6 ng/g, and 0.01–1.5 ng/g, respectively (Malmquist et al., 2003; Table 3). They are also higher than those in Devon Island lake cores (Canadian Arctic) for DDTs, max. 0.20 ng/g, HCHs, 0.33, ng/g, PCBs, 2.7, ng/g, PBDEs, 0.25, ng/g, chlordanes, 0.08, ng/g, dieldrin, 0.43, ng/g, and endosulfans, 0.60 ng/g (Stern et al., 2005). A comparison of the mean core concentrations in NOW5 and the mean top 2 cm from lake sediment in Alaska (Elusive, Schrader, Feniak and Desperation Lakes from the Brooks Range) shows that the concentrations of HCB, 0.17 ng/g, HCHs, 0.090 ng/g, PCBs, 0.12 ng/g, DDTs, 0.15 ng/g, endosulfans, below detection limit, and chlordanes, 0.030 ng/g (Allen-Gil et al., 1997) are higher in the seabird influenced Greenland polynya lake (Tables 2 and 3). The organohalogen concentrations in NOW5 are similar to those found in other remote Canadian Lakes such as Yukon Lakes (Rawn et al., 2001) concerning DDTs, 0.86–21 ng/g, HCB, 1.1–1.9 ng/g, and HCHs, 0.46–1.6 ng/g, or lakes located between 49°N and 82°N (Muir et al., 1996) for HCB, 0.3–1.8 ng/g, HCHs, 0.05–2.9 ng/g, chlordanes, 0.08–3.3 ng/g, and dieldrin, 0.05–3.2 ng/g. However, these Canadian lakes exhibit higher PCB concentrations, 2.5–59 ng/g (Tables 2 and 3). PCBs are also found in higher concentrations than NOW5 lake in cores from Svalbard, 2.6–14 ng/g (Rose et al., 2004) and Ellasjøen, 72 ng/g (Bear Island; Evenset et al., 2007b). In this last site, the concentrations of DDTs, 4.0 ng/g, and PBDEs, 0.73 ng/g, are lower than in NOW5.

3.2. Depositional fluxes

The sedimentation fluxes of all organochlorine and organobromine compounds considered for study were higher in the core of the NOW5 lake than in the cores of the other two reference lakes (NOW14 and Q5; Table 4). The medians of the fluxes of DDTs, PBDEs, PCBs, and chlordanes in NOW5 core, 10 pg cm^{-1} y^{-1}, 4.2 pg cm^{-1} y^{-1}, 5.9 pg cm^{-1} y^{-1}, and 0.15 pg cm^{-1} y^{-1}, respectively, are about 1.9–4.2

Table 2
Statistical parameters of the concentrations of the organohalogen compounds found in the studied cores (ng/g dry weight).

	NOW5						NOW14						Q5					
	Min	Max	Top[i]	Mean	Median	SD[j]	Min	Max	Top[i]	Mean	Median	SD[j]	Min	Max	Top[i]	Mean	Median	SD[j]
HCB[a]	0	0.65	0.35	0.30	0.36	0.23	0.010	0.030	0.020	0.018	0.020	0.0075	0.010	0.060	0.011	0.023	0.020	0.014
PCBs[b]	0.14	3.8	1.7	1.5	1.2	0.96	0.10	0.48	0.26	0.28	0.26	0.10	0.070	0.90	0.48	0.43	0.44	0.22
HCHs[c]	0	1.2	0.71	0.29	0.18	0.30	0	0.020	0	0.011	0.010	0.0094	0	0.010	0	0.0029	0	0.0047
Drins[d]	0.020	7.9	0.16	1.6	0.74	2.2	0.040	0.19	0.050	0.078	0.050	0.052	0.020	0.16	0.020	0.078	0.050	0.052
DDTs[e]	0.12	16	0.12	2.7	1.9	3.4	0.35	0.80	0.35	0.60	0.64	0.14	0.19	1.7	1.1	0.56	0.43	0.38
Chlordanes[f]	0	0.47	0.19	0.080	0.040	0.12	0	0.040	0.010	0.014	0.010	0.010	0	0.020	0.0060	0.048	0	0.0070
PBDEs[g]	0.22	6.2	2.5	1.6	1.3	1.5	0.27	0.48	0.37	0.35	0.37	0.061	0.11	1.1	0.27	0.29	0.22	0.26
Endosulfans[h]	0	0.25	0.25	0.062	0.020	0.083	0	0	0	0	0	–	0	0.010	0.0010	0.00071	0	0.0024

[a] Hexachlorobenzene.
[b] Polychlorobiphenyls (28 + 52 + 101 + 118 + 138 + 153 + 180 congeners).
[c] Hexachlorocyclohexanes (α + β + γ isomers).
[d] Aldrin + dieldrin + endrin.
[e] 2,4′-DDE + 4,4′-DDE + 2,4′-DDD + 4,4′-DDD + 2,4′-DDT + 4,4′-DDT.
[f] cis + trans chlordanes.
[g] 17 + 28 + 47 + 66 + 71 + 85 + 99 + 100 + 138 + 153 + 154 + 183 + 190 + 209 congeners.
[h] α- + β-endosulfans + endosulfan sulphate.
[i] Value at the top of the core.
[j] Standard deviation.

times higher than the medians in NOW14 and Q5 lake cores, 2.4–4.2 pg cm^{-1} y^{-1}, 1.3–2.2 pg cm^{-1} y^{-1}, 1.7–2.8 pg cm^{-1} y^{-1}, and 0–0.080 pg cm^{-1} y^{-1}, respectively. In the case of the drin pesticides and HCB, the NOW5 core medians of 5.2 pg cm^{-1} y^{-1} and 1.4 pg cm^{-1} y^{-1}, respectively, are about 9.5–13 times higher than in NOW14-Q5 core, 0.48–0.55 pg cm^{-1} y^{-1} and 0.11–0.12 pg cm^{-1} y^{-1}, respectively. The medians of HCHs and endosulfans in NOW5 core, 0.84 pg cm^{-1} y^{-1} and 0.070 pg cm^{-1} y^{-1}, respectively, are more than 21 times

Table 3
Sedimentary concentrations and fluxes of organohalogen compounds from other remote lakes.

Sites	Location	Compound	Concentrations (ng/g)	Flux (pg cm^{-2} y^{-1})
Pyrenees (Lake Redon)	42°38′34″N 0°46′13″E	DDTs	Max[a]: 15; Top[b]: 15	
(Grimalt et al., 2004a)		PCBs	Max: 7.3; Top: 7.3	
(1942–1992)		HCB	Max: 1.6; Top: 1.6	
Tatras	49°10′0″-49°13′36″N 20°0′39″-20°10′0″E	DDTs	Max: 30–190; Top: 1–50	
(Grimalt et al., 2004a)		HCHs	Max:1–10; Top: 1	
(1942–2001)		PCBs	Max: 36–86; Top: 5.6–45	
		HCB	Max: 0.5–3.2; Top: 1	
Canadian Arctic	75°34.420′N 89°18.545′W	DDTs	Max: 0.20; Top: 0.05	Max: 1.5; Top 0.71
Devon Island		HCHs	Max: 0.33; Top: 0.22	Max: 3.8; Top: 3.1
(Stern et al., 2005)		PCBs	Max: 2.7; Top: 2.6	Max: 37; Top 37
(1908–1997)		PBDEs	Max:0.25; Top: 0.17	Max: 2.8; Top: 2.8
		Chlordanes	Max: 0.08; Top: 0.05	Max: 1.3; Top: 1.3
		Dieldrin	Max: 0.43; Top: 0.28	Max: 4.6; Top: 4.0
		Endosulfan	Max: 0.60; Top: 0.60	Max: 0.040; Top: 0.040
Ellasjøen (Bear Island)	74°30′N 19°00′E	PCBs	Max: 72; Top: 48	
(Evenset et al., 2007b)		DDTs	Max: 4.0; Top: 1.6	
(1881–1994)		PBDEs	Max: 0.73; Top: 0.73	
Svalbard	77°33′-79°48′N	PCBs	Max: 2.6–14; Top: 2.6–14	
(Rose et al., 2004)	9°30′-15°00′E			
(1980–1998)				
Kangerlussaq (Greenland)	67°16′-67°02′N	PCBs	Max: 0.60–1.3; Top: 0.11–1.2	Mean: 3.0
(Malmquist et al., 2003)	51°46′-51°07′W	PBDEs	Max: 0.001–0.02; Top: 0–0.02	
(1940–2000)		Chlordanes	Max: 0.03–0.6; Top: 0–0.6	1.0–4.0
		HCB	Max: 0.01–1.5; Top: 0–0.2	0.10–2.0
Yukon Lakes (Canada)	59°47′-64°00′N	PCBs	Max: 33.5–11; Top: 33.5–2.2	135–1150
(Rawn et al., 2001)	128°46′-136°10′W	DDTs	Max: 0.86–21; Top: 0.86–3.5	6.6–1300
		HCHs	Max: 0.46–1.6; Top: 0.13–1.4	7.5–36
		HCB	Max: 1.1–1. 9; Top: 0.06–1.1	4.2–87
Canadian Arctic	49°42′-81°45′N	PCBs	Max: 2.5–59; Top: 2.5–40	11–425
(Muir et al., 1995, 1996)	71°30′-126°16′W	HCB	Max: 0.3–1.8; Top: 0.1–1.8	3.2–3.9
(1895–1990)		DDTs	Max: 0.1–12; Top: 0.1–9.5	11–69
		Chlordanes	Max: 0.08–3.3; Top: 0–1	3.8–4.2
		HCHs	Max: 0.05–2.9; Top: 0–1	3–5.3
		Dieldrin	Max: 0.05–3.2; Top: 0–1	4.3–4.7
Alaska	68°16′-68°50′N	HCB	Mean top 2 cm: 0.17	
(Allen-Gil et al., 1997)	144°60′-158°45′W	HCHs	Mean top 2 cm: 0.090	
		PCBs	Mean top 2 cm: 0.12	
		DDTs	Mean top 2 cm: 0.15	
		Endosulfans	Mean top 2 cm: 0	
		Chlordanes	Mean top 2 cm: 0.030	

[a] Maximum value of the core.
[b] Value at the top of the core.

Table 4
Statistical parameters of the sedimentary deposition fluxes of the organohalogen compounds found in the studied cores (pg cm^{-2} y^{-1}).

	NOW5						NOW14						Q5					
	Min	Max	Top[i]	Mean	Median	SD[j]	Min	Max	Top[i]	Mean	Median	SD[j]	Min	Max	Top[i]	Mean	Median	SD[j]
HCB[a]	0	4.9	4.9	1.5	1.4	1.3	0.030	0.30	0.28	0.14	0.12	0.11	0.045	0.67	0.067	0.18	0.11	0.17
PCBs[b]	0.77	25	24	7.7	5.9	6.3	0.30	3.6	3.6	1.9	1.7	1.2	0.44	5.5	2.9	2.7	2.8	1.3
HCHs[c]	0	9.9	9.9	1.6	0.84	2.1	0	0.20	0	0.058	0.040	0.071	0	0.073	0	0.017	0	0.028
Drins[d]	0.080	34	2.2	7.7	5.2	8.9	0.17	0.70	0.70	0.43	0.48	0.18	0.12	0.98	0.12	0.50	0.55	0.28
DDTs[e]	1.7	47	1.7	12	10	10	1.9	7.2	7.2	3.8	4.2	1.8	1.0	10	6.4	3.6	2.4	2.3
Chlordanes[f]	0	3.6	2.7	0.53	0.15	0.94	0	0.14	0.14	0.10	0.080	0.11	0	0.44	0.036	0.048	0	0.11
PBDEs[g]	1.5	35	35	8.4	4.2	8.2	0.80	5.1	5.1	2.5	2.2	1.7	0.57	7.1	1.7	2.0	1.3	1.9
Endosulfans[h]	0	3.5	3.5	0.41	0.070	0.78	0	0	0	0	0	–	0	0.061	0.0061	0.0043	0	0.015

[a] Hexachlorobenzene.
[b] Polychlorobiphenyls (28 + 52 + 101 + 118 + 138 + 153 + 180 congeners).
[c] Hexachlorocyclohexanes (α + β + γ isomers).
[d] Aldrin + dieldrin + endrin.
[e] 2,4′-DDE + 4,4′-DDE + 2,4′-DDD + 4,4′-DDD + 2,4′-DDT + 4,4′-DDT.
[f] cis + trans chlordanes.
[g] 17 + 28 + 47 + 66 + 71 + 85 + 99 + 100 + 138 + 153 + 154 + 183 + 190 + 209 congeners.
[h] α- + β-endosulfans + endosulfan sulphate.
[i] Value at the top of the core.
[j] Standard deviation.

higher than in NOW14-Q5 core, 0–0.040 pg cm^{-1} y^{-1} and below detection limit, respectively.

Comparison of the data from Tables 3 and 4 shows that these sedimentation fluxes of all POPs in the lakes of the present study are lower than those described in lacustrine cores from Kangerlussuaq (Greenland; Malmquist et al., 2003), the Canadian Arctic (Muir et al., 1995, 1996) and Yukon Lakes (Rawn et al., 2001). However, there are two exceptions, the drins in the Canadian Arctic cores which have similar mean fluxes than NOW5 core, 4.3–4.7 pg cm^{-1} y^{-1} and 5.2 pg cm^{-1} y^{-1}, respectively (Tables 3 and 4), and the mean flux of PCBs in the Kangerlussuaq (3.0 pg cm^{-1} y^{-1}) which are lower than those of NOW5 core, 7.7 pg cm^{-1} y^{-1}. Comparison of the results of the present study with the POP composition in the cores from North West Greenland and Devon Island (Stern et al., 2005) shows that the latter had higher sedimentation fluxes than cores NOW14 and Q5 for of all POPs except in the case of DDTs whose maximum sedimentation rates were 1.5 pg cm^{-1} y^{-1}, 7.2 pg cm^{-1} y^{-1} and 10 pg cm^{-1} y^{-1}, respectively, and therefore higher in North West Greenland (Tables 3 and 4). Conversely, for all POPs except PCBs, sedimentation fluxes are higher in the NOW5 core, which is influenced by the bird polynya, which values are 27 pg cm^{-1} y^{-1} and 37 pg cm^{-1} y^{-1}, respectively.

3.3. Influence of birds on lacustrine POP accumulation

The specific conditions of sedimentation in NOW5 are strongly influenced by the bird population, as shown by the sedimentary concentration and flux differences between the three lakes chosen for study (Tables 2 and 4, respectively), resulting in the observed significant increase in organochlorine and organobromine compounds compared to the seabird free lakes.

Because POPs tend to partition from gas and liquid phases to organic phases, the accumulation of atmospheric POPs is also driven in part by gradients in organic carbon content of soils and sediments (Nizzetto et al., 2010). The fertilizing effects of guano deposits are the main sources of organic carbon in the lakes. Furthermore, eutrophication and the accumulation of organic matter can be related with chlorophyll *a* concentration. Phytoplankton in the water column is a transport driver of organohalogen compounds to the sediments both in lacustrine (Meijer et al., 2006) and marine environments (Dachs et al., 2002). In lacustrine environments, the sedimentation fluxes of the organohalogen compounds driven by phytoplankton sinking in the water column have been related to the water column chlorophyll *a* concentrations by Eq. (1) (Meijer et al., 2006),

$$F_{sed} = 1.8 \cdot C_p \cdot 10^{(1.82+0.62\log(Chla))}/(69Chla + 146.8) \quad (1)$$

where F_{sed} is the sedimentation flux of one organohalogen compound (ng m^{-2} d^{-1}), Chla is the concentration of chlorophyll *a* (kg m^{-3}) and C_p is the concentration of the organochlorine compound in phytoplankton (per volume of water; ng m^{-3}).

The estimated coefficients for the C_p values in lakes NOW5, NOW14 and Q5, 0.16 m d^{-1}, 0.024 m d^{-1} and 0.015 m d^{-1}, respectively, are obtained by calculating the chlorophyll *a* values defined by Eq. (1) using the chlorophyll concentrations of Table 1. These result in ratios of 6.5 and 10 for the relative sinking rates for NOW5/NOW14 and NOW5/Q5, respectively.

These values are intermediate between the ratios of the measured concentrations or deposition rates, in the range of 1.9–21 for NOW5/NOW14 and 2.1–13 for NOW5/Q5 when calculated using the median values (Table 5). These ratios are consistent with the enhanced effect of the bird deposition. As shown in a previous study (Meijer et al., 2009), significant transport from air to water occurs in the gas phase at air to water constants, log Kaw, higher than −2.4, and in the particulate phase at octanol to air constants, log Kow, higher than 9. Accumulation from the water column into sediments is observed at octanol to water constants, log Kow, higher than 6.8 (Meijer et al., 2009). These conditions are fulfilled by most congeners of the ΣPCBs and ΣPBDEs and DDT metabolites (Table 5). The chlordanes also have constants close to these threshold values (Table 5). Accordingly, these compounds are those having lower NOW5/NOW14 and NOW5/Q5 ratios (1.9–4.2) because their deposition and accumulation in the sediments already occurs irrespectively of bird mediation. The other compounds do not have physical chemical constants favouring transport from air to water (HCB, some HCHs, α- and β- endosulfans) or accumulation in the sediments (HCB, HCHs, drins, endosulfans) (Table 5). In these cases, the difference in the accumulation is more relevant if enhanced by bird deposition and the NOW5/NOW14 and NOW5/Q5 ratios are much higher (≥ 9.5).

Furthermore, the rates of Table 5 indicate that bird-mediated deposition has a preservation effect of the less stable compounds, e.g. endosulfans (Guerin and Kennedy, 1992), whose concentrations and fluxes are much higher in NOW5 than in the other lakes.

The effect of the birds in transporting POPs to the high arctic lakes can reflect two processes: 1) from lower to higher latitudes when they migrate and 2) from the marine environment to inland where they feed and transport meal for their chicks. This transport is in the same direction as that described in the global distillation model and the tendency for semi-volatile POP chemicals to become concentrated in cold environments (Wania and Mackay, 1993, 1996; Grimalt et al., 2001; Grimalt et al., 2004a, 2004b) but through specific biogenic mechanisms. In any case, the polynya effect leads to higher rates of POPs in

Table 5
Ranges of the physical-chemical constants of the organohalogen compounds found in the lakes.

	Log Kaw[a]	Log Koa[b]	Log Kow[c]	NOW5/NOW14[d]	NOW5/Q5[d]
HCB[e]	−1.158	7.38	5.73	12	13
PCBs[f]	(−2.087, −3.388)[g]	(7.71, 11.66)	(5.62, 8.24)	3.4	2.1
HCHs[h]	−3.677	(7.82, 8.88)	(3.93, 4.14)	21	>20
Drins[i]	(−1.801, −3.388)	(7.86, 8.59)	(5.20, 6.06)	11	9.5
DDTs[j]	(−2.769, −3.468)	(9.12, 10.38)	(5.87, 6.91)	2.4	4.2
Chlordanes[k]	−2.702	8.92	6.22	1.9	–
PBDEs[l]	(−3.516, −6.131)	(9.40, 18.42)	(5.88, 12.11)	1.9	3.2
Endosulfans[m]	(−2.576, −4.877)	(6.41, 8.54)	(3.66, 3.83)	>20	>20

[a] Air-water constants.
[b] Octanol-air constants.
[c] Octanol-water constants.
[d] Calculated from the median values of the calculated sedimentation rates.
[e] Hexachlorobenzene.
[f] Polychlorobiphenyls (28 + 52 + 101 + 118 + 138 + 153 + 180 congeners).
[g] Range of values for the compounds included in the group.
[h] α + β + γ Hexachlorocyclohexanes.
[i] Aldrin + dieldrin + endrin.
[j] 2,4′-DDE + 4,4′-DDE + 2,4′-DDD + 4,4′-DDD + 2,4′-DDT + 4,4′-DDT.
[k] cis + trans chlordanes.
[l] Polybromodiphenyl ethers (17 + 28 + 47 + 66 + 71 + 85 + 99 + 100 + 138 + 153 + 154 + 183 + 190 + 209 congeners).
[m] α- + β-endosulfans + endosulfan sulphate. Constant data from US EPA (2022) and Beyer et al. (2002).

the lake sediments which are not diluted by the organic matter increases due to the higher productivity associated to the increase of nutrients from the guano deposits.

3.4. Temporal trends

With the major threat of climate change looming over the Arctic, favouring snowmelt re-emission of POPs that were deposited long ago in the various environmental compartments in the cold climate (Arellano et al., 2011, 2015, 2018; Grimalt et al., 2009; Gustavsson et al., 2019; AMAP, 2021), multiple new sources of POPs may emerge, leading to changes in transport rates and additional deposition in the lakes. Consequently, monitoring lakes such as NOW5 with high sedimentation rates and supplies of contaminants from multiple sources is extremely beneficial since changes in contaminant input are reflected in the lake sediments.

Examination of the temporal trends of the sedimentary deposition fluxes of the measured pollutants (Fig. 2) show much higher values for NOW5 than the other lakes. This is consistent with the overall results of Table 4 and highlights the biogenic POP transport effect linked to guano deposits once more. The most distinct feature of the majority of time profiles from this core is the increase to highest values in the most recent core sections, e.g. 2014, for many of the compounds examined, PCBs, HCHs, drins, chlordanes, PBDEs, HCB and endosulfans. Total DDTs are the lone exception showing a maximum peak in 1980. The values in the upper sections (most recent years) in the other two cores are significantly lower, with no increase. These temporal trends in core NOW5 show that despite the banning of many of the POPs, the pollutants released into the environment at lower latitudes are still transported to Arctic areas and have an impact on their ecosystems and that migratory bird activity is a main agent of long-range transport in the polynya.

In addition to this main feature, the cores from NOW5 show other patterns such as a maximum of the sedimentation fluxes of drins, PCBs, HCHs, DDTs, PBDEs, and endosulfans at 1980–1985 (Fig. 2). This maximum likely reflects an episode of highest pollution by all these organohalogen pollutants and is coincident with the largest flux of DDTs recorded in this core. It is also coincident, with dating uncertainties, with a maximum of 4,4′-DDT and chlordanes in a lacustrine core from Devon Island (75°34.420′N 89°18.545′W; Stern et al.,

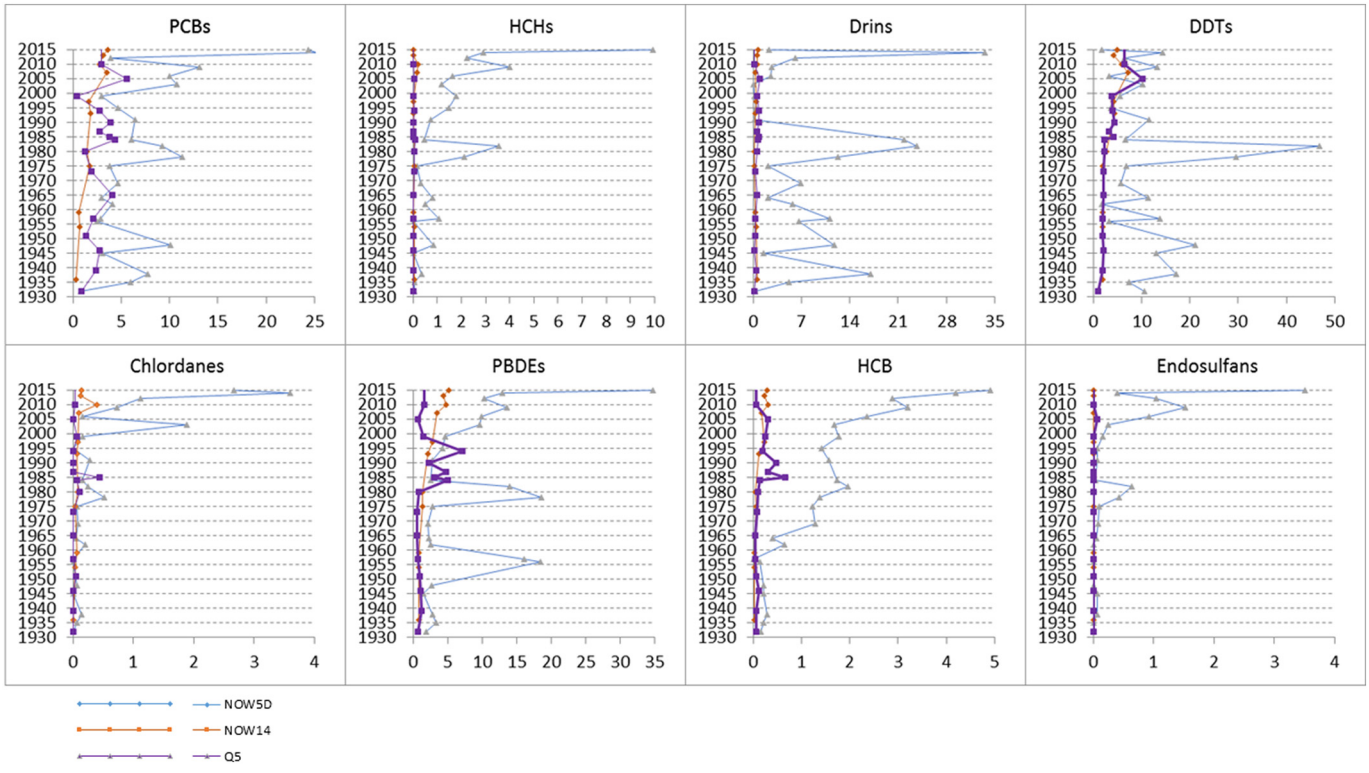

Fig. 2. Downcore sedimentary deposition fluxes of the organohalogen compounds found in the studied cores (pg cm^{-2} y^{-1}).

2005). Other lower maxima reflected higher inputs from specific comments, e.g. PBDEs in 1955, PCBs, drins, and DDTs before 1955.

The fluxes of HCB followed a different pattern showing a continuous increase from 1960 to 2015 and a maximum value in this last year (Fig. 2). HCB has been shown to display quite constant concentrations in the atmosphere in different remote sites, 35–85 pg m^{-3} in Europe (Van Drooge et al., 2004), 39–50 pg m^{-3} in North America (Daly et al., 2007), 56 pg m^{-3} in the Tibetan Plateau (Zhu et al., 2014) and 60 pg m^{-3} in Brazil (Guida et al., 2018) which is close to background pollution levels, while the other organohalogen compounds identified in the lakes may reflect episodic inputs.

In general, the temporal changes of POPs in Arctic samples reported in the literature were showing decreasing trends for most organochlorine compounds and increases for the PBDEs. However, recent reports are describing that the global warming is leading to re-emission of POPs already deposited in cold areas which effects in the Arctic regions (AMAP, 2021). Concerning PBDEs, a study of sediment cores from Søndre Strømfjord, near Kangerlussuaq (West Greenland), performed in 2000 showed maximum concentrations in the top sediment sections of four of the seven cores studied (Malmquist et al., 2003). de Wit et al. (2010) also showed increasing trends for PBDEs in the freshwater sediments from the Canadian Arctic and from Greenland. In the sediment core of Lake Ellasjøen (Bear Island; Barents Sea, with a seabird colony), the PBDEs concentration of the congeners (BDE-28, 47, 99, 100, 153), 0.73 ng/g, also peaked in the surface sediments (Evenset et al., 2007b).

PCBs concentration trends in Arctic biota have been reported to be decreasing (Rigét et al., 2010a, 2010b). Decreasing trends were also identified in cores from Kangerlussuaq, West Greenland, where the concentration maximum of these pollutants peaked in 1970 (Malmquist et al., 2003). Similar decreasing trends were recorded in Lake Ellasjøen where the concentration maximum was observed in the core section of 1966 (Evenset et al., 2007b). In other studies, i.e. Alaska (Gubala et al., 1995) and Finland (Kjeller and Rappe, 1995), PCBs were primarily found in layers starting 1950s with maxima in the 1970–1980s. A study from the Baltic, on the other hand, found PCBs appearing early in the 20th century (Muir et al., 1996). Sanders et al. (1992) also reported low levels of PCBs (mostly low molecular weight PCBs) in early 1900s. PCBs were commercially produced between the 1930s and 1980s (Bigus et al., 2014). However, on Devon Island, the concentrations of these pollutants in the sediment cores of lakes with strong bird influence (Cape Vera) show highest concentrations in the most recent core sections (Michelutti et al., 2009a, 2009b). This study likewise showed a strong contrast between the PCB concentrations in the core with bird influence (3.8 ng/g at the top) and no bird inputs (almost below limit of detection) which is consistent with the observations of the present study (Fig. 2). The PCB profiles from Devon Island lake sediment cores located at 75°34.420′N 89°18.545′W also showed maximum concentrations in the top sections (19 μg m^{-2} y^{-1}; Stern et al., 2005).

Lindane (γ-HCH) was used until recently when it was banned globally under the Stockholm Convention in 2009 (Kirk and Gleason, 2015). Arctic biota, especially seabird population, have showed decreasing trends for α- and γ-HCH (lindane) in Arctic Canada and Greenland but increasing trends of β-HCH in East Greenland black guillemot eggs (Rigét et al., 2016). Since β-HCH has stronger affinity for organic matter than α-HCH and γ-HCH, is found in higher concentrations in biota (Li and Macdonald, 2005). However, in NOW5, the concentrations of all three isomers of HCHs were similar and showed highest concentrations in the top sections, indicating a distinct temporal trend than in the cores lacking bird influence, which showed much lower concentrations and fluxes (Fig. 2). The HCH profiles in cores from Devon Island located at 75°34.420′N 89°18.545′W also showed maximum concentrations in the top sections and in the section dated in 1975 (1.95 and 2.2 μg m^{-2} y^{-1}, respectively; Stern et al., 2005).

Dieldrin, aldrin, endrin and chlordanes were banned or heavily restricted prior to the year 2000 (Kirk and Gleason, 2015). Although aldrin was widely used, it is readily degraded to dieldrin in the environment, which is the form of major concern in the Arctic. Most of the studies have focused solely on dieldrin, but in the present study all three drins were considered. Dieldrin and endrin were found in equally high concentrations in the core sections of highest sedimentation in NOW5.

HCB was first used in the 1950s with peak usage between 1970s and 1980. Despite the fact that it is currently banned it is commonly found in remote environments. For instance, in one study of freshwater lakes from Alaska, it was detected at concentrations of 0.17 ng/g dw in the top 2 cm of the sediment cores (Allen-Gil et al., 1997). In the current study, this compound is again found in highest concentration in the lake core of strong guano deposition with highest fluxes in the most recent core sections whereas the cores from the lakes free from bird influence show much lower concentrations and no discernable temporal trend.

As stated previously, the temporal profile of DDTs in the core from lake NOW5 was the only contaminant that did not show maximum values in the top sections of the core but in the section that corresponded to the year 1980. This temporal trend is in agreement with the banning policies implemented in European and north American countries. This profile is equivalent, within model age uncertainty, with the profile of 4,4′-DDT in a core from Devon Island which showed maximum concentrations in the section dated in 1988 (DV09; 1.6 μg m^{-2} y^{-1}; Stern et al., 2005). However, the lake core temporal trend of Lake Ellasjøen (Bear Island; Barents Sea) which also has a seabird colony shows the highest DDT concentrations at 1966 (4 ng/g; Evenset et al., 2007b). These comparisons of the ages from different core records are tentative because the resolution of the time models is not the same. In any case, the NOW5 core witnesses that the DDT restrictions successfully decreased the transport of this insecticide and metabolites to the Arctic regions which is in contrast with the observations of the other organohalogenated POPs.

4. Conclusions

According to the findings of this study, the levels of contamination in the lake NOW5 are positively correlated to the presence of birds in the lake catchment. The other two lakes are also polluted, albeit to a much lesser extent and mainly as a result of atmospheric deposition. The median concentrations of DDTs, PBDEs, PCBs, and chlordanes in the polynya lake are about 2.7–6 times higher than the median concentrations in the lakes with no bird influence. In the case of the drin pesticides and HCB, the former have a median that is about 9.5–18 times higher than the latter, and these ratios are more than 18 times higher for HCHs and endosulfans. When the changes in sedimentation fluxes between these lakes are considered, similar ratios are found, indicating that bird-mediated deposition has a preservation effect of the less stable and more volatile compounds.

The results have also shown that the highest sedimentary deposition fluxes of PCBs, HCHs, drins, chlordanes, PBDEs, HCB and endosulfans of the polynya lake were found in the upper sediment layer, corresponding to 2014. Thus, despite the fact that many of the organochlorine and organobromine compounds have been banned, those that have already been released to the environment at lower latitudes are still being transported to Arctic areas and impacting the ecosystems there.

In contrast, the maximum sedimentation fluxes of DDTs were found at the layer corresponding to 1980 which, within age model uncertainties, is consistent with the maximum sedimentation flux of this pesticide found in Devon Island (Stern et al., 2005) and could reflect that the restrictions in the use of this compound successfully decreased the transport of this insecticide and metabolite to the Arctic regions, even when mediated by bird metabolism.

CRediT authorship contribution statement

NN analysis, interpretation of results, writing. MB conceptualization, supervision, interpretation of results, review and editing. SB conceptualization, supervision, interpretation of results, TAD sampling, conceptualization, interpretation of results, review and editing. EJ interpretation of results, review and editing. JOG supervision, interpretation of results, writing, review and editing, funding acquisition.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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