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Final Thesis

**Temporal dynamics of anthropogenic
contaminants in sediments of the
Kongsfjorden-Krossfjorden system
(Svalbard, Norway)**

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*“We stand now where two roads diverge.
But unlike the roads in Robert Frost's familiar poem,
they are not equally fair.
The road we have long been traveling is deceptively easy,
a smooth superhighway on which we progress with great speed,
but at its end lies disaster.
The other fork of the road — the one less traveled by —
offers our last, our only chance
to reach a destination that assures the preservation of the earth.”*

Rachel Carson – *Silent Spring* (1962)

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Resumé

Four marine sediment cores have been collected from the Kongsfjorden-Krossfjorden system (Svalbard, Norway) to assess the occurrence, concentration levels and temporal trends of selected legacy and emerging contaminants, to identify potential sources of contamination. Two sampling campaigns were conducted 10 years apart: one in 2011, yielding a single core (NYA11_09); and another in 2021, which produced three cores (NYA21_01, NYA21_03 and NYA21_04). The study targeted emerging contaminants, including seven organic UV Filters (UV-Fs) and six synthetic fragrances (SFs), analyzed in the 2011 core. Additionally, thirty-eight polybrominated diphenyl ethers (PBDEs), classified as legacy contaminants, were analyzed in the 2021 cores. Radiocarbon (^{14}C) and ^{210}Pb age-depth models were constructed to evaluate the historical deposition of these contaminants. To the best of our knowledge, this study is the first to investigate the historical trends of these contaminants in sediment cores from KKS while simultaneously exploring the deposition of selected organic UV-Fs and SFs in Arctic marine sediments.

Chemical analyses involved extraction from sediments using Pressurized Liquid Extraction (PLE) for both legacy and emerging contaminants, followed by compound identification and quantification. Gas chromatography-tandem mass spectrometry (GC-MS/MS) was employed for emerging contaminants, while gas chromatography-mass spectrometry (GC-MS) was used for legacy contaminants. Among the UV-Fs detected were: 4-MBC (Enzacamene), EHMC (Octinoxate), EHS (Octisalate) and HMS (Homosalate). Detected SFs included: HHCB (Galaxolide), AHTN (Tonalide) and OTNE (Iso-E Super). In core NYA11_09, total concentrations of $\Sigma_4\text{UV-Fs}$ and $\Sigma_3\text{SFs}$ ranged from <LOD to 10.4 ng g⁻¹ d.w. and <LOD to 6.4 ng g⁻¹ d.w., respectively. EHMC and OTNE were the most abundant compounds. PBDEs congeners detected included: BDE-28, BDE-47, BDE-49, BDE-71, BDE-99, BDE-100, BDE-119, BDE-116, BDE-173+190 and BDE-183. Total concentrations of $\Sigma_{11}\text{PBDEs}$ ranged from <LOD to 15.33 ng g⁻¹ d.w. in core NYA21_01, <LOD to 3.30 ng g⁻¹ d.w. in core NYA21_03 and 0.12 to 6.01 ng g⁻¹ d.w. in core NYA21_04. Penta- and hepta-BDEs were the dominant PBDE homologues across all cores.

Historical trends revealed a marked increase in PBDE concentrations in all cores starting in the late 1970s to early 1980s, peaking in the mid-2000s, followed by a decline. For emerging contaminants, total concentrations of UV-Fs and SFs generally increased from the early 1970s and 1980s respectively, peaking in the late 1990s to early 2000s, and then declined. These patterns align with the production and usage trends of the studied contaminants. These findings underscore the value of sediment cores as natural archives for reconstructing historical environmental contamination.

Environmental contamination in the study area arises from various sources, including long- and medium-range atmospheric and oceanic transport, local anthropogenic activities, and climate-change-induced 'secondary sources'. Marine sediments serve as critical sinks for organic contaminants due to the accumulation and settling of organic matter. Despite the challenges of sampling in Arctic environments, this study highlights the importance of analyzing modern age temporal trends in sediment cores. Such investigations offer crucial insights into contaminant sources and the historical deposition of anthropogenic chemicals in remote ecosystems.

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CHAPTER 1 – Introduction

1.1 Rationale and objectives

This PhD project aims to provide new insights into the contamination of the Arctic marine environment. Although several studies on this topic already exist in literature, data on marine sediment cores are still limited. This project analyzed four sediment cores collected from the Kongsfjorden-Krossfjorden system (KKS) in the Svalbard Archipelago (Norway). KKS serves as an ideal location for studying the effects of ongoing environmental changes due to its strategic geographic position, lying adjacent to both Arctic and Atlantic water masses, and its proximity to the village of Ny-Ålesund, which offers valuable context for assessing human impact on the surrounding environment. The sediment cores were sampled during two campaigns that took place ten years apart: one core was collected in 2011 and three in 2021. Specifically, analyses on the 2011 core started in February 2020 at the University of Cádiz (Spain). Additional laboratory analyses and data processing for this core resumed in 2021, at the beginning of the second year of the PhD program. Analyses for the three cores collected in 2021 were conducted at CNR-ISP Bologna and CNR-ISP Montelibretti (RM).

The specific objectives of this PhD project are to: (1) assess the presence and determine concentration profiles of selected anthropogenic organic contaminants (UV-Fs, SFs and PBDEs); (2) reconstruct contaminants introduction in the fjord system, identifying temporal trends and distinct periods of deposition; and (3) unveil potential contamination sources in this region.

To the best of our knowledge, this study is the first to examine historical trends of these contaminants in sediment cores from KKS and to simultaneously investigate the deposition of selected UV-Fs and SFs in Arctic marine sediments.

1.2 Background

1.2.1 Differences between selected legacy and emerging contaminants

The anthropogenic contaminants analyzed in this work include both legacy Persistent Organic Pollutants (POPs) and Contaminants of Emerging Concern (CECs). POPs are strictly regulated, with production banned for many years due to their persistence and toxicity, even though residues are still detectable in the environment. In contrast, CECs are substances that are partially or not yet regulated; they may be either newly recognized or have been used for decades, with increasing awareness in recent decades (Field et al., 2006).

POPs encompass various organic chemicals characterized by persistence, bioaccumulation, toxicity (PBT) and the potential for long-range transport (LRT). These

include pesticides, industrial chemicals, and by-products formed unintentionally during industrial processes, degradation, or combustion. POPs have been regulated under the Stockholm Convention by the United Nations Environment Programme (UNEP) since 2001 (UNEP, 2001).

Among POPs, polybrominated diphenyl ethers (PBDEs) are industrial halogenated flame retardants, used to reduce the flammability in materials like plastics, furniture coatings, upholstery products, paints, textiles, electrical equipment and electronic devices (UNEP, 2017). PBDEs can be either reactive (covalently bonded to materials) or additive (dissolved in materials without bonding) (Rahman et al., 2001), which increases the likelihood of their leaching and environmental dispersion (Wu et al., 2019, Alaee et al., 2003). Major sources of PBDE emission include manufacturing processes, volatilization from products containing them, and leaching from disposal and recycling sites (UNEP, 2017). Controlled incineration or open burning also release PBDEs into the atmosphere (Xu et al., 2021).

Since the 1960s, the synthetic organic chemicals industry has expanded rapidly, leading to the widespread use of PBDEs as a replacement for polychlorinated biphenyls (PCBs), resulting in increasing environmental concentrations through the 1990s (UNEP, 2009). By the late 1990s, global PBDE production was estimated at nearly 70,000 tons annually (Wania and Dugani, 2003), with cumulative use estimated at 100,000 tons in 2001 (UNEP, 2009).

Structurally, PBDEs are halogenated aromatic hydrocarbons containing one to ten bromine atoms bonded to an aromatic double ring (diphenyl), which are in turn joined by an oxygen atom to form an ether bridge (Fig. 1). Depending on the number of bromine substituent atoms present and their position, it is possible to obtain 209 unique structures (congeners). Congeners with the same number of bromine atoms are called homologues and are divided into ten groups (mono to deca) (Table 1). However, only three commercial PBDE mixtures have been widely produced: c-pentaBDE, c-octaBDE, and c-decaBDE (La Guardia et al., 2006). The c-pentaBDE mixture contains mainly tetra-, penta- and hexa- congeners; c-octaBDE contains mainly heptaBDE plus hexa- and octaBDE; and c-decaBDE consists mainly of BDE-209 (de Wit et al., 2010). The latter is the most widely used mixture globally (UNEP, 2017), indeed the estimated world market demand for penta-, octa- and deca-BDEs in 1999 amounted to 8,500, 3,825 and 54,800 tons, respectively (de Wit, 2002). Due to their physico-chemical characteristics and effects on humans and ecosystems, penta- and octa- BDE commercial mixtures have been classified as PBT substances and were listed in the Stockholm Convention in 2004, while tetra-BDEs, penta-BDEs, hexa-BDEs, hepta-BDEs, octa-BDEs, and nona-BDEs were listed in 2009 (UNEP, 2009). Deca-BDE – used as a replacement for penta- and octa-BDEs mixtures – was listed only in 2017 (EC, 2017). Despite the ban on the manufacturing and use of PBDEs first introduced in Europe, USA and Canada and consequently adopted by

other countries, these contaminants are still detected in the environment around the world (Turner, 2022).

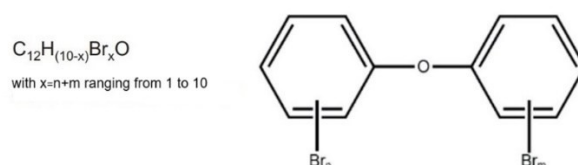


Figure 1 - Molecular structure of PBDEs.

Table 1 - Some physico-chemical properties of PBDEs.

Molecular Formula	Name	Isomers No.	IUPAC No.	Molecular mass (g/mol)
C ₁₂ H ₉ BrO	Mono-BDE	3	1-3	248.97
C ₁₂ H ₈ Br ₂ O	Di-BDE	12	4-15	327.87
C ₁₂ H ₇ Br ₃ O	Tri-BDE	24	16-39	406.77
C ₁₂ H ₆ Br ₄ O	Tetra-BDE	42	40-81	485.66
C ₁₂ H ₅ Br ₅ O	Penta-BDE	46	82-127	564.56
C ₁₂ H ₄ Br ₆ O	Esa-BDE	42	128-169	643.45
C ₁₂ H ₃ Br ₇ O	Epta-BDE	24	170-193	722.35
C ₁₂ H ₂ Br ₈ O	Otta-BDE	12	194-205	801.25
C ₁₂ HBr ₉ O	Nona-BDE	3	206-208	880.14
C ₁₂ Br ₁₀ O	Deca-BDE	1	209	959.04

As a result of the widespread use of products containing PBDEs, their dispersion patterns have made these compounds ubiquitous in the environment, with concentrations increasing considerably over the decades, also due to improper waste disposal and obsolete electrical and electronic equipment (EEE) dismantling activities (also called ‘E-waste’) (Da et al., 2019). E-waste contains many hazardous substances that require special disposal, and PBDEs are one of these substances (Cai et al., 2020). Moreover, electronics, along with textiles, are considered the major commercial sectors in which large quantities of PBDEs have reportedly been used (Sharkey et al., 2020). The seven largest producers of e-waste worldwide are the EU (10.07 Mt), China (7.21 Mt), USA (6.30 Mt), Japan (2.14 Mt), India (1.96 Mt), Brazil (1.53 Mt) and Indonesia (1.27 Mt) (Baldé et al.,

2017). In this context, the rise in the production and use of EEE (e.g. mobile phones, computers and kitchen appliances) has resulted in an increasing volume of E-waste. For this reason, since 2003, EU has restricted PBDEs use in electrical and electronic equipment under the Restriction of Hazardous Substances (RoHS) Directive (EC, 2003).

Although PBDE demand declined in industrialized countries in the early 2000s, economic growth in less industrialized regions led to increased consumption there, often accompanied by waste exports from industrialized nations for cheaper informal recycling (Chang et al., 2022, Breivik et al., 2016). This latter process, often involving open burning or acid leaching, has elevated global PBDE emissions (Cai et al., 2020, Abbasi et al., 2019, Shang et al., 2013). Hence, without unified international regulations, these practices may continue to release PBDEs into the environment.

Regarding Contaminants of Emerging Concern (CECs), this represents a diverse group of compounds, also including personal care products (PCPs). PCPs are common in daily personal and household products (e.g., toothpaste, cosmetics, detergents, household products) and have raised concern recently due to their increasing use and PBT characteristics (Brausch and Rand, 2011). Two classes of PCPs analyzed in this study, organic UV filters (UV-Fs) and synthetic fragrances (SFs), are increasingly studied due to their prevalence in daily-use products. Some physico-chemical properties of the selected UV-Fs and SFs are reported in Table 2. Some UV-Fs and SFs can disrupt endocrine systems, interfere with thyroid and reproductive functions, and affect brain development in both aquatic and terrestrial species (Huang et al., 2021, Barón et al., 2013, Brausch and Rand, 2011, Fent et al., 2008, Luckenbach and Epel, 2005).

In the EU, UV-Fs, SFs and fragrance allergens are regulated under the Cosmetic Products Regulation (EC) N° 1223/2009. Currently, the EU permits 27 UV filters in cosmetics at concentrations ranging from 0.5% to 15% (EC, 2009). In USA, New Zealand, Canada and Australia, UV filters are managed under drug regulations, whereas in China, Japan, South Africa, and in some countries in South America, they are regulated as cosmetic products (Jesus et al., 2022, Chisvert and Salvador, 2018).

Historically, UV-Fs were primarily used as sunscreen agents. It was in 1935 that the first UV-B filters were developed, then in 1956 was introduced the concept of the sun protection factor (SPF) and at the end of 1960s–early 1970s, formulators begin to develop water-resistant sunscreens and regulatory bodies for sunscreen were introduced (Drissi (Drissi et al., 2022, Ma and Yoo, 2021, Svarc, 2015). Nowadays, they are also used as stabilizers in industrial products (e.g., plastics, paints, textiles) to prevent photodegradation of polymers and pigments (Huang et al., 2021, Díaz-Cruz M. Silvia. and Damià, 2015).

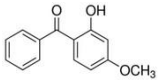
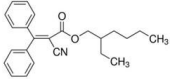
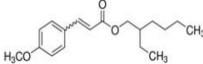
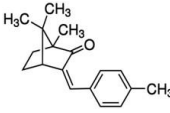
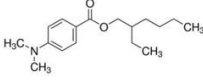
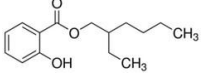
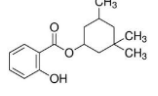
As for UV-filters, also fragrances are used since ancient times to provide a pleasant scent. Initially, these were exclusively products with ingredients of natural origin (e.g. essential oils derived from plants). In the late 19th century, synthetic fragrances began to be

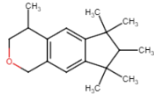
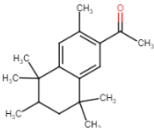
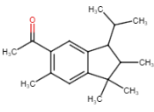
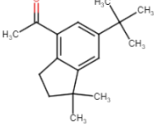
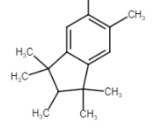
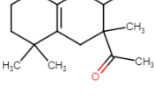
synthesized (Gautschi et al., 2001), expanding the introduction of these compounds in many functional products like detergents and personal care items (Bester, 2009, Daughton and Ternes, 1999). Both UV-Fs and SFs are now globally consumed at an estimated rate of 10'000 tons per year (Díaz-Cruz M. Silvia. and Damià, 2015).

UV-Fs and SFs enter the environment directly through water recreational activities and indirectly from wastewater treatment plants (WWTP) effluents following cosmetic use (Wong et al., 2019, Díaz-Cruz M. Silvia. and Damià, 2015, Balmer et al., 2005). Their environmental behavior and accumulation depend on factors like physico-chemical compound properties (e.g., log K_{ow} , log K_{oc} , vapor pressure, water solubility), and surrounding environmental conditions.

Both legacy PBDEs and the emerging UV-Fs and SFs have limited studies regarding their presence in the Arctic marine environment, especially concerning temporal trends. This study aims to increase understanding and implement the framework of anthropogenic contamination in the Arctic.

Table 2 - Some physico-chemical properties of selected UV-Fs and SFs.

IUPAC name	Abbreviations	CAS No.	Molecular Formula	Molecular Weight (g/mol)	Structure
Organic UV-Filters (UV-Fs)					
(2-Hydroxy-4-methoxyphenyl)(phenyl)methanone or Benzophenone-3 (Oxybenzone) or Benzophenone-3	BP-3	131-57-7	C ₁₄ H ₁₂ O ₃	228.24	
2-Ethylhexyl 2-cyano-3,3-diphenylacrylate (Octocrylene)	OC	6197-30-4	C ₂₄ H ₂₇ NO ₂	361.48	
2-Ethylhexyl (2E)-3-(4-methoxyphenyl)acrylate or 2-Ethylhexyl 4-methoxycinnamate (Octinoxate)	EHMC	5466-77-3	C ₁₈ H ₂₆ O ₃	290.40	
3-(4-methylbenzylidene) camphor (Enzacamene)	4-MBC	36861-47-9	C ₁₈ H ₂₂	254.37	
2-Ethylhexyl 4-(dimethylamino) benzoate (Padimate O)	ODPABA	21245-02-3	C ₁₇ H ₂₇ NO ₂	277.40	
2-Ethylhexyl salicylate (Octisalate)	EHS	118-60-5	C ₁₅ H ₂₂ O ₃	250.33	
3,3,5-Trimethylcyclohexyl salicylate (Homosalate)	HMS	118-56-9	C ₁₆ H ₂₂ O ₃	262.35	

Synthetic fragrances (SFs)					
4,6,6,7,8,8-Hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta[g]isochromene (Galaxolide)	HHCB	1222-05-5	C ₁₈ H ₂₆ O	258.40	
1-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydro-2-naphthalenyl)ethenone (Tonalide)	AHTN	1506-02-1	C ₁₈ H ₂₆ O	258.40	
1-(3-Isopropyl-1,1,2,6-tetramethyl-2,3-dihydro-1H-inden-5-yl)ethenone (Traseolide)	ATII	68140-48-7	C ₁₈ H ₂₆ O	258.40	
1-[1,1-Dimethyl-6-(2-methyl-2-propanyl)-2,3-dihydro-1H-inden-4-yl]ethenone (Celestolide)	ADBI	13171-00-1	C ₁₇ H ₂₄ O	244.37	
1-(1,1,2,3,3,6-Hexamethyl-2,3-dihydro-1H-inden-5-yl)ethenone (Phantolide)	AHMI	15323-35-0	C ₁₇ H ₂₄ O	244.37	
1-(2,3,8,8-Tetramethyl-1,2,3,4,5,6,7,8-octahydro-2-naphthalenyl)ethanone	OTNE (or Iso-E super)	54464-57-2	C ₁₆ H ₂₆ O	234.38	

1.2.2 Mechanisms controlling the transport and behavior of anthropogenic contaminants in the Arctic

The study of air pollution in the Arctic dates back to the 19th century, when pioneering explorers and scientists noticed a peculiar ‘white’ and ‘dense’ haze in the sky, seasonally. This description corresponds to the earliest evidence of the ‘Arctic haze’ phenomenon, which became known in 1957 thanks to U.S. Air Force meteorologist J. Murray Mitchell (Garrett and Verzella, 2007). What emerged from later studies conducted by K. Rahn and colleagues was that the Arctic haze was mainly composed of sulphur in the form of sulphate and that there was a strong seasonal variation, with the maximum occurrence between late winter and early spring, a period followed by a rapid drop of intensity (Shaw, 1995). By 1980s, through chemical fingerprinting methods to determine the origin and chemical composition analyses of the aerosol, it was determined that the Arctic was heavily influenced by anthropogenic pollution sources from Eurasia and North America, as a result of long-range atmospheric transport (LRAT) ((Shaw, 1995, Heintzenberg et al., 1981). However, the ability of these substances to undergo LRAT from mid-latitudes (where they are most often produced) to polar areas, depends on both their physico-chemical properties (e.g., volatility, partitioning coefficients in environmental media) and the physical factors of the environment (e.g. temperature, precipitation, winds, currents) (Wania and Mckay, 1996). Contaminants with different volatility will also have a different migration velocity, as well as a specific range of temperatures or latitudes of condensation, dictated by their atmosphere-surface partitioning. As a result, the ‘global fractionation’ process occurs, that is, the more volatile constituents will remain more in the atmospheric phase and migrate faster, while the less volatile ones will distribute more in the liquid or non-gaseous solid media of water, soil and vegetation (Wania and Mackay, 1996) (Fig.2). By developing a global distribution model of organic chemicals, (Wania and Mackay, 1995) also demonstrated that, contrary to mid-latitudes where high temperatures favor the evaporation from the soil and ocean surface, in polar areas, the very low temperatures and reduced sunlight conditions are responsible for the ‘cold condensation’ and accumulation of these contaminants in polar ecosystems, resulting in elevated contaminant concentration also due to reduced degradation mechanism.

Precipitation, atmospheric transfer and anthropogenic activities are processes that favor the deposition and, subsequently, the accumulation in the surrounding environment (Beard et al., 2022a). In this context, climate change (CC) at a global level, but especially in the Arctic, where its effects are occurring three times faster than in the rest of the world (IPCC, 2023), is responsible for the alteration of fluxes (release, transport, degradation) contaminants are subjected to. Climate oscillation indices, in particular the Arctic Oscillation (AO) and the North Atlantic Oscillation (NAO), are considered significant patterns responsible for atmospheric circulation variability in the Northern Hemisphere, (AMAP, 2021). Moreover, their potential to affect the transport and distribution of POPs in the Arctic environment has been demonstrated, given their positive correlation with changing mass balance of glaciers, as well as with precipitation, wind patterns and

moisture fluxes, with strong regional expressions (Kallenborn et al., 2012, Serreze and Barry, 2011, Nesje et al., 2000).

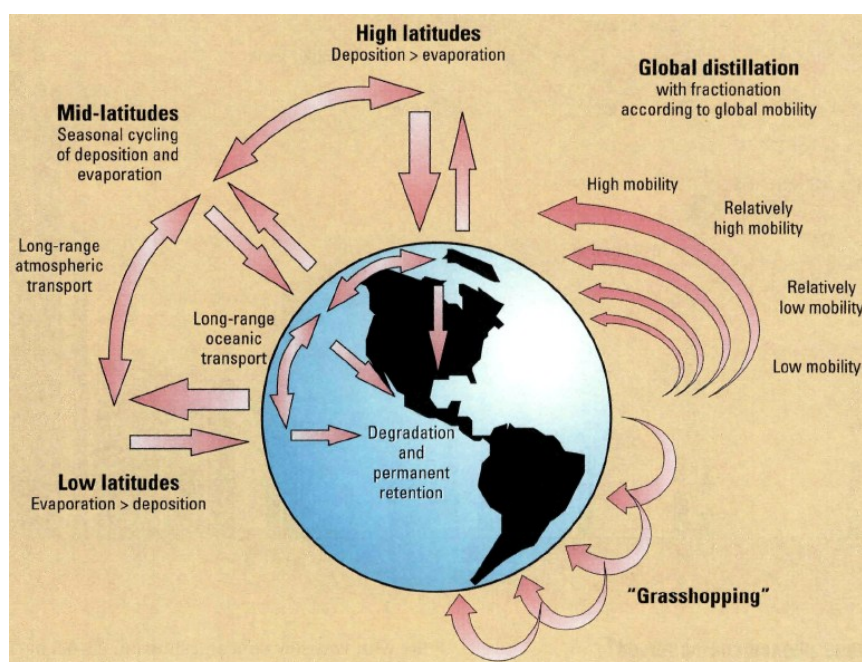


Figure 2 – POPs migration processes (modified from Wania and McKay, 1996).

Although during most of the last 10'000 years (the Holocene) there have been natural variations in climate, over the last two millennia and especially in the last two centuries, Arctic ecosystems have experienced a transient increase in almost all contaminants emitted by anthropogenic activities (Macdonald et al., 2005). Multiple drivers influence the so called 'Arctic amplification' – enhancement of near surface temperature as a response to increasing atmospheric greenhouse gas concentrations in the Arctic region in comparison to the northern hemisphere or the globe as a whole, especially during the autumn and winter seasons (Previdi et al., 2021, Serreze and Barry, 2011) – reflecting in ecosystem impacts (Descamps et al., 2017). Moreover, CC has re-defined the role of environmental reservoirs such as air, water, glaciers, snow, permafrost, soil, vegetation and sediments, making them significant 'secondary sources' of contaminants (Hung et al., 2022, Xie et al., 2022). This is possible because the exchange of these substances between reservoirs is critically related to temperature-dependent properties (i.e., vapour pressure - P_A , Henry's Law constant - H , partition coefficients for octanol–air - K_{OA} and octanol–water - K_{OW}), susceptibility to degradation or transformation (e.g., photolysis, metabolism, hydrolysis) of the chemical and environmental conditions (Ma et al., 2016) (Fig. 3). Generally, chemicals with low P_A and high K_{OA} show low gaseous concentrations in air and greater tendency to sorb to air-borne particles, likely more easily deposited close to the source region (Ma et al., 2016). These latter are considered 'heavier' chemicals, such as highly brominated PBDE congeners (octa- to deca-BDEs), and are less

susceptible to be transported over long distances (Qiao et al., 2020). However, the increasing temperature and sea-ice retreat, caused by the ongoing CC, results in an increase of P_A and a decrease of K_{OA} , favoring the volatilization and higher gaseous concentrations in air, but also an increase in H , promoting higher partitioning from seawater into air (Ma et al., 2011). Nevertheless, CC acts on biogeochemical processes involving contaminants in an opposite way. Indeed, while increasing ambient temperature favors the volatilization of chemicals, thus enhancing their mobility in the atmosphere and the potential for LRAT, on the other hand, increasing precipitation favors the scavenging, deposition and removal of chemicals from the atmosphere (Hung et al., 2022). Specifically, wet precipitation - the process whereby particulates and contaminants in the atmosphere are washed out through rain, snow or fog - is considered the most efficient mechanism in removing particulate matter and associated contaminants from the atmosphere (Beard et al., 2022b). As a result of CC, the Arctic has also experienced a widespread increase in precipitation in the last century, with the greatest evidence observed in autumn and winter (Box et al., 2019, Førland et al., 2011). The latter becomes relevant when combined with melting glaciers, snow and sea-ice, which contribute to increased meltwater runoff (Hagen et al., 2003) and the accumulation of contaminants in receiving environments (Macdonald et al., 2005). Melting glaciers are also responsible for changes in the dynamics of rivers, which will provide more fresh water and suspended particles in the catchment area (Hagen et al., 2003). Thus, fjords, being closely located to glaciers and more sheltered from ocean currents than open sea conditions, could become repositories for contaminants (Beard et al., 2022a). Nonetheless, it has been demonstrated that POPs can also be transported to the Arctic via oceanic currents, to a greater extent from by North Atlantic water passing through the Fram Strait, that represents the only deep connection to the Arctic Ocean, and partly from the Barents Sea; and a minor influx of Pacific water through the Bering Strait (Ma et al., 2018, Beszczynska-Möller et al., 2012, Stemmler and Lammel, 2010, Gioia et al., 2008). Once released in seawater, many anthropogenic contaminants being hydrophobic and with a tendency to bind with organic matter, are adsorbed or partitioned onto organic carbon or carbon-rich particles and a fraction of it may eventually reach deep waters and the seafloor with settling particles deposited over time by 'vertical sinking', driven primarily by biogeochemical processes operating in productivity near-surface waters (Hung et al., 2022, Galbán-Malagón et al., 2012, Dachs et al., 2002). Specifically, the mechanisms involving contaminants in the water column, from their initial presence at the surface to their deposition on the seafloor, are: (i) partitioning onto colloidal and suspended/sedimented particulate material, (ii) degradation of dissolved compounds, (iii) incorporation into trophic chains, and (iv) transport due to mixing of water masses by turbulent diffusion and vertical advection (Jurado et al., 2007, Dachs et al., 2002). Settling fluxes in the water column dominates over other removal processes and represents the final step controlling the surface recycling, impact and deposition of contaminants (Dachs et al., 2002).

Thus, marine sediments constitute stationary ‘end points’ for contaminants to be stored for a long period of time, and particularly sediment cores represent valuable natural archives of environmental contamination, by which sources and historical contaminant trends may be recognized.

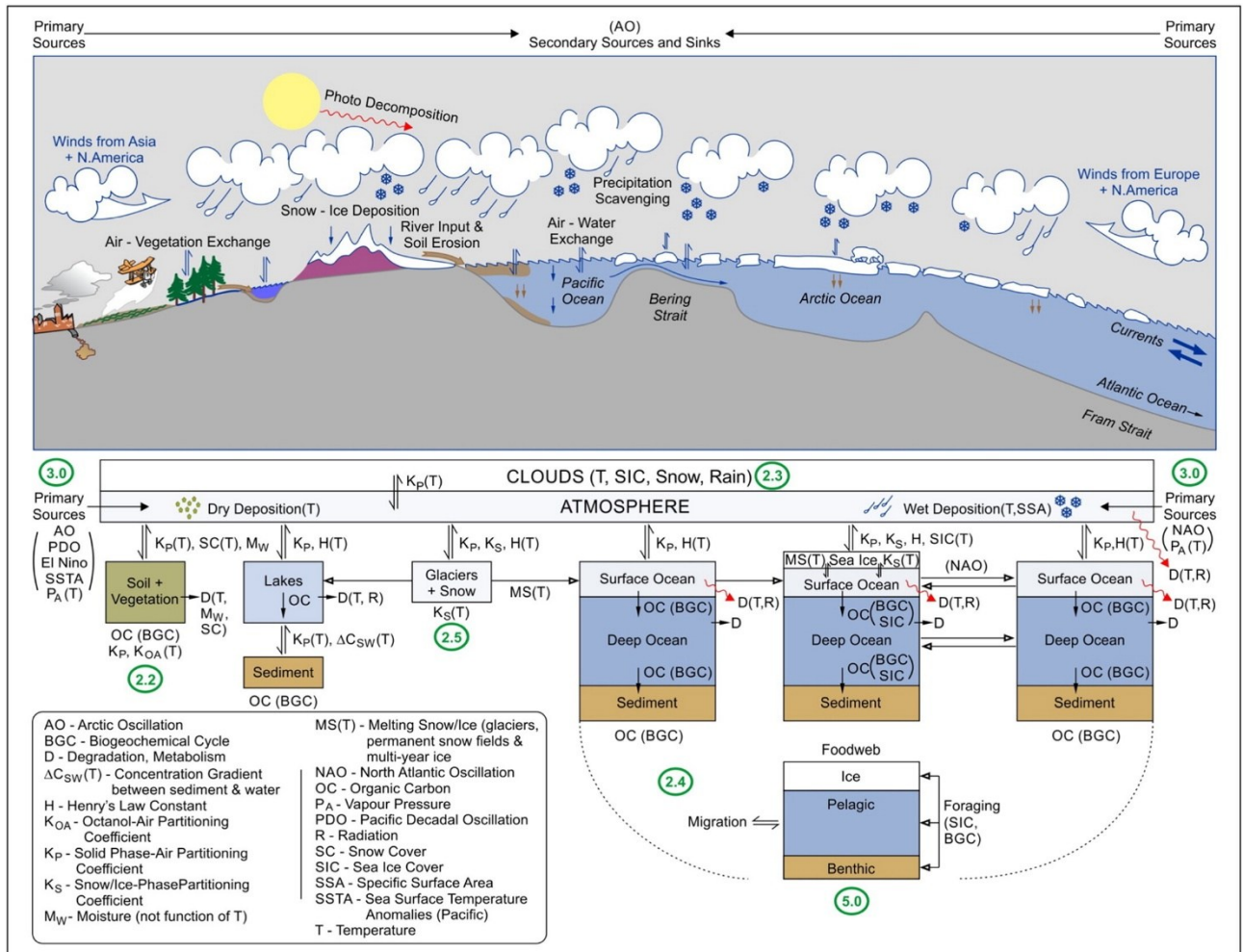


Figure 3 - Key climate-related processes influencing contaminant levels and fate in Arctic ecosystems (Ma and Macdonald, 2016).

1.2.3 Long-term data series as temporal trend indicators of pollution in the Arctic, with a focus on selected organic contaminants

Long-term monitoring data spanning several years or even decades are essential for identifying concentration trends related to the production and use of contaminants over time, and for assessing their persistence and fate within ecosystems. Temporal trends for these substances are influenced by local and seasonal factors specific to each location, such as geomorphology, ambient temperature, elevation, humidity, precipitation, proximity to open or ice-covered ocean surfaces, and distance to potential sources. These factors contribute to variations in contaminant presence across different locations (Hung et al., 2010). Additionally, studies on temporal trends may reflect the effectiveness

of regional and global regulatory actions intended to phase out or restrict harmful chemicals, as these trends are assumed to mirror changes in primary emissions directly (Vorkamp et al., 2022).

The adoption of the Stockholm Convention has emphasized the importance of monitoring POPs in the environment, and Arctic research on POPs has since become a significant focus (Lohmann et al., 2007). Initial measurements of Arctic haze and aerosols in the European Arctic began in the 1970s, following a mining accident in Ny-Ålesund (Svalbard) in 1962. In summer 1982, the first measurements of organic pollutants in the European Arctic were initiated across several locations – Bear Island, Hopen, Longyearbyen, and Ny-Ålesund – and in spring 1983 at Ny-Ålesund (Platt et al., 2022). The establishment of the Arctic Monitoring and Assessment Programme (AMAP) by the Arctic Council in 1991 furthered research on contaminants in the Arctic environment, enabling ongoing monitoring of an expanding range of chemicals in different matrices (Reiersen et al., 2024).

For this purpose, numerous studies have analyzed time-series data on organic chemical concentrations, especially legacy contaminants, in Arctic biotic and abiotic matrices. Regarding CECs, (Provencher et al., 2022) reported a 44-year temporal trend (1975-2019) of 26 UV filters (including 4-MBC, HMS, EHS and BP-3) analyzed in archived egg samples of three seabird species from the Canadian Arctic, revealing different peak concentrations for each compound in relation to their production and usage. Regarding legacy contaminants, (Daugaard-Petersen et al., 2018) investigated skull size and bone mineral density (BMD) in polar bears from East Greenland and Svalbard, sampled from 1892–2015 and 1964–2004 respectively, concluding that certain POPs (including PBDEs) impacted polar bear bone density and size over time. Studies on legacy contaminants in polar bears tissues from Hudson Bay (1991–2007) (McKinney et al., 2010) and from Alaska to Svalbard (2005–2008) (McKinney et al., 2011), revealed that PBDE levels significantly increased, though they were lower in 2007 than in 2003. (Rotander et al., 2012) analyzed selected PBDEs congeners in marine mammals from Arctic and North Atlantic regions, spanning 1986–2009, and found peak levels in samples from the late 1990s to early 2000, which likely reflected increased global production of PBDE mixtures during the 1990s. (Vorkamp et al., 2008) analyzed POP concentrations (including PBDEs) in ringed seals from Central West Greenland collected between 1982 and 2006, finding that while all organochlorines POPs displayed decreasing trends, BDE-47 showed a significant annual increase of 5%. Increasing PBDE trends were also documented in South Greenland peregrine falcon eggs collected between 1981 and 2003 (Vorkamp et al., 2005) and in seabird eggs collected in Northern Norway and Svalbard region from 1983 to 1993, before leveling off (Helgason et al., 2008). (Rigét et al., 2019) reviewed over 1,000 POP time-series in Arctic marine and freshwater biota, noting an overall decrease in concentrations over the last two to three decades. Specifically, PBDEs followed a pattern of rising concentration up to the mid-2000s, after which levels began to decline. Similar trends

were observed in Great Lakes (Canada) predator fish from 1979 to 2016, with PBDE concentrations significantly increasing in the period 1990-2000, then rapidly decreasing from 2000-2007, and remaining relatively stable therefore (Zhou et al., 2019). PBDE temporal trends were also analyzed in sediment cores from seven West Greenland lakes (Malmquist et al., 2003) and three Canadian Arctic lakes (Nunavut) (Muir et al., 2003), both of which showed increasing concentrations in recent sediment layers. Collectively, these studies indicate similar rising PBDE trends over time across biota and sediment matrices.

Available time series for air concentrations are generally shorter than those for biota and sediments. However, since the 1990s, an increasing number of chemicals have been monitored in Arctic air samples from various locations. (Hung et al., 2016), as part of the AMAP network, analyzed a 20-years temporal trend in POPs concentrations in Arctic air samples. Most POPs showed slowly declining trends, consistent with reduced primary emissions in recent decades compared to the increase in emissions from secondary sources; while, other POPs (including PBDEs) increased at specific locations, possibly due to warming in the region and ongoing primary emissions. Air samples collected in the Canadian High Arctic (Alert, Nunavut) from 2002–2004 showed inter-annual PBDE concentrations increases, with doubling times of 2–6 years (Su et al., 2007). Temporal PBDE trends in the Canadian Great Lakes atmosphere (2005–2014) showed a decreasing level, although chemicals persisted in the environment (Shunthirasingham et al., 2018). (Bossi et al., 2016) studied atmospheric POP concentrations (including PBDEs) at Villum Research Station, Station Nord (North Greenland) in the period 2008-2013, but found no discernible trend due to high inter-annual variability and the short monitoring period.

These findings underscore that these chemicals do not exhibit a uniform seasonal pattern with winter minimum and summer maximum concentrations, nor do they behave identically at different locations. Each site has unique physical environmental conditions and distinct processes influencing chemical fate (Wong et al., 2021). Some time-series data reveal recent disruptions in declining trends, indicating both a reduction in primary emissions and potential climate-related secondary emissions (de Wit et al., 2022) (Fig. 4). The lack of long-term studies on temporal trends for selected CECs (synthetic fragrances and organic UV-filters) in the Arctic environment, despite their presence in Arctic matrices (D'Amico et al., 2024, D'Amico et al., 2022, Xie et al., 2022, Sonne et al., 2021, Vecchiato et al., 2018, Tsui et al., 2014, Xie et al., 2007, Kallenborn et al., 1999), prevents determination of whether their levels are increasing or decreasing over time and, consequently, whether regulation is necessary. Therefore, there is a pressing need for monitoring networks conducting continuous sampling to generate long-term data on the sources and fate of these contaminants in the Arctic.

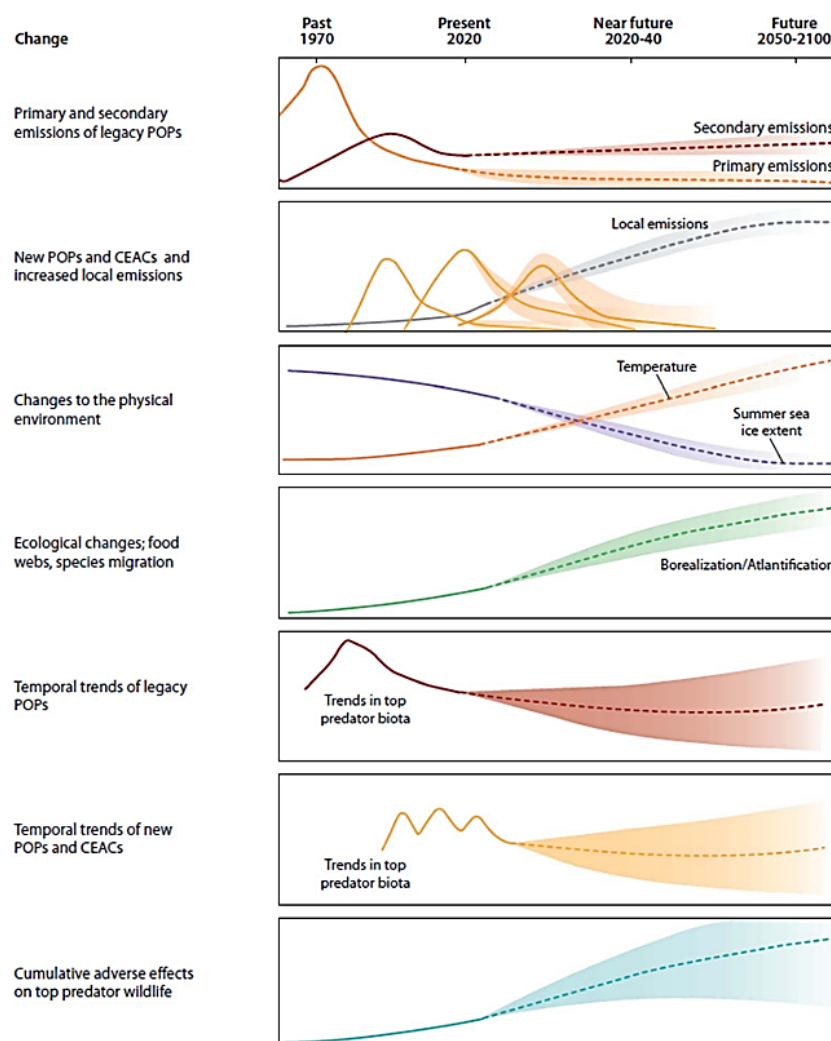


Figure 4- Temporal trends of direct and indirect effects of climate change on biological, chemical and physical processes that influence the fate of contaminants (POPs: Persistent Organic Pollutants; CEACs: Chemicals of Emerging Arctic Concern) within a rapidly warming Arctic. Dashed lines indicate predicted relative trends compared to modelled or measured trends (solid lines) for the period 1970–2020. Shaded areas indicate relative uncertainty in projected trends (de Wit et al., 2022).

1.2.4 Population growth and its implications in contaminants distribution in the Arctic

The 21st century marked the beginning of a rapid increase in global population and anthropogenic activities, and this has contributed significantly to global warming, with a higher incidence in the Arctic than in other regions of the world (IPCC, 2023, Larsen and Fondahl, 2014). Some northern latitude states (i.e. Arctic Canada, Iceland and Alaska) have also seen a substantial increase in population, with higher migration from small settlements to urban centres (Heleniak, 2020). The migration and urbanization trends, as stated in the latest report by the Intergovernmental Panel on Climate Change (IPCC, 2023), are also responsible for increasing climatic hazards exposure.

In this regard, the latest AMAP report (AMAP, 2021) showed that in a changing context where the climate will tend to be ever warmer, Arctic and sub-Arctic populations will also grow and, consequently, so will human activities. In a recent review, (Muir et al., 2025) analyzed and discussed the future implications and emissions of contaminants in relation to human activities (i.e. tourism, infrastructure development, shipping and fishing, oil and gas production) in the Arctic. Therefore, human socio-economic development results in new exposure pathways and an increase in the primary sources of these contaminants in the Arctic region (Muir et al., 2025; Hung et al., 2022).

For this reason, the analysis of human presence becomes a key issue within the understanding of both legacy and emerging contaminant release dynamics, as climate change is already altering, and will continue to do so in the future, the ecosystem balances as they have been known so far.

CHAPTER 2 - Study Area

2.1 Geography

Fjords act as ‘bridges’ between terrestrial and marine environments and, in the Arctic, their dynamics are characterized by strong seasonality, rapid melting rates and consequent freshwater release, sea-ice formation and persistent orographic winds (Cottier et al., 2005). The fjords along Svalbard’s west coast, especially are considered sentinels for environmental change, influenced by both Arctic and Atlantic currents as well as by inputs originating within the fjord itself. The Kongsfjorden–Krossfjorden system (KKS) located along the north-western coast of Spitsbergen (the largest island of the Svalbard archipelago, Norway), includes two fjords located between 78°40’ and 77°30’N and 11°03’ and 13°06’E, along the north-western coast of Spitsbergen, the largest island of the Svalbard archipelago (Norway). Kongsfjorden forms the southern arm of the fjord system, extending in SE-NW direction; while Krossfjorden forms the northern arm and is oriented in N-S direction (Svendsen et al., 2002). The estimated total volumes of Kongsfjorden and Krossfjorden are 29.4 and 25 km³, respectively (Ito and Kudoh, 1997). At their seaward end, the outer basins of both fjords merge to form the main submarine glacial trough, the Kongsfjordrenna, which provides a deep-water connection across the shelf (Cottier et al., 2010). Kongsfjorden is 20 km long, with a variable width of 4–10 km, featuring a series of deep basins (between 250–300 m or >300 m depth) decreasing to less than 100 m towards the inner part of the fjord near the Blomstrandhalvøya peninsula. In the innermost part, towards the Lovénøyane islands and the glacier fronts, water depths decrease further to less than 50 m (Husum et al., 2019). Krossfjorden, by comparison, is approximately 30 km long with 3–6 km in width, reaching a maximum depth of 374 m. The inner region is divided by Kongs Haakon Halvøya into two smaller fjords: Lilliehöökfjorden and Möllerfjorden (MacLachlan et al., 2010). Unlike Kongsfjorden, the Krossfjorden seabed is relatively smooth, interrupted by two small across-fjord channels, likely formed by riverine sediment transport from rivers on the western shore, located around 15 and 22 km from the Lilliehöökreen glacier in the north (Howe et al., 2003).

2.2 Oceanic currents and water masses

The main ocean currents influencing the hydrology of the KKS are the West Spitsbergen Current (WSC) and the Spitsbergen Polar Current (SPC), both flowing along the West Spitsbergen Shelf (WSS) in the Fram Strait (Guruvayoorappan et al., 2020) (Fig. 5). The eastern branch of the WSC represents the major source of warm and saline Atlantic Water (AW) entering the Arctic Ocean. As this eastern branch of AW flows northward along the western coast of Spitsbergen, it undergoes cooling and freshening through mixing with ambient waters and interaction with the atmosphere (Cottier et al., 2007). The WSC is separated from the western Spitsbergen fjords by a shallow shelf, along which the SPC

flows northward, carrying colder and fresher Arctic water (ArW) originating from Storfjorden and the Barents Sea (Svendsen et al., 2002; Cottier et al., 2005). As a result, the interaction between AW and ArW results in denser meltwater flowing northward, due to ice melting and heat loss to the atmosphere, gradually making the shelf water gradually warmer and more saline. Consequently, the northern fjords on the west Spitsbergen shelf, such as KKS, exhibit more Atlantic characteristics compared to fjords further south on the shelf (Cottier et al., 2010).

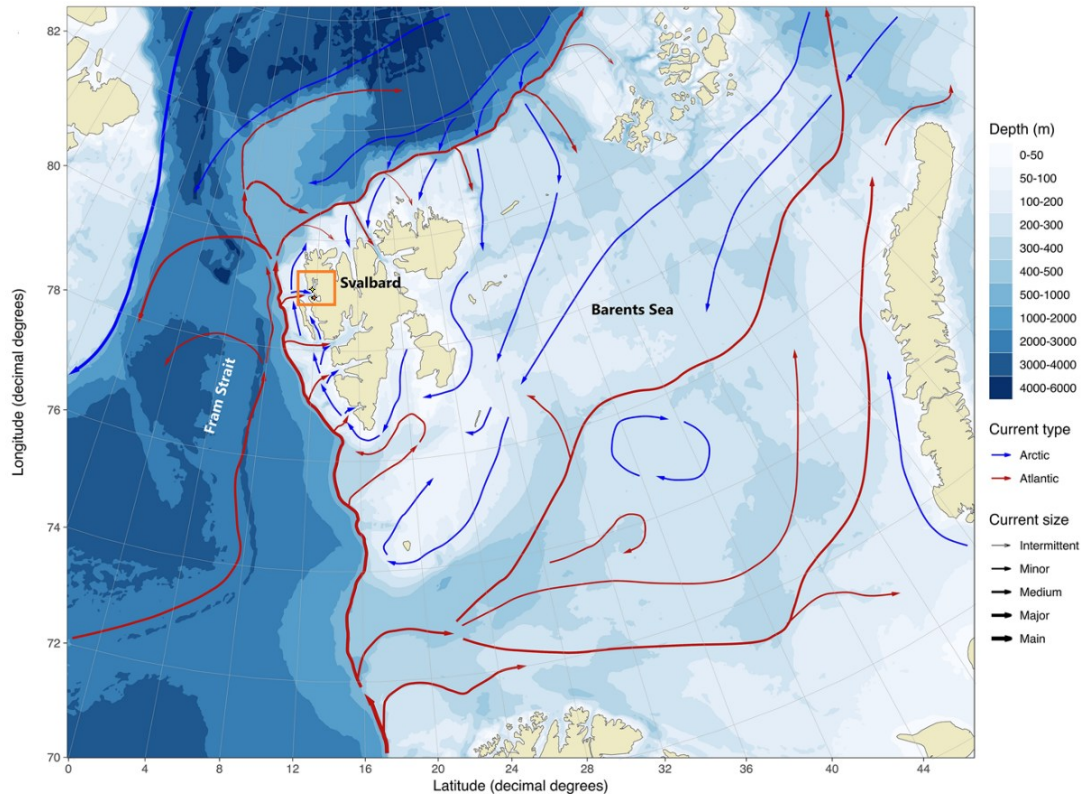


Figure 5 - Map of Svalbard, with two main current types influencing the hydrology of Kongsfjorden-Krossfjorden system (within the orange box) (Modified from Guruvayoorappan et al., 2020).

The water column stratification in the Kongsfjorden varies seasonally and interannually, influenced by winter cooling and sea-ice formation, freshwater discharge and the inflow of external water masses (Cottier et al., 2005). Three primary water masses are typically observed in Kongsfjorden: (1) surface waters, composed of fresh water from glaciers, basal melting and terrestrial sources such as snowmelt and rivers; (2) intermediate mixed water masses, where fresher, colder waters combine with advected warm AW; and (3) the deepest, densest water masses, characterized by high salinity, such as AW entering the fjord through geostrophic control at the shelf-edge (Nilsen et al., 2016, Cottier et al., 2005) (Fig. 6). Local winds significantly influence internal fjord circulation. Fresh surface waters are driven along the fjord's axis by wind, moving towards the northern shore and then flowing out the fjord. Simultaneously, on the southern shore this outward flow of fresh

water is balanced by the inflow of AW deeper in the water column (Sundfjord et al., 2017, Ingvaldsen et al., 2001).

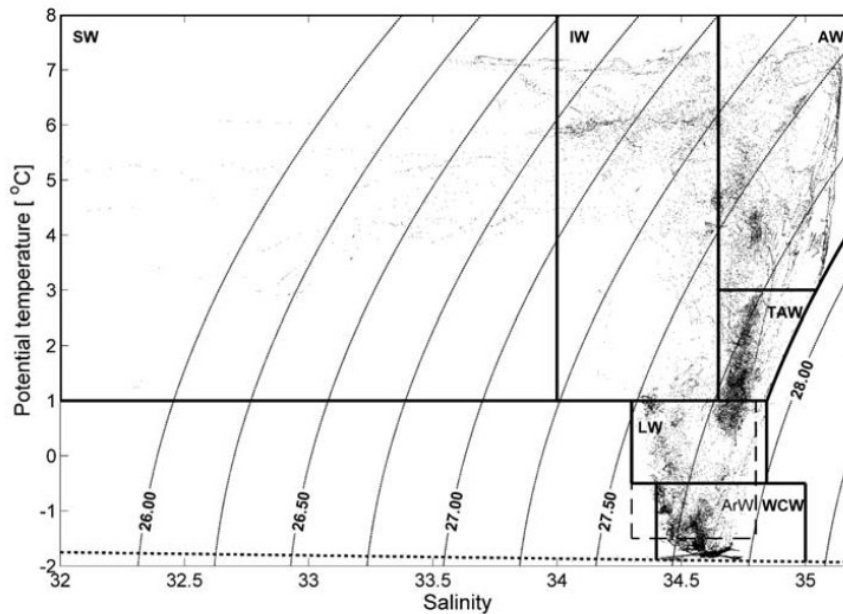


Figure 6 – Temperature-Salinity diagram for the water masses described for the Kongsfjorden and adjacent shelf region [External water masses: Atlantic Water (AW) and Arctic Water (ArW); Internal water masses: Winter Cooled Water (WCW), Local Water (LW), Surface Water (SW), Transformed Atlantic Water (TAW) and Intermediate Water (IW). Isopycnals are at 0.25 intervals, and the dotted line indicates the freezing point (Cottier et al., 2005).

However, although Atlantic water has always entered the fjord in summer, there has been a gradual increase in the volume of AW entering in winter as well, creating the conditions for a gradual “Atlantification” of the KKS ((Tverberg et al., 2019, Divya and Krishnan, 2017, Cottier et al., 2007). The Atlantification of the eastern Fram Strait has been a rapid and early process, beginning in the 20th century, with notable impacts on the Arctic ecosystem. These effects include rapid retreat of the sea ice edge, warmer summer waters, increased winter convection, and shifts in benthic foraminiferal communities (Tesi et al., 2021). Together with rising precipitation in the region, these processes have led to increased snowmelt and terrestrial runoff, which in turn influence the stability and dynamics of tidewater glacier margins that are highly sensitive to ambient ocean temperatures (Skirbekk et al., 2010, Maclachlan et al., 2010).

2.3 Freshwater input and sediment supply

The KKS receives freshwater inputs from both land and marine-terminating glaciers. Krossfjorden is fed by five calving glaciers along its eastern coast draining into it, with Lilliehöökreen at its head being the major contributor (Howe et al., 2003; Svendsen et al., 2002). As for the Krossfjorden, in the Kongsfjorden the glacier runoff is the major contributor of freshwater entering the fjord, since more than 80% of the land area

drainage is covered by glaciers (Svendsen et al., 2002). Additional freshwater inputs include snowmelt, precipitation, run-off, groundwater discharge and rivers. The largest and most studied river is Bayelva, in the Kongsfjorden, which receives runoff from the two small land-terminating glaciers Austre and Vestre Brøggerbreen (Hagen et al., 2003). Kongsfjorden is surrounded to the south by small land-terminating glaciers, whereas to the east and north, large tidewater glaciers contribute to the majority of freshwater runoff to the fjord (Pramanik et al., 2018). Kronebreen and Kongsvegen are among the fastest-flowing glaciers in Svalbard, making them major sources of freshwater and sediments input in the fjord (Streuff et al., 2015). These two glaciers can also serve as tracers for sediment provenance due to the close relationship between the geology of the glacier's hinterland and the mineralogical composition of the marine sediments (Shi et al., 2018). Specifically, higher iron concentrations are likely associated with Kronebreen supply, while higher calcium concentrations suggest Kongsvegen as the dominant sediment source (Streuff et al., 2015).

The sediment supply in this fjord system is predominantly controlled by the settling of fine-grained sediments from meltwater plumes and ice rafting, leading to high stratification in fjord coastal waters (Husum et al., 2019). At the interface between fresh and salt water, particles can aggregate and form larger particles or “flocs” with faster settling velocities, in a process known as “flocculation”. This process is strongly influenced by suspended particulate matter (SPM) concentration, turbulence and salinity gradient (Meslard et al., 2018) (Fig. 7). SPM concentrations tend to decrease with distance from the glacier front due to the sedimentation of coarser, flocculated particles (Meslard et al., 2018).

Tidal glaciers and rivers are key contributors to the transport of fine-grained material such as clays and silts across considerable distances, with some sand deposits occurring close to glacier front (Dallmann, 2015). In contrast, coarse-grained material, or ice-rafted debris (IRD), is carried offshore by icebergs or sea ice, while fine sediments travel with meltwater plumes. This leads to lower IRD concentrations in the inner fjord, with higher concentrations in the central fjord and at certain points in the Kongsfjordrenna (Husum et al., 2019). Sediment runoff is typically higher in summer and lower in winter. However, sediment inputs from tidewater glaciers continues year-round, unlike rivers, which freeze for at least half of the year and contribute only seasonally (Dallmann, 2015). Sedimentation rates vary based on several factors, including distance from the sediment source and local bathymetry. The thickest sediment deposits are found near tidewater glaciers, river mouths, and in seafloor depressions, which act as sediment traps. In contrast, deposition is reduced further from sediment sources and in shallow areas, where higher bottom current velocities may even cause erosion. For example, at the grounding-line fan of Kronebreen glacier in Kongsfjorden, sedimentation rates can exceed 300 mm per year, corresponding to an average sediment yield of 12 kton/km² per year (Dallmann, 2015). Studies by (Svendsen et al., 2002) and (Zajaczkowski, 2008) also show

a marked decrease in sedimentation rates from the glacier fronts to the fjord's outer regions on the continental shelf, with rates decreasing by two orders of magnitude over this distance.

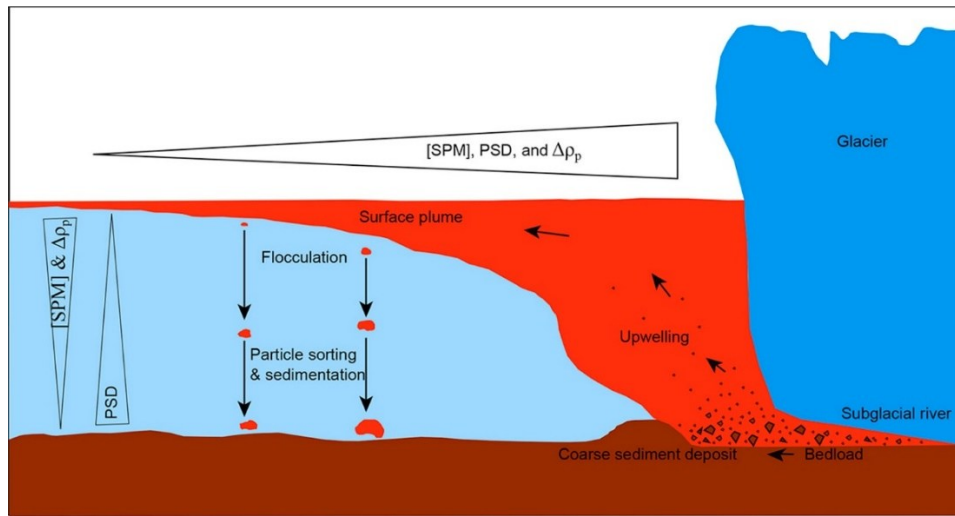


Figure 7 – Conceptual model of the processes involved in the particles transport (river inputs, upwelling, gravitational sorting, and flocculation) occurring in front of a coastal glacier in an Arctic fjord. [SPM: suspended particulate matter; PSD: in-situ particle size distribution; $\Delta\rho_p$: effective density of particle assemblage (in kg m^{-3})] (Meslard et al., 2018).

2.4 Human presence

Since the discovery of Svalbard in 1596, the human presence in this region has undergone significant changes, starting with whalers in the 17th century, followed by miners in several coal mines throughout the territory in the 19th century (Avango et al., 2010). However, it was the Svalbard Treaty of 1920 that declared this territory under Norwegian sovereignty, facilitating a permanent Norwegian presence (Paglia, 2020).

The KKS is located far from most local contaminant sources, but a small village hosting a research community, Ny-Ålesund, is located on the southern side about mid-way between the inner and outer Kongsfjorden. In the 20th century, in Ny-Ålesund, as well as for other parts of the Svalbard territory, the main activity was coal mining (1916-1962), with the mine workers and their families settled (~300 people) in the village (Reymert, 2016) (Fig. 8). By 1964, after the mining operation was stopped, the village of Ny-Ålesund was defined a center for international Arctic research and environmental surveillance (Fride Eeg-Henriksen and Sjørmæling, 2016).

Figure 9 shows the temporal trend of the population on Svalbard from 1923 to 2012, including residents in the main settlements from 1981 to 2012. After the arrival of the first inhabitants in the 1920s, there was a reduction in population due to the onset of World War II. After the war ended, in the late 1940s-early 1950s, there was an increase in population that peaked in the early 1980s. This could probably be explained by the easier access to Svalbard, as an airport became operational in Longyearbyen in 1975

(Andreassen Ivar et al., 2009). The decline observed between the late 1980s and mid-1990s may be due to the 'coalmining crisis', which at the time was still the major activity responsible for human presence on the land. After that, the almost depletion of the reserves of coal and its falling price contributed to the shift from coalmining to scientific research territory (Paglia, 2020).



Figure 8 - Ny-Ålesund in 1920 (Reymert, 2016).

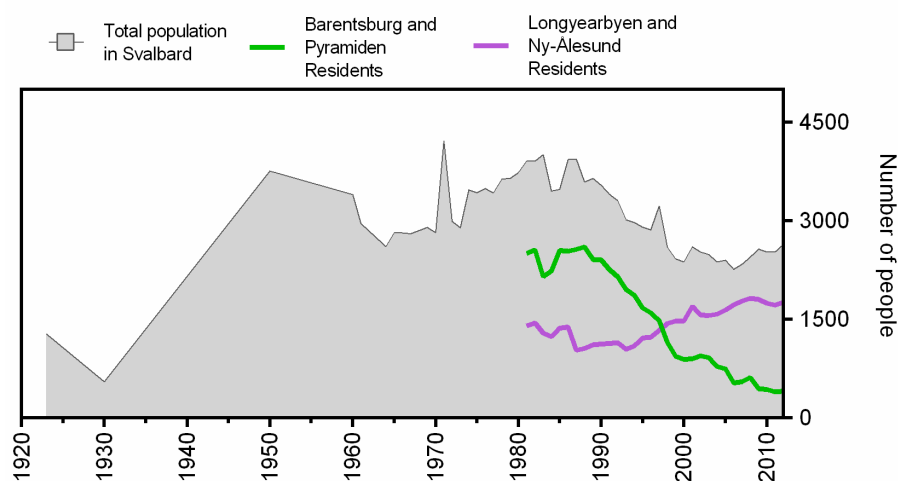


Figure 9 - Time series of the total population in Svalbard (1923-2007) and residents in the main settlements: Longyearbyen and Ny-Ålesund; Barentsburg and Pyramiden (1981-2010). ('Resident' here means all those living in the archipelago and who intend to stay for more than 6 months) (Source: Kristiansen, 2014).

After that, in the early 1990s in the settlements of Barentsburg and Pyramiden, inhabited by Russians, and Longyearbyen and Ny-Ålesund, inhabited by Norwegians, there was a decline in population. Since then, the number of Russians has continued to fall, while the same cannot be said for Norwegians (Andreassen Ivar et al., 2009). Indeed, in early 1990s, the commercial focus on tourism started up in Longyearbyen, growing substantially from 1999 (Kristiansen, 2014).

For this reason, from the late 1980s, Ny-Ålesund has undergone a fundamental transformation, moving from industrial coalmining activity to international scientific research (Paglia, 2020; Reymert, 2016). In that period Norway was exploring strategies to diversify Svalbard's economy due to declining coal prices, and this occurred in conjunction with the advent of the ever-increasing interest for the emergence of climate change and polar ozone depletion as major political issues (Paglia, 2020). Therefore, Norwegian authorities began to actively encourage and facilitate the establishment of research stations managed by national polar institutes, with contributions from the Kings Bay AS company (Paglia, 2020). However, it was only from the 1990s onwards that research became the main activity in Ny-Ålesund (Fride Eeg-Henriksen & Sjørmæling, 2016). In 1990, Kings Bay AS specialized in service provider, including technical support, repurposing buildings and construction of customized scientific infrastructure, operating on the settlement's transformation from underutilized post-industrial site to thriving international research base, reaching an ever-increasing number of registered research days year by year (Paglia, 2020, Sanders et al., 2006). Figure 10 depicts a timeline indicating the installation of the relevant instrumentation and international research bases, in comparison with the overnight stays in Ny-Ålesund in the period 1989-2010. Except for 1989 and 1990, data from before 1994 are not available. It was only in the early 1990s that Norway decided to extend the possibility of scientific research at Ny-Ålesund to other countries. Since then, the overnight stays of all visitors have been recorded continuously since 2004, when the Ny-Ålesund Science Managers Advisory Committee (NySMAC) was established with the aim of close co-ordination of research activities and associated logistics. Nowadays, Ny-Ålesund counts around 150 people (including researchers and Kings Bay AS locals) during the summer period, compared to a maximum of 30-35 during wintertime (McGovern et al., 2022a).

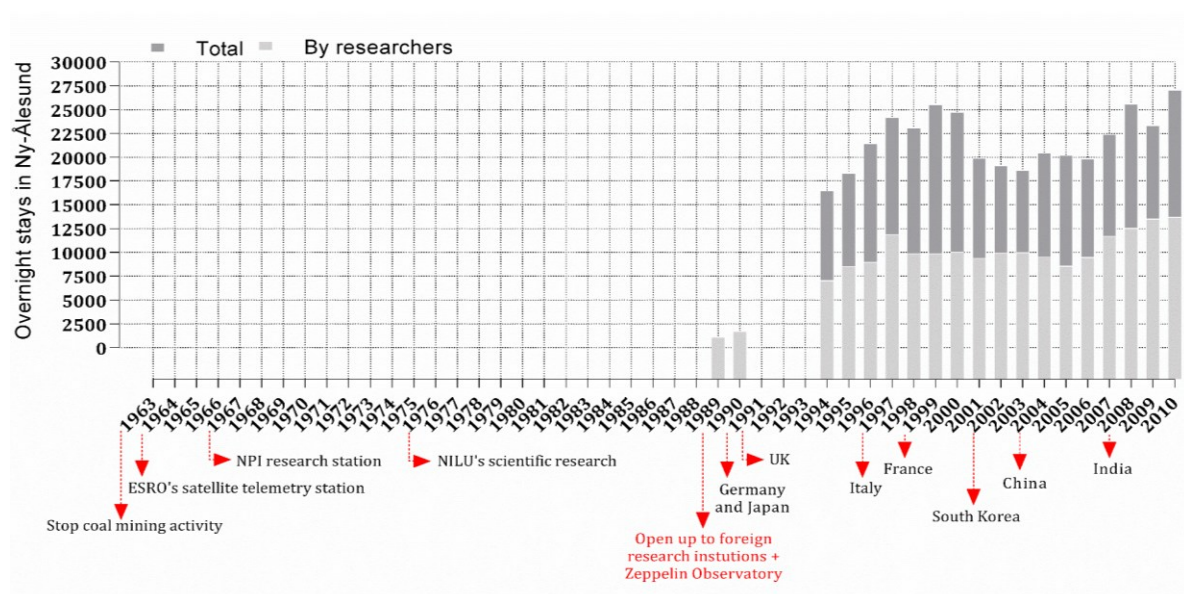


Figure 10 - Timeline of the installation of the relevant instrumentation and international research bases, in comparison with the overnight stays in Ny-Ålesund in the period 1989-2010 (Source: Kings Bay AS).

In 1995, following a rapid expansion of human activity and facilities in Ny-Ålesund the NySMAC committee considered appropriate to assess the potential effects this might have on the surrounding environment. Thereby, in early 1996 the NySMAC committee drafted an Environmental Impact Assessment (EIA), also approved by the board of Kings Bay Kull Compani (KBKC) A/S, with the objective to examine the impact of human presence on the environment at Ny-Ålesund (Shears et al., 1998). It already emerged at that time and was confirmed by other reports, in 2006 (Sanders et al., 2006) and in 2019 (Granberg et al., 2019), that the increasing human activities had a significant impact on the local environment, such as: habitat loss and damage to wildlife, especially for tundra; disturbance of marine soft sediments and benthic communities due to shrimp trawling and pollution caused by organic contaminants leaching from rubbish dumps; soils contamination by diesel fuel spills; pollution related to local emissions by the power plant, airport, cruise ships, open burning and disposal of sewage and environmentally hazardous material (Shears et al., 1998; Sanders et al., 2006; Granberg et al., 2019).

CHAPTER 3 – Materials and methods

3.1 Sediment cores collection and pre-treatment

In this study, four sediment cores were analyzed and the two sampling campaigns (one in 2011 and the other in 2021) took place in the Kongsfjorden-Krossfjorden system (KKS) (Fig. 11). Information on individual cores is provided in Table 3.

Cores have been collected on board the MS Teisten operated by Kings Bay AS using a SW104 light gravity corer able to preserve the sediment water interface and minimize the sediment compaction. The locations chosen for sediment core collection, both in 2011 and 2021, were identified based on a high-resolution seismic survey conducted in September 2010. During this survey, over 130 miles of sub-bottom profiles were acquired to delineate morpho-bathymetric features and surface seismic-stratigraphy (Miserocchi et al., 2016). Sites where modern sedimentation seems to be active were selected to ensure a continuous and undisturbed sedimentary record.

After collection, the cores were stored at +4 °C before shipping. After arriving in Italy, at the CNR-ISP of Bologna, the cores were splitted in two halves and one half was subsampled at a resolution of 0.5 and 1 cm. The cores have been described for visual characteristics and scanned with X-Ray to highlight the inner structures of the sediment column (Fig. 12). From each sub-sample, two aliquots were obtained: one was freeze-dried, homogenized using an agate mortar and pestle, for organic carbon, retene (only for the three cores collected in 2021) and contaminants analyses; one was dried in oven at 60°C for 24 hours, for sediment properties characterization (e.g. water content and grain size). The freeze-dried aliquots have been stored until subsequent chemical analyses. Sediment samples were weighed before and after heating to account for water content loss during the drying process. Water content was calculated by subtraction of dry weight from wet weight and used to calculate the dry bulk density (DBD).

Table 3 – Metadata of the studied sediment cores.

Location	Core label	Data of collection	Latitude	Longitude	Water Depth (m)	Core length (cm)
Kongsfjorden	NYA11_09	September 2011	78°56.457'	012°09.111'	171	101
Krossfjorden	NYA21_01	September 2021	79°07.879'	011°43.814'	318	89
Kongsfjorden	NYA21_03	September 2021	78°56.940'	012°09.115'	190	117
Kongsfjorden	NYA21_04	September 2021	78°59.763'	011°39.423'	320	108

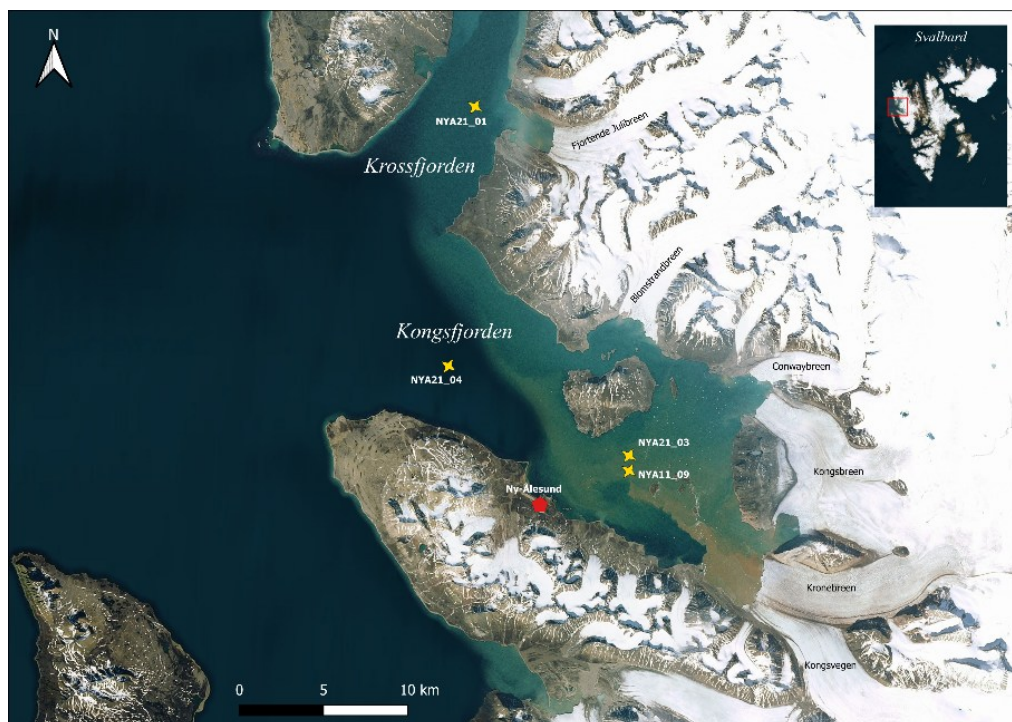


Figure 11 – Study area and cores locations.

3.2 Analyses for physical and compositional characteristics of sediments

3.2.1 Non-destructive analyses: XRF core-scanning

Immediately after opening, each core was examined by the III^o generation XRF (X-Ray Fluorescence) Core Scanner (XRF-core scanner, Avaatech) at the CNR-ISMAR XRF lab, in order to evaluate the elemental composition of the sediment. Acquired XRF scanning data is semi-quantitative and is reported as ratios of counts per unit time per unit area (cps) or elemental ratios (Croudace et al., 2006). Technical specifications of the instrument are described in detail in (Richter et al., 2006) and (Croudace and Rothwell, 2015). As well as for high-resolution digital photos and colour scanning of sediments, this instrument is used to perform a complete scan for major elements, to obtain the bulk geochemistry of the core at a resolution of 1 cm (Fig. 12).

3.2.2 Grain size analysis

Grain size analysis was performed by soaking the samples in a solution of water and hydrogen peroxide (H₂O₂, 35%) (1:10, v/v) for three days, to remove salts and organic matter that aggregate individual granules. Then, they were passed through a 63-µm sieve, resulting in two fractions: mud (<63µm) and sand (>63µm) (Wentworth, 1922). The gravel fraction (>2mm) was removed in preliminary sedimentological analysis.

3.2.3 Total Organic carbon (TOC) content

For all sediment cores, a small aliquot (ca. 5 mg) of freeze-dried samples was treated with 10% HCl for 24h to remove carbonates prior to analysis (EA-IRMS-FLASH 2000 Elemental Analyzer coupled to a mass spectrometer Finnigan DeltaQ+XP, Thermo Fisher Scientific) to measure the organic carbon (OC) and the stable isotopes contents of C ($\delta^{13}\text{C}$).

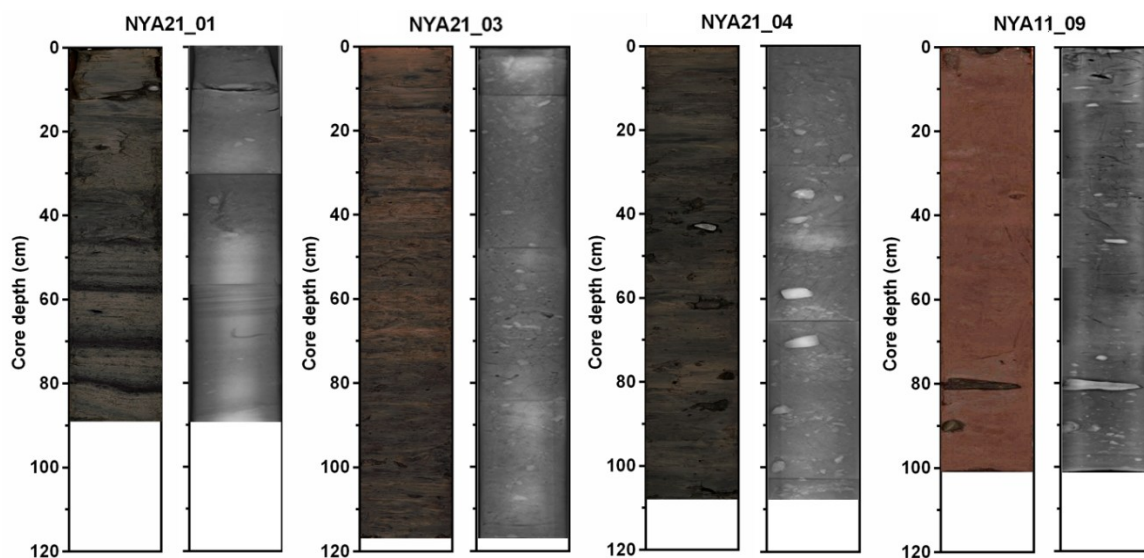


Figure 12 – Sediment cores high-resolution photos and x-ray scan acquired with XRF-core scanner.

3.3 Analyses of organic ultraviolet filters (UV-Fs), synthetic fragrances (SFs) and polybromodiphenyl ethers (PBDEs)

3.3.1 Chemicals and solvents

Emerging contaminants. Regarding the emerging contaminants, the target analytes comprised seven UV-Fs and stabilizers, six synthetic fragrances (SFs) (Tab. 4). Among the UV-Fs, 3-(4-Methylbenzylidene) camphor (4-MBC), 2-Hydroxy-4-methoxybenzophenone (BP-3), Ethylhexyl methoxycinnamate (EHMC), Benzoic acid, 2-hydroxy-, 2-ethylhexyl ester (EHS), 3,3,5-Trimethylcyclohexyl salicylate (HMS), 2-Ethylhexyl 4-(dimethylamino) benzoate (OD-PABA), octocrylene (OC), and benzophenone d10 were purchased from Sigma–Aldrich (Madrid, Spain). Among the SFs, 4-acetyl-1,1-dimethyl-6-tert-butylindane (ADBI, celestolide), 6-acetyl-1,1,2,3,3,5-hexamethylindane (AHMI, phantolide), 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindane (ATII, traseolide), and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN, tonalide) were purchased from LGC Standards (Barcelona, Spain), while 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(g)-2-benzopyran (HHCB, galaxolide) was purchased from Dr Ehrenstorfer GmbH (Augsburg, Germany), and (1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethylnaphthalen-2yl)ethan-1-one (OTNE, Iso E Super) was purchased from Bordas Chinchurreta Destilations (Seville, Spain). Labeled standards triphenylphosphate d15

(TPP-d15), purchased from Chiron (Trondheim, Norway), and benzophenone d10 (BP-d10), purchased from Sigma–Aldrich (Madrid, Spain) were used as surrogate standards; whereas a mixture of isotopically labelled compounds (acenaphthene-d10, chrysene-d12, phenanthrene-d10, and perylene-d12), purchased from Dr Ehrenstorfer GmbH (Augsburg, Germany) was used as internal standard. Solvents dichloromethane (DCM), acetone and ethyl acetate were of chromatography quality, purchased from Sigma–Aldrich (Madrid, Spain) and Scharlau (Barcelona, Spain).

Legacy contaminants. Regarding the legacy contaminants, the target analytes comprised 38 polybromodiphenyl ethers (PBDEs) congeners: BDE-17, -25, -28, -30, -47, -49, -71, -66, -74, -75, -99, -85, -97+118, -100, -101, -116, -119, -138, -139, -153, -154, -155, -156, -173+190, -182, -181, -183, -185, -191, -196, -197+204, -198, -203, -206, -208). The analytical Standard Reference Material (SRM) NIST 2257 for 38 congeners of PBDEs in 2,2,4-trimethylpentane was purchased from Sigma-Aldrich (Steinheim, Germany) (Tab. 5). Labeled standards PBDE47 (^{13}C -PBDE-47) and PBDE183 (^{13}C -PBDE-183) (purity $\geq 99\%$), were used as internal standards for PBDEs analyses. Solvents hexane (Hex) and acetone (Ace) were of high-performance liquid chromatographic quality (HPLC).

Retene. Regarding retene, docosane was purchased from Sigma-Aldrich (Steinheim, Germany), and used as internal standard. Solvents dichloromethane (DCM) and hexane (Hex) were of high-performance liquid chromatographic quality (HPLC).

3.3.2 Extraction and clean-up

Emerging contaminants. Regarding the emerging contaminants, the extraction of the selected UV-Fs and SFs has been carried out using the Pressurized liquid extraction (PLE) technique, also known as Accelerated Solvent Extraction (ASE), based on the extraction and in-cell clean-up method described by (Pintado-Herrera et al., 2016). PLE of target compounds was achieved using an accelerated solvent extractor ASE (Dionex-350 system (Thermo Co., Sunnyvale, CA, USA) equipped with 11-mL stainless steel extraction cells and 30-mL collection vials (Fig. 13). In cell clean-up was performed simultaneously by placing sorbents (activated alumina and copper) inside the cell. Briefly, 3.5 g freeze dried sediment sample was weighed and twenty-four hours before extraction, sediment samples were spiked (20 μL) with a solution of deuterated surrogates (BP-d10 and TPP-d15) at a final concentration of 100 ng mL $^{-1}$ to account for losses during the extraction procedure. Each cell was prepared as follows: a cellulose filter was placed at the bottom of the cell followed by 0.5 g of activated copper (to remove sulfur residues from the sediment), 1 g of activated alumina, and 3.5 g of sediment samples previously homogenized with 0.75 g of alumina. All these layers in the cell were separated by cellulose filters. Procedural blanks were also performed, filling the cell with sorbents and no sediment, to check the presence of interferences. The compounds detected in small amounts in the procedural blanks were octocrylene, EHMC and OTNE, so the average

blank concentrations were subtracted from the concentration detected in each sample. Dichloromethane was selected as the best solvent, using three static extraction cycles of 5 min each (purge time = 60 s, flush volume = 60%), 100 °C and 1500 psi. The extracts (30 mL) were evaporated to dryness using a Syncore Polyvap (Büchi, Switzerland) and dissolved in 1 mL of dichloromethane. Afterwards, the samples were again evaporated to dryness and re-dissolved in 500 µL of ethyl acetate, then filtered through PTFE centrifuge filters (0.22 µm pore size). A mixture of isotopically labelled compounds (acenaphthene-d10, chrysene-d12, phenanthrene-d10, and perylene-d12) used as internal standards (10 µL) and N-(tert-butyldimethylsilyl)-N-methyltrifluoroacetamide (MTBSTFA), as a derivatizing agent (10 µL), were added to the final extracts at least 30 min before GC-MS analysis.

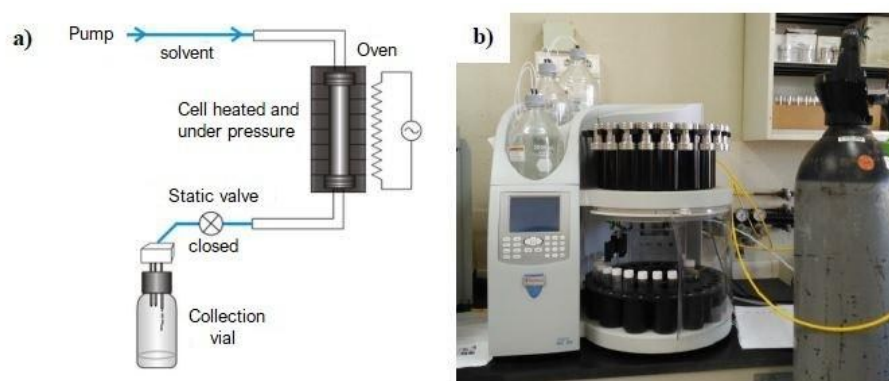


Figure 13 – a) PLE process; b) Dionex-350 system.

Legacy contaminants. Regarding the legacy contaminants, the extraction of the selected PBDEs has been carried out using the Pressurized Liquid Extraction (PLE) technique, making a set-up and optimization from existing analytical methods in the literature (Da Da et al., 2019, Carlsson et al., 2018). PLE procedure was performed on a PLE extractor (Speed Extractor E-916 system, Büchi, Italy) (Fig. 14) equipped with 20 mL stainless steel extraction cells. Each cell was prepared as follows: a bottom glass fibre was placed at the bottom of the cell followed by 1.5 g of sediment sample previously homogenized with diatomaceous earth; then, diatomaceous earth to fill the cell and a cellulose filter at the top of the cell. Procedural blanks were also performed, filling the cell with sorbent and no sediment. Hexane was selected as the best solvent, using three static extraction cycles of 5 min each (purge time: 60s, flush volume: 100%), temperature at 100 °C and pressure at 1500 psi. The extracts obtained (approximately 60 mL) did not require further purification and were evaporated (Syncore, Büchi, Italia) to a final volume of 1 mL, and subsequently analyzed by gas chromatography-mass spectrometry (GC-MS). Stable isotope-labelled compounds (^{13}C -PBDE-47 and ^{13}C -PBDE-183) were used as internal standards, added to both standard solutions and extracts prior to GC analysis up to a final

concentration of 5 µg/L, to minimize the effects of suppression or enhancement of the MS signal due to matrix interference.

To test the recovery efficiency of the extraction technique, 1 mL of hexane solution prepared from the stock solution (4.14 mg/L) of the reference standard (NIST SRM 2257) was added to approximately 2 g of dried sediment free of PBDEs. From the stock solution, two further solutions in hexane were prepared (2.07 and 1.035 mg/L) and three replicates were prepared for each spike, such that the final concentration of the PBDE mixture in the sediment was 0.258 (test 1), 0.5175 (test 2) and 1.035 (test 3) µg/g. The final concentration of the individual congeners is given in Table 6. Then, the sediment was left to dry at room temperature for at least 24 hours. The reproducibility of the method was expressed as the coefficient of variation (CV, %) calculated from the results of analyses performed in triplicate of standard solutions with internal standards. An initial extraction test was carried out using an acetone-hexane mixture (1:1) as extraction solvent, however, the recoveries obtained were between 40-55% and were not reproducible (CV>20%). Therefore, it was subsequently decided to modify the extraction solvent by using only hexane, considering the better affinity between the extraction solvent and the compounds, and the samples were processed under the conditions described above. By comparing the initial theoretical concentrations with those obtained with the method under investigation, a percentage recovery emerged in the range of 65-95% depending on the congener, with RSD (Relative Standard Deviation) values between 2 and 8 % and CV<10%.



Figure 14 - Speed Extractor E-916 system.

Retene. Regarding retene analysis, the extraction of retene has been carried out using the sonicated extraction technique. Freeze-dried sediments (0.5 g) were transferred into precombusted vials. A stocking solution of internal standard (docosane) was prepared in hexane, with a final concentration of 0.4052 mg/mL, and stored at +4 °C. A known amount of internal standard was added to the samples, followed by addition of a solvent mixture [(DCM:Hex), 9:1, v/v]. Vials were sonicated (10 min at 50°C) and centrifuged (2500 rpm, 2 min), and the supernatant was transferred in precombusted vials. Extraction steps were

repeated were repeated three times in total. The total lipid extracts were dried (N₂ stream; 40°C) and redissolved in 750 µl of Hex:DCM (3:2, v/v) before purification via silica gel columns. Hexane was used as elution solvent. Reduced extracts were dried (N₂ stream; 30°C) and redissolved in 500 µl before GC-MS analysis. An external standard consisting of long-chain alkanes (C-20 to C-35) was also injected between batches to evaluate the response of our internal standard to GC-MS analysis.

3.3.3 Instrumental analysis and quality control

Emerging contaminants. Regarding the emerging contaminants, the separation, identification and quantification of selected UV-Fs and SFs were achieved by using gas chromatography -tandem mass spectrometry (GC-MS/MS) technique. The gas chromatographer (SCION 456-GC, Bruker) was equipped with a BR-5 ms column (30 m × 0.25 mm i.d. × 0.25 µm film thickness) (Fig. 15a). Injection volume was 1 µL in splitless mode and the solvent delay was set to 4.5 min. The column temperature ramp was as follows: 70 °C for 3.5 min, increased at 25 °C min⁻¹ to 180 °C, then at 10 °C min⁻¹ to 300 °C, and held for 4 min. A triple quadrupole mass spectrometer (SCION TQ from Bruker with CP 8400 Autosampler) was coupled to GC analysis for the determination of UV-Fs and SFs. The carrier gas flow (helium) was set at 1 mL min⁻¹, and the transfer line and the injection port temperatures at 280°C. The mass detector was operated in multiple reaction monitoring (MRM) mode using an electron ionization (EI) source set at 70 eV and argon as collision gas (2 mTorr). Target compounds were identified and quantified by comparison with ions listed in Table 7. Data were processed using the software “Bruker MS Workstation 8”.

Calibration curves were prepared in ethyl acetate from 0.001 to 200 ng g⁻¹. The correlation coefficients (R^2) were higher than 0.99 for all the target compounds, showing calibration curves good linearity. Method limits of detection (mLODs) and method limits of quantification (mLOQ) were calculated as three times the signal-to-noise ratio and ten times the signal-to-noise ratio, respectively (Tab. 8). The mLODs for UV-Fs and SFs ranged from 0.01 to 0.41 ng g⁻¹ and 0.01 to 2.40 ng g⁻¹, respectively. The mLOQs for UV-Fs and SFs ranged from 0.03 to 1.36 ng g⁻¹ and 0.04 to 8.00 ng g⁻¹, respectively. The recoveries for target SFs and UV-Fs were in the range 78-100 % and 53-107 %, respectively. More details on this method are reported by (Pintado-Herrera et al., 2016).

Legacy contaminants. Regarding the legacy contaminants, the separation, identification and quantification of PBDEs were performed using gas chromatography (GC) (Thermo Fisher Trace 3000) coupled to mass spectrometry (MS) (Thermo Fisher ISQ7000) (Fig. 15b). Capillary gas chromatography analysis was carried out on a ZB-5HT Inferno column (15m x 0.25mm x 0.10µm, Phenomenex, France), a fused silica capillary column with a (5%) phenyl- (95%) dimethylpolysiloxane stationary phase suitable for high temperatures. The carrier gas flow (high purity helium, over 99.99%) was kept constant at 1.2 mL min⁻¹,

and the transfer line and the injection port temperatures at 320 and 280 °C, respectively. Injection volume was 1 µL in splitless mode. Chromatographic separation of the compounds was carried out using a temperature program showing a gradual and progressive increase, allowing selective separation of the 38 congeners present in the standard mixture. To achieve the optimum conditions, several chromatographic runs were carried out by changing the temperature schedule by varying both the rate of temperature rise (°C/min) and the target temperature in order to maximize peak resolution. The column temperature ramp operating conditions were optimized and set as follows: 60 °C for 2 min, increased at 15 °C min⁻¹ to 280 °C held for 2 min, then at 15 °C min⁻¹ to 360 °C held for 10 min. For the identification of congeners and their retention times, MS acquisition was initially carried out in Full Scan mode; then, in Selected Ion Monitoring (SIM) mode using the ions listed in Table 9 for qualification and quantification. The identification of the target contaminants was performed based on the m/z ion ratios, the ion transition intensity ratios and the comparison with retention times (RT) of the product ions in the extracts with those in the analytical standards, considering the criteria difference of 0.2 min. The ionization mode was electron impact (EI). Data was processed using the software “Chromeleon 7” Thermo Fisher (v 7.2.7).

Two calibration curves were obtained at different concentration ranges (2.5; 5; 10; 25; 50 µg/L and 0.1; 0.25; 0.5; 1 and 1.5 mg/L). The curves were produced by analysing standard solutions in hexane obtained by dilution from a stock solution of PBDE mixture, having an initial total concentration of 4.14 mg/L and containing all the congeners under investigation. The good linearity was confirmed by the determination coefficient (R²) of the calibration curves obtained for the individual congeners and ranging between 0.9683 and 0.9999 (Fig. 16). The limits of detection (LOD) were calculated in accordance with the IUPAC method (Thompson et al., 2002), from the lowest concentration that produces a peak that can be reliably distinguished from background noise (three times the signal-to-noise ratio). The limits of quantification (LOQ) were calculated as three times the LOD value. LOD values were in a range between 0.001 and 0.026 ng/g, and LOQ values between 0.003 and 0.078 ng/g depending on the congener (Tab. 9).

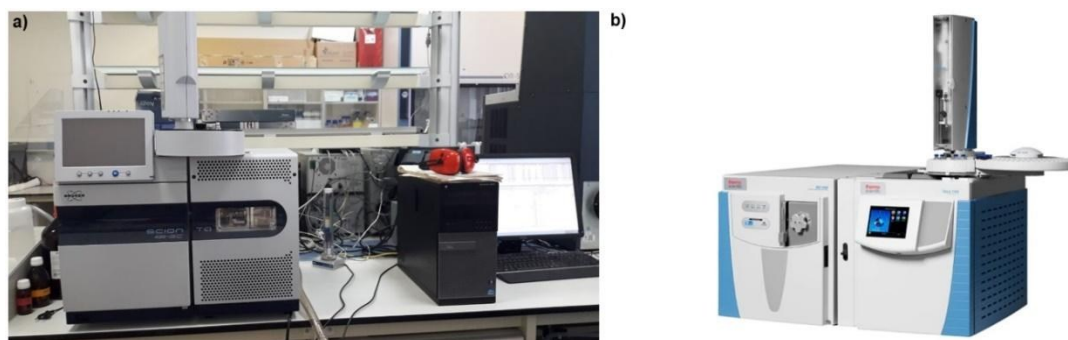


Figure 15 – a) SCION 456-GC coupled with CP 8400 Autosampler (Bruker); b) Trace 3000 coupled to ISQ7000 (Thermo Fisher).

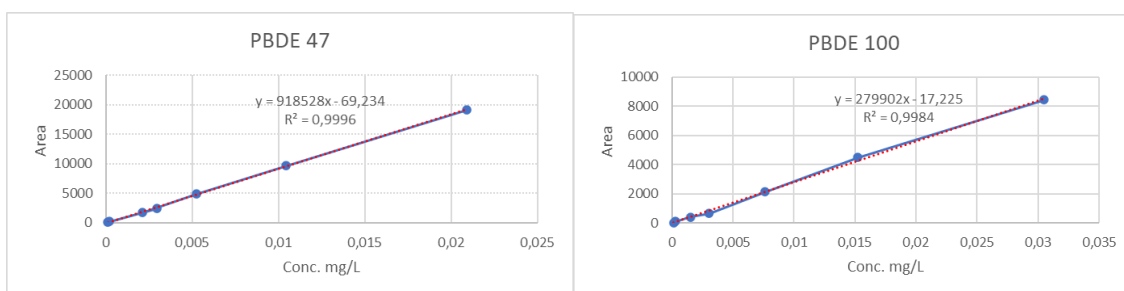


Figure 16 - Example of calibration curves of two PBDE congeners (BDE-47, BDE-100) and correlation coefficient (R^2).

Retene. Regarding retene analysis, the separation, identification and quantification of retene was performed using gas chromatography (GC) (7820A, Agilent) coupled to mass spectrometry (MS) (5977B mass selective detector, Agilent), fitted with BP5MS column (30m x 320µm x 0.25µm, SGE Analytical Science), a column with a 5% Phenyl Polysilphenylene-siloxane stationary phase suitable for high temperatures. Injection volume was 1 µL in splitless mode. The column temperature ramp started with a temperature of 70 °C, then increased at 6 °C min⁻¹ to 300 °C, and held for 17 min. The carrier gas flow (helium) was set at 1.2 mL min⁻¹, and the transfer line and the injection port temperatures at 260°C. The mass detector was operated in both selective ion monitoring (SIM) and SCAN modes. Retene concentrations were calculated based on the integrated area of TIC or ion m/z 234 depending on the concentration. Integrated peaks of m/z 234 were adjusted for a correction factor based on retene-rich samples to obtain the total ion chromatogram (TIC). Integrated TIC areas were then compared with the response of the internal standard to obtain the retene concentration values. Data was processed using software “Agilent Mass Hunter Qualitative Analysis Navigator v. 3.8”.

3.4 Chronology

3.4.1 ²¹⁰Pb age-depth model

For the sediment core NYA11_09, the chronology was constructed by integrating ²¹⁰Pb and ¹³⁷Cs activity profiles. ²¹⁰Pb activity (Bq kg⁻¹) was quantified by alpha particle spectrometry according to the method of (Frignani et al., 2005), and ¹³⁷Cs by gamma spectrometry (Frignani et al., 2004). ²¹⁰Pb is a natural radionuclide of the ²³⁸U radioactive chain with a half-life ($t_{1/2}$) of 22.23 ± 0.12 years (Heijnis, 2001). It has been applied as a radiotracer to study many processes (e.g. atmospheric deposition and contamination, sedimentary processes, accumulation rates of organic carbon) (Sanchez-Cabeza and Ruiz-Fernández, 2012) of recent sediments over a time span of ~100–150 years. ¹³⁷Cs is a bomb-produced radionuclide ($t_{1/2} = 30.15$ years) that started to appear in 1954 with the onset of weapon testing and peaked in 1963 after the 1986 Chernobyl (1986) nuclear accident in the Northern Hemisphere. The age-depth model was computed using ²¹⁰Pb data combined

with ^{137}Cs as an age-equivalent marker. The age-depth model was built using Plum package version 0.1.4 (Aquino-López et al., 2018), a Bayesian forward age-depth model (Blaauw et al., 2020, Blaauw and Christen, 2011) in R version 4.0.0 (R Core Team, 2020).

3.4.2 Radiocarbon (^{14}C) age-depth model

For the sediment cores NYA21_01, NYA21_03 and NYA21_04, the chronology was constructed by integrating several elements, including ^{14}C (radiocarbon) analyses performed on bulk sediments and planktonic foraminifera at ETH SMS ^{14}C facilities of Zürich. ^{14}C is an unstable radioactive isotope of carbon with a half-life of about $5,720 \pm 30$ years (Blais et al., 2015). Considering that ^{14}C presence doubled in the atmosphere after nuclear weapons-testing in late 1950s-early 1960s, its content in post-bomb samples must be interpreted in relation to the concentration in the atmosphere or ocean reservoir (Reimer et al., 2004). Nowadays, radiocarbon dating is the most widely used method to date marine fossils and sediments covering the last ca. 50,000 years (Hillaire-Marcel et al., 2022). Selected depth levels were chosen to achieve greater resolution in the more superficial layers, given the relatively recent time range (last 100 years) in which we assume to find the contaminants of interest, than in the deeper layers (Tab.10) When radiocarbon samples are small ($< 100 \mu\text{g C}$) or very small ($< 25 \mu\text{g C}$), they are analyzed in gas form. Indeed, an elemental analyser (EA) or carbonate handling system (CHS) is used to convert the organic samples or carbonates to CO_2 , which is then injected into the gaseous ion source of the MIni CARbon DAting Systems (MICADAS) (Wertnik et al., 2023, Synal et al., 2007).

For the construction of the age-depth models, radiocarbon dates of each core were modeled using OxCal4.4 with the P_Sequence deposition procedure (Ramsey, 2009). To calibrate radiocarbon dates, the Marine20 curve was used (Heaton et al., 2020). The applied local reservoir effect (ΔR) before calibration corresponds to the reservoir correction for the study region. This was previously calculated by (Tesi et al., 2021) using retene excess as time marker and the value is $\Delta R = 305 \pm 75$ years. The OXCal output confirmed a good robustness for all age-depth models, with agreement indices always $> 95\%$, higher than the suggested critical threshold of 60% (Ramsey, 2009).

Also in this case, retene was used as a proxy for the identification of the beginning of coal mining activities in the fjord, which took place in Ny-Ålesund from 1916 to 1963 (Paglia, 2020). However, unlike in (Tesi et al., 2021), retene in this study was only used as an external time marker: the estimated depth interval corresponding to AD 1916 (start of the increase in retene concentration caused by the opening of the mining activity) was compared to the results obtained from the age-depth model, in order to double check the accuracy of the dating methods and modelling.

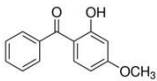
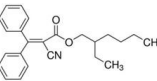
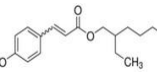
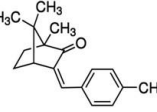
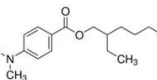
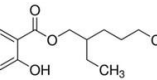
Table 10 – NYA21 cores depth levels analyzed for radiocarbon dating.

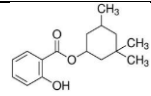
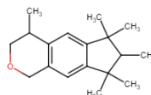
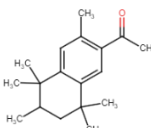
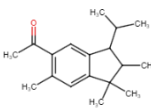
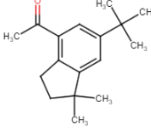
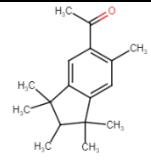
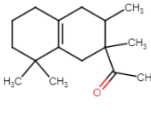
Core	Depth (cm)	Matrix	Age BP 14C	±1σ
NYA21_01	26-27	Foraminifera	964	75
NYA21_01	88-89	Bulk	7253	133
NYA21_03	0-0.5	Bulk	4942	89
NYA21_03	14-15	Foraminifera	303	76
NYA21_03	38-40	Foraminifera	1905	95
NYA21_03	45-47	Foraminifera	995	82
NYA21_03	116-117	Foraminifera	1092	75
NYA21_04	1-1.5	Foraminifera	-10	67
NYA21_04	14-15	Foraminifera	797	56
NYA21_04	26-27	Foraminifera	746	52
NYA21_04	107-108	Foraminifera	1626	58

3.5 Statistical analysis

Statistical analysis of data was performed using the software Primer v.6 and GraphPad Prism v.6.01. The normal distribution of data was examined using the ShapiroWilk test. Significant correlations between samples were calculated based on the Spearman correlation coefficient (r). Statistical differences ($p < 0.05$, with a confidence interval of 95%) between target contaminant concentrations in the sediment cores were evaluated with PERMANOVA analysis. Principal Component Analysis (PCA) was used to identify correlations between samples based on contaminant concentrations in the sediment cores (Maćkiewicz and Ratajczak, 1993).

Table 4 - Trade names, chemical structures, and physico-chemical properties of organic UV-Fs and SFs analyzed in the sediment core NYA11_09.

IUPAC Name	Abbreviations	CAS N.	Molecular formula	Molecular weight (g/mol)	Henry's Law constant (atm m ³ /mol)	Vapour pressure at 25 °C (mm Hg)	Log K _{ow}	Log K _{oc}	Water solubility at 25 °C (mg/L)	Structure
Organic UV-Filters (UV-Fs)										
(2-Hydroxy-4-methoxyphenyl)(phenyl)methanone (Oxybenzone or Benzophenone-3)	BP-3	131-57-7	C ₁₄ H ₁₂ O ₃	228.24	2.900 x 10 ⁻⁸	6.62 x 10 ⁻⁶	3.52 ^a 3.79 ^a 3.64	3.103	68.56 ^a 210	
2-Ethylhexyl 2-cyano-3,3- diphenylacrylate (Octocrylene)	OC	6197-30-4	C ₂₄ H ₂₇ NO ₂	361.48	3.935 x 10 ⁻⁷	3.15 x 10 ⁻⁹	6.88	5.614	3.808 ₃ x 10 ⁻⁷	
2-Ethylhexyl (2E)-3-(4-methoxyphenyl)acrylate (2-Ethylhexyl 4-methoxycinnamate or Octinoxate)	EHMC	5466-77-3	C ₁₈ H ₂₆ O ₃	290.40	3.406 x 10 ⁻⁵	1.38 x 10 ⁻⁵	5.8	4.089	0.155	
3-(4-methylbenzylidene) camphor (Enzacamene)	4-MBC	36861-47-9	C ₁₈ H ₂₂	254.37	2.588 x 10 ⁻⁵	1.52 x 10 ⁻⁵	5.92 ^a 4.95 5.47	4.087	0.197	
2-Ethylhexyl 4-(dimethylamino) benzoate (Padimate O)	ODPABA	21245-02-3	C ₁₇ H ₂₇ NO ₂	277.40	6.536 x 10 ⁻⁵	3.54 x 10 ⁻⁵	5.77 ^a 6.15	3.382	0.198	
2-Ethylhexyl salicylate (Octisalate)	EHS	118-60-5	C ₁₅ H ₂₂ O ₃	250.33	3.275 x 10 ⁻⁶	7.13 x 10 ⁻⁶	5.97	3.933	0.717	
3,3,5-Trimethylcyclohexyl salicylate (Homosalate)	HMS	118-56-9	C ₁₆ H ₂₂ O ₃	262.35	2.296 x 10 ⁻⁶	2.79 x 10 ⁻⁶	6.16	4.032	0.419	

										
Synthetic fragrances (SFs)										
4,6,6,7,8,8-Hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta[g]isochromene (Galaxolide)	HHCB	1222-05-5	C ₁₈ H ₂₆ O	258.40	1.749 x 10 ⁻⁴	2.52 x 10 ⁻⁴	5.43	3.799	0.886	
1-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydro-2-naphthalenyl)ethenone (Tonalide)	AHTN	1506-02-1	C ₁₈ H ₂₆ O	258.40	2.278 x 10 ⁻⁴	1.6 x 10 ⁻⁴	5.80	3.716	0.209	
1-(3-Isopropyl-1,1,2,6-tetramethyl-2,3-dihydro-1H-inden-5-yl)ethenone (Traseolide)	ATII	68140-48-7	C ₁₈ H ₂₆ O	258.40	2.588 x 10 ⁻⁴	1.95 x 10 ⁻⁴	5.76	3.771	0.149	
1-[1,1-Dimethyl-6-(2-methyl-2-propenyl)-2,3-dihydro-1H-inden-4-yl]ethenone (Celestolide)	ADBI	13171-00-1	C ₁₇ H ₂₄ O	244.37	7.05 x 10 ⁻⁶	1.44 x 10 ⁻⁴	5.93	3.697	1.154	
1-(1,1,2,3,3,6-Hexamethyl-2,3-dihydro-1H-inden-5-yl)ethenone (Phantolide)	AHMI	15323-35-0	C ₁₇ H ₂₄ O	244.37	1.787 x 10 ⁻⁴	4.17 x 10 ⁻⁴	5.30	3.464	0.424	
1-(2,3,8,8-Tetramethyl-1,2,3,4,5,6,7,8-octahydro-2-naphthalenyl)ethanone	OTNE (or Iso-E super)	54464-57-2	C ₁₆ H ₂₆ O	234.38	3.150 x 10 ⁻⁴	1.1 x 10 ⁻³	5.18	3.508	10.066	

^a Physical-chemical properties from ChemSpider (<http://www.chemspider.com/>)

Table 5 – PBDE congeners included in NIST Standard SMR 2257.

IUPAC Name	Compound name	CAS Number	Mass fraction (µg/g)
PBDE 17	2,2',4-Tribromodifenilether	147217-75-2	5.87 ± 0.35
PBDE 25	2,3',4-Tribromodifenilether	147217-77-4	3.19 ± 0.39
PBDE 28	2,4,4'-Tribromodipenylether	41318-75-6	1.88 ± 0.14
PBDE 30	2,4,6-Tribromodifenilether	N/A	3.08 ± 0.10
PBDE 47	2,2',4,4'-Tetrabromodifenilether	5436-43-1	2.09 ± 0.16
PBDE 49	2,2',4,5'-Tetrabromodifenilether	243982-82-3	3.95 ± 0.31
PBDE 66	2,3',4,4'-Tetrabromodifenilether	189084-61-5	2.162 ± 0.089
PBDE 71	2,3',4',6-Tetrabromodifenilether	189084-62-6	2.86 ± 0.10
PBDE 74	2,4,4',5-Tetrabromodifenilether	N/A	3.56 ± 0.10
PBDE 75	2,4,4',6-Tetrabromodifenilether	189084-63-7	3.45 ± 0.15
PBDE 85	2,2',3,4,4'-Pentabromodifenilether	182346-21-0	3.359 ± 0.092
PBDE 97 + 118	2,2',3',4,5-Pentabromodifenilether + 2,3',4,4',5-Pentabromodifenilether	N/A	5.29 ± 0.19
PBDE 99	2,2',4,4',5-Pentabromodifenilether	60348-60-9	2.127 ± 0.090
PBDE 100	2,2',4,4',6-Pentabromodifenilether	189084-64-8	3.05 ± 0.15
PBDE 101	2,2',4,5,5'-Pentabromodifenilether	N/A	3.784 ± 0.080
PBDE 116	2,3,4,5,6-Pentabromodifenilether	N/A	3.042 ± 0.067
PBDE 119	2,3',4,4',6-Pentabromodifenilether	189084-66-0	4.11 ± 0.14
PBDE 138	2,2',3,4,4',5'-Hexabromodifenilether	182677-30-1	2.522 ± 0.053
PBDE 139	2,2',3,4,4',6-Hexabromodifenilether	N/A	3.514 ± 0.082
PBDE 153	2,2',4,4',5,5'-Hexabromodifenilether	68631-49-2	2.048 ± 0.068
PBDE 154	2,2',4,4',5,6'-Hexabromodifenilether	207122-15-4	1.622 ± 0.057
PBDE 155	2,2',4,4',6,6'-Hexabromodifenilether	35854-94-5	0.895 ± 0.026
PBDE 156	2,3,3',4,4',5-Hexabromodifenilether	N/A	2.77 ± 0.13
PBDE 173 + 190	2,2',3,3',4,5,6-Heptabromodifenilether + 2,3,3',4,4',5,6-Heptabromodifenilether	N/A 189084-68-2	3.01 ± 0.13
PBDE 181	2,2',3,4,4',5,6-Heptabromodifenilether	189084-67-1	2.859 ± 0.079
PBDE 182	2,2',3,4,4',5,6'-Heptabromodifenilether	N/A	1.502 ± 0.060
PBDE 183	2,2',3,4,4',5',6-Heptabromodifenilether	207122-16-5	2.183 ± 0.049
PBDE 185	2,2',3,4,5,5',6-Heptabromodifenilether	N/A	2.37 ± 0.18
PBDE 191	2,3,3',4,4',5',6-Heptabromodifenilether	N/A	2.085 ± 0.055
PBDE 196	2,2',3,3',4,4',5,6'-Octabromodifenilether	N/A	2.46 ± 0.11
PBDE 197 + 204	2,2',3,3',4,4',6,6'-Octabromodifenilether + 2,2',3,4,4',5,6,6'-Octabromodifenilether	N/A	2.823 ± 0.070
PBDE 198	2,2',3,3',4,5,5',6-Octabromodifenilether	N/A	1.898 ± 0.057
PBDE 203	2,2',3,4,4',5,5',6-Octabromodifenilether	N/A	1.373 ± 0.034
PBDE 206	2,2',3,3',4,4',5,5',6-Nonabromodifenilether	N/A	1.982 ± 0.063
PBDE 208	2,2',3,3',4,5,5',6,6'-Nonabromodifenilether	N/A	1.108 ± 0.026

Table 6 - Theoretical concentrations used for the three recovery tests, mean recovery ($\pm$ RSD) e CV (%).

Congener	Recovery tests				CV (%)
	PBDEs theoretical concentrations in sediments			Mean recovery	
	Test 1 ($\mu\text{g/g}$)	Test 2 ($\mu\text{g/g}$)	Test 3 ($\mu\text{g/g}$)	(% $\pm$ RDS)	
PBDE 17	0.015	0.030	0.088	65 $\pm$ 3	8
PBDE 25	0.008	0.017	0.048	67 $\pm$ 4	6
PBDE 28	0.005	0.010	0.028	84 $\pm$ 2	9
PBDE 30	0.008	0.016	0.046	86 $\pm$ 3	9
PBDE 47	0.005	0.011	0.031	82 $\pm$ 7	8
PBDE 49	0.010	0.020	0.059	83 $\pm$ 6	9
PBDE 71	0.007	0.015	0.043	80 $\pm$ 8	9
PBDE 66	0.006	0.011	0.032	87 $\pm$ 8	4
PBDE 74	0.009	0.018	0.053	84 $\pm$ 5	6
PBDE 75	0.009	0.018	0.052	82 $\pm$ 3	6
PBDE 99	0.006	0.011	0.032	83 $\pm$ 3	6
PBDE 85	0.009	0.017	0.050	95 $\pm$ 5	1
PBDE 97-118	0.014	0.027	0.079	92 $\pm$ 6	3
PBDE 100	0.008	0.016	0.046	85 $\pm$ 2	5
PBDE 101	0.010	0.020	0.057	80 $\pm$ 3	7
PBDE 119	0.011	0.021	0.062	78 $\pm$ 4	9
PBDE 116	0.008	0.016	0.046	78 $\pm$ 3	8
PBDE 138	0.007	0.013	0.038	78 $\pm$ 2	8
PBDE 139	0.009	0.018	0.053	75 $\pm$ 5	9
PBDE 153	0.005	0.011	0.031	77 $\pm$ 3	7
PBDE 154	0.004	0.008	0.024	78 $\pm$ 5	3
PBDE 155	0.002	0.005	0.013	75 $\pm$ 5	7
PBDE 156	0.007	0.014	0.042	81 $\pm$ 3	7
PBDE 173-190	0.008	0.016	0.045	78 $\pm$ 4	8
PBDE 182	0.004	0.008	0.023	77 $\pm$ 3	7
PBDE 181	0.007	0.015	0.043	77 $\pm$ 7	8
PBDE 183	0.006	0.011	0.033	95 $\pm$ 8	3
PBDE 185	0.006	0.012	0.036	98 $\pm$ 4	3
PBDE 191	0.005	0.011	0.031	82 $\pm$ 5	2
PBDE 196	0.006	0.013	0.037	85 $\pm$ 4	2
PBDE 197-204	0.007	0.015	0.042	78 $\pm$ 3	5
PBDE 198	0.005	0.010	0.028	82 $\pm$ 8	3
PBDE 203	0.004	0.007	0.021	78 $\pm$ 4	7
PBDE 206	0.005	0.010	0.030	81 $\pm$ 5	6
PBDE 208	0.003	0.006	0.017	75 $\pm$ 6	4

Table 7 - Compound, retention time (RT) and MS ions used for quantification and qualification.

Compound	RT (min)	MS ions for quantification	MS ions for qualification
<i>Synthetic fragrances (SFs)</i>			
OTNE	10.790	191	109
HHCB	12.310	243	213
AHTN	12.350	243	187
ATII	12.250	215	173
ADBI	11.110	229	173
AHMI	11.510	229	187
<i>Organic UV-Filters (UV-Fs)</i>			
4-MBC	14.060	254	155
EHS	14.870	195	159
HMS	15.590	195	177
EHMC	16.060	178	132
BP-3	16.120	285	242
OC	18.820	248	165
ODPABA	15.700	165	164

Table 8 - Method limits of detection (mLODs) and quantification (mLOQs) of the target UV-Fs and SFs (ng g⁻¹).

Class	Compound	mLOD (ng g ⁻¹)	mLOQ (ng g ⁻¹)
Synthetic fragrances (SFs)	Tonalide (AHTN)	0.02	0.04
	Galaxolide (HHCB)	0.01	0.04
	Traseolide (ATII)	0.15	0.51
	Celestolide (ADBI)	0.04	0.14
	Phantolide (AHMI)	2.40	8.00
	OTNE	0.03	0.11
Organic UV-filters (UV-Fs)	Homosalate (HMS)	0.02	0.07
	Benzophenone-3 (BP-3)	0.01	0.03
	Octocrylene (OC)	0.02	0.08
	2-Ethylhexyl 4-(dimethylamino) benzoate (OD-PABA)	0.41	1.36
	4-methylbenzylidene camphor (4-MBC)	0.22	0.74
	Ethyl hexyl salicylate (EHS)	0.06	0.22
	2-ethylhexyl methoxycinnamate (EHMC)	0.04	0.13

Table 9 - Congener, LOD (ng g⁻¹) and LOQ (ng g⁻¹), retention time (TR) and MS ions used for PBDE quantification and qualification.

Congener	LOD (ng g ⁻¹)	LOQ (ng g ⁻¹)	RT (min)	MS ions for quantification
PBDE 17	0.002	0.006	11.055	246
PBDE 25	0.001	0.003	11.626	246
PBDE 28	0.002	0.006	11.821	246
PBDE 30	0.002	0.006	11.962	246
PBDE 47	0.003	0.009	12.862	326
PBDE 49	0.004	0.012	12.977	326
PBDE 71	0.005	0.015	13.027	326
PBDE 66	0.004	0.012	13.197	326
PBDE 74	0.006	0.018	13.272	326
PBDE 75	0.011	0.033	13.377	326
PBDE 99	0.007	0.021	14.185	404
PBDE 85	0.008	0.024	14.245	404
PBDE 97+118	0.005	0.015	14.282	404
PBDE 100	0.006	0.018	14.467	404
PBDE 101	0.005	0.015	14.567	404
PBDE 116	0.007	0.021	14.960	404
PBDE 119	0.003	0.012	15.125	404
PBDE 138	0.014	0.042	15.240	484
PBDE 139	0.008	0.024	15.766	484
PBDE 153	0.007	0.021	16.112	484
PBDE 154	0.01	0.03	16.302	484
PBDE 155	0.007	0.021	16.438	484
PBDE 156	0.004	0.012	16.525	484
PBDE 173+190	0.026	0.078	16.702	562
PBDE 182	0.022	0.066	16.782	562
PBDE 181	0.026	0.078	16.832	562
PBDE 183	0.017	0.051	17.000	562
PBDE 185	0.011	0.033	17.204	562
PBDE 191	0.015	0.045	17.240	562
PBDE 196	0.007	0.021	17.594	642
PBDE 197+204	0.022	0.066	17.787	642
PBDE 198	0.003	0.009	18.377	642
PBDE 203	0.007	0.021	18.382	642
PBDE 206	0.006	0.018	18.867	642
PBDE 208	0.004	0.012	18.879	720

CHAPTER 4 – Results

4.1 Sediment characteristics

The main physico-chemical characteristics of the sediments were highlighted by means of certain parameters, such as grain size distribution, elemental ratios (Ca/Ti, Br/Cl and Zr/Rb), organic carbon (OC) content and stable carbon isotopic composition ($\delta^{13}\text{C}$), in order to describe the principal depositional processes occurring in this Arctic fjord environment. Specifically, elemental ratios from XRF core scanning were examined to address additional aspects of the sediment accumulation processes. For example, the Ca/Ti ratio is a useful indicator of relative changes in biogenic versus lithogenic sedimentation and recording carbonate content, and Ca has better application with Ti is inert (Croudace and Rothwell, 2015). In this study, Ca/Ti has been used as a proxy for assessing the glacial sediment supply since, in this fjord environment, Ca-rich sediments are primarily associated with the Kronebreen and Kongsvegen glaciers (Streuff et al., 2015). The Br/Cl has been used to evaluate marine organic matter content, since organic Br molecules are primarily synthesized by marine organisms (Croudace and Rothwell, 2015). The Zr/Rb ratio has been used as a grain-size proxy, since Zr is mostly found in coarser sediment fraction than Rb, which is most abundant in clay minerals (Croudace and Rothwell, 2015).

Distribution and characterization of organic matter (OM), stable carbon isotopic composition ($\delta^{13}\text{C}$) and the relative contribution of terrestrial (F_{terr}) and marine (F_{mar}) OM were analyzed according to (Kim et al., 2011) and (Wu et al., 2023), in order to define potential sources (marine versus terrestrial) in Arctic marine sediments. $\delta^{13}\text{C}$ is widely used for identifying sources of OM in the Arctic (Winkelmann and Knies, 2005). Particularly, terrestrial (C3) plants, typical from arid environments have a $\delta^{13}\text{C}$ content that ranges from -29.3 to -25.5‰; while C4 plants are enriched in $\delta^{13}\text{C}$ content but it is unlikely to be found in the Arctic (Kim et al., 2011). For this reason, the soils in this high latitude area have $\delta^{13}\text{C}$ values within the range of C3 plants (Kim et al., 2011). On the contrary, OM of marine origin (phytoplankton production) in Kongsfiorden-Krossfiorden area has been found to have higher $\delta^{13}\text{C}$ content (i.e., -20.6 ‰, Winkelmann and Knies, 2005; -21.4 ‰ in the central Arctic Ocean, (Schubert and Calvert, 2001)).

The F_{terr} was calculated as reported by (Wu et al., 2023) using the following equation:

$$F_{\text{terr}} = \frac{\delta^{13}\text{C}_{\text{sample}} - \delta^{13}\text{C}_{\text{marine}}}{\delta^{13}\text{C}_{\text{terrestrial}} - \delta^{13}\text{C}_{\text{marine}}} \times 100\%$$

where F_{terr} is the percentage of terrestrial organic carbon in the samples, $\delta^{13}\text{C}_{\text{sample}}$ is $\delta^{13}\text{C}$ measured in the samples, and $\delta^{13}\text{C}_{\text{terrestrial}}$ and $\delta^{13}\text{C}_{\text{marine}}$ are the end-member values for terrigenous (-26.8‰) and marine (-20.6‰) OM according to previous studies in Svalbard region. Based on the above equation, the F_{mar} value corresponding to the percentage

content of organic carbon of marine origin found in the four analyzed cores was also calculated.

Regarding the OC content, it varied between 0.3 and 0.5%, with an average value $0.4 \pm 0.06 \%$ ($n=40$). $\delta^{13}\text{C}$ content varied between -24.0 and -22.9‰, with an average value $-23.5 \pm 0.30 \text{‰}$ ($n=40$). F_{terr} varied between 37.7 and 55.4%, with an average value $46.1 \pm 4.9 \%$ ($n=40$). F_{mar} varied between 44.6 and 62.3%, with an average value $53.9 \pm 4.9 \%$ ($n=40$) (Fig. 17a).

In the 2011 sediment core, from 10 cm depth up to the top of the core, a tendency of the organic matter towards slightly more marine values was observed, which is confirmed by the $\delta^{13}\text{C}$ values and the Br/Cl ratio. According to the Zr/Rb ratio, the grain size distribution remained almost unchanged throughout the core. The Ca/Ti ratio showed Ca rich level around 32-33 cm depth, which was interpreted as the last surge of the Kongsvegen glacier occurred in 1948 (Kehrl et al., 2011) (Fig.17b). This latter parameter has been used as forcing in the ^{210}Pb age-depth model.

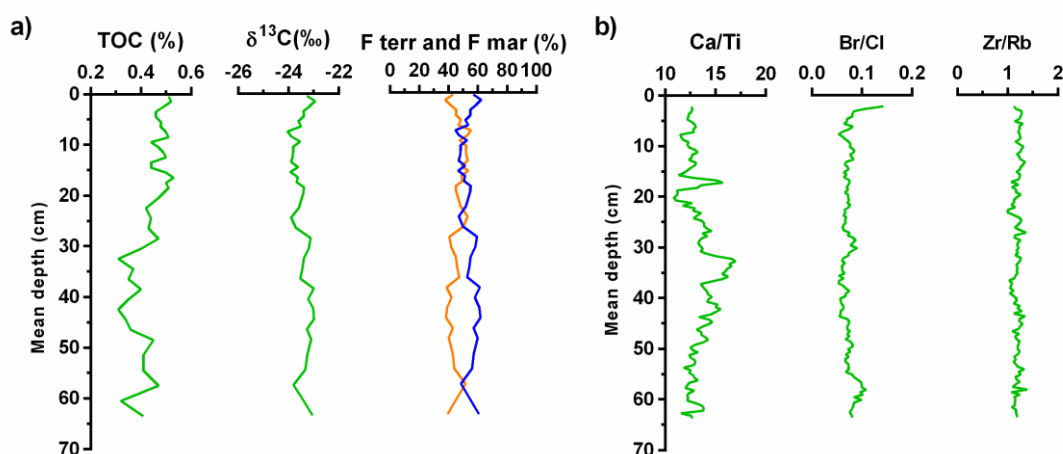


Figure 17 – a) TOC (%), $\delta^{13}\text{C}$ (‰), F_{terr} (%) (orange line) and F_{mar} (%) (blue line), and b) elemental ratios depth profiles in the sediment core collected in 2011.

In the sediment core NYA21_01, the OC content varied between 0.1 and 0.9%, with an average value $0.5 \pm 0.3 \%$ ($n=24$). $\delta^{13}\text{C}$ content varied between -23.1 and -21.3‰, with an average value $-22.3 \pm 0.47 \text{‰}$ ($n=24$). F_{terr} varied between 12.5 and 39.7%, with an average value $26.8 \pm 7.7 \%$ ($n=24$). F_{mar} varied between 60.3 and 87.5%, with an average value $73.2 \pm 5.1 \%$ ($n=24$) (Fig 17a).

In the sediment core NYA21_03, the OC content varied between 0.3 and 0.6%, with an average value $0.4 \pm 0.09 \%$ ($n=27$). $\delta^{13}\text{C}$ content varied between -23.7 and -22.6‰, with an average value $-23.0 \pm 0.31 \text{‰}$ ($n=27$). F_{terr} varied between 37.7 and 51.4%, with an average value $39.4 \pm 5.1 \%$ ($n=27$). F_{mar} varied between 48.6 and 67.3%, with an average value $60.6 \pm 5.1 \%$ ($n=27$) (Fig 17a).

In the sediment core NYA21_04, the OC content varied between 0.6 and 1.6%, with an average value $1.3 \pm 0.18 \%$ ($n=26$). $\delta^{13}\text{C}$ content varied between -23.2 and -22.2‰, with an average value $-22.6 \pm 0.27 \text{‰}$ ($n=26$). F_{terr} varied between 25.6 and 41.3%, with an average value $31.7 \pm 4.4 \%$ ($n=26$). F_{mar} varied between 58.7 and 74.4%, with an average value $68.3 \pm 4.4 \%$ ($n=26$) (Fig 18a).

Regarding the three sediment cores collected in 2021, NYA21_01 showed a sharp decrease in Ca/Ti and Zr/Rb ratios at 48–50 cm depth, with a slight increase in Br/Cl ratio towards the top of the core; NYA21_03 showed a peak in Ca/Ti ratio at ~40–41 cm depth, while Br/Cl and Zr/Rb ratios remained relatively stable throughout the core; NYA21_04 showed a peak in Ca/Ti and Zr/Rb ratios at 49–50 cm depth, along with a slight decrease in Br/Cl ratio (Fig.18b). These results highlight the interactions between grain size, organic carbon and pollutant behavior, as well as the influence of environmental processes on sediment composition and contaminant distribution in the fjord system.

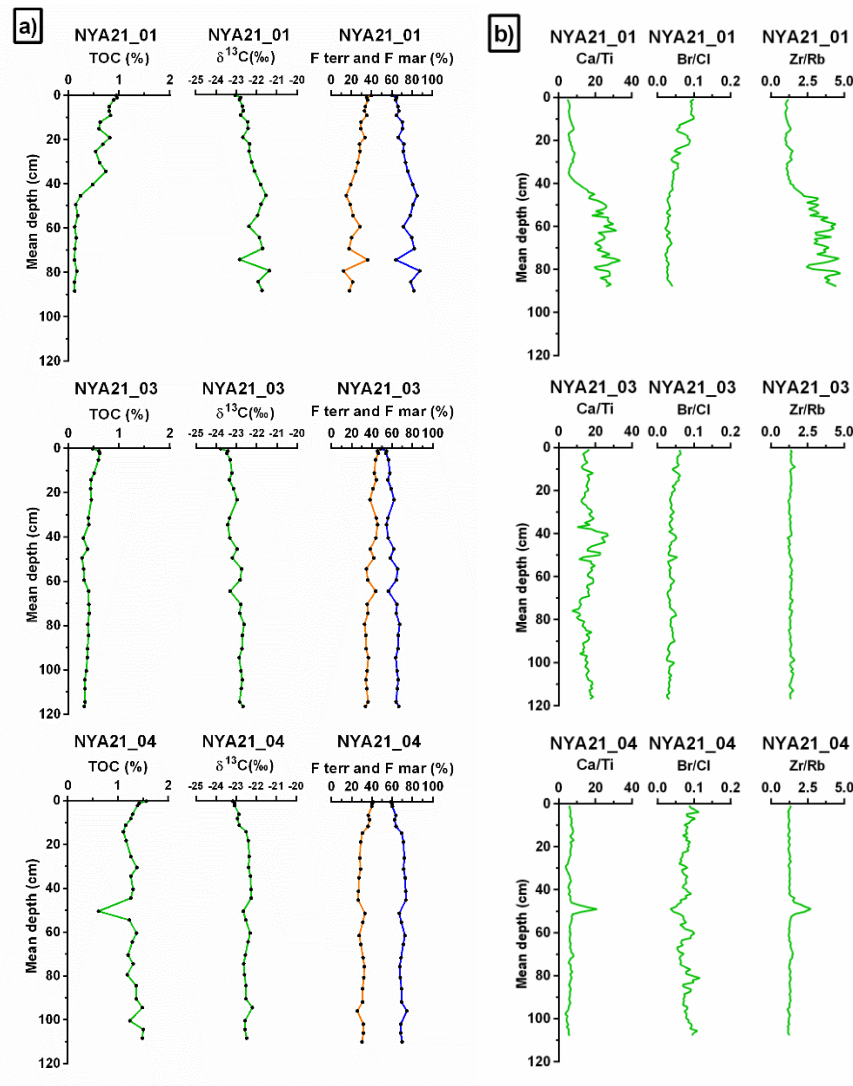


Figure 18 – a) TOC (%), $\delta^{13}\text{C}$ (‰), F_{terr} (%) (orange line) and F_{mar} (%) (blue line), and b) elemental ratios depth profiles in the sediment cores collected in 2021.

Grain-size distribution and organic carbon content are key factors influencing the behavior of organic pollutants in complex aquatic sediment systems (Spasojević et al., 2017). Across all the three sediment cores collected in 2021, fine fraction ($<63\mu\text{m}$) was predominant, constituting more than 80% of the total composition (Fig. 19). In the three cores, the Zr/Rb ratio acts as a proxy for grain size. However, this is most evident in core NYA21_01 where, consistent with the analysis of the grain size distribution, the Zr/Rb value increased markedly as the sand increased from 48-50 cm depth to the bottom. On the other hand, the prevalence of the fine fraction is particularly significant as it serves as the primary surface for the adsorption and accumulation of hydrophobic contaminants (Awad et al., 2019).

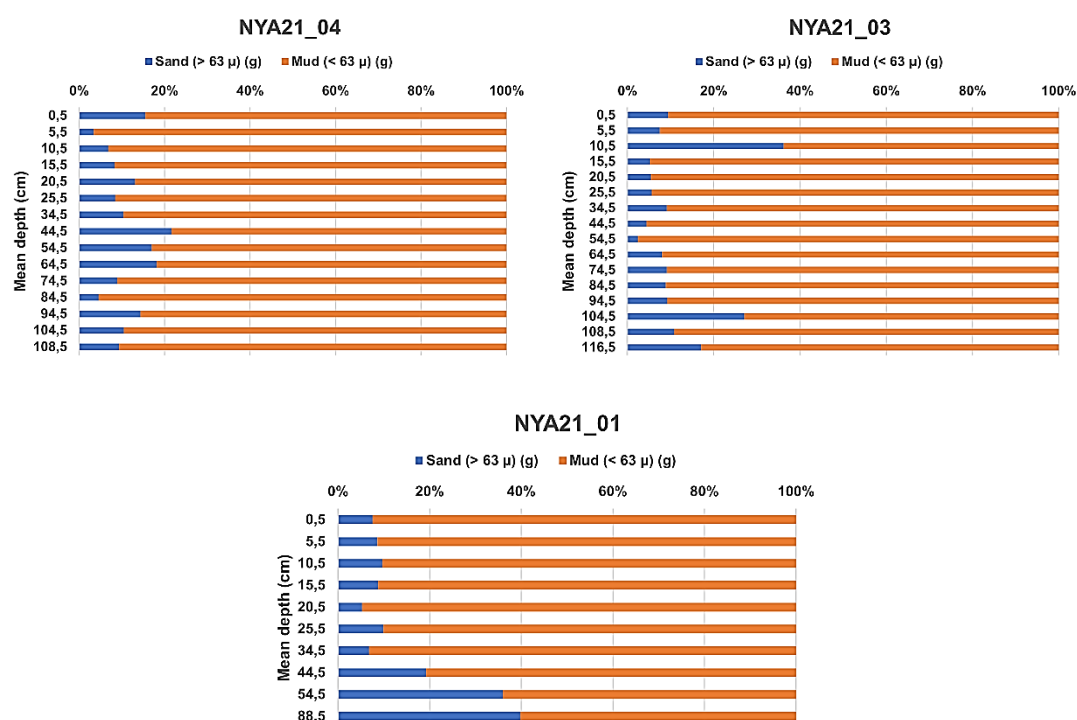


Figure 19 – Grain-size distribution in the three sediment cores collected in 2021.

4.2 Contaminant concentrations in the sediment cores

4.2.1 Occurrence and patterns of UV-Fs and SFs

Concentrations of UV-Fs and SFs in the sediment core NYA11_09 are presented in Tab. 11. Three UV-Fs (BP-3, OC, OD-PABA) and three SFs (ATII, ADBI, AHMI) were not detected in any sediment sample from the sediment core. Consequently, the following discussion will only include four UV-Fs and three SFs.

The total concentrations of UV-Fs ($\Sigma\text{UV-Fs}$) and SFs (ΣSFs) ranged from $< \text{LOD}$ to 10.4 ng g^{-1} ($2.1 \pm 2.6 \text{ ng g}^{-1}$) and $< \text{LOD}$ to 6.4 ng g^{-1} ($0.9 \pm 1.2 \text{ ng g}^{-1}$), respectively. Total and individual UV-Fs and SFs depth profiles are shown in Figure 20.

With reference to individual UV-Fs, EHMC, 4-MBC, EHS and HMS were detected in 95%, 18% and in 28 – 38% of the sediment samples, respectively, and their concentrations increased in the following order: EHMC ($< \text{LOD} - 6.6 \text{ ng g}^{-1}$) $>$ 4-MBC ($< \text{LOD} - 4.5 \text{ ng g}^{-1}$) $>$ HMS and EHS ($< \text{LOD} - 0.99 \text{ ng g}^{-1}$). 4-MBC profile revealed only a few detections, and an erratic trend. For this reason, it has not been reported in Fig. 19.

EHMC was the prevailing organic ultraviolet filter and contributed to $83 \pm 24\%$ of the total UV-Fs compounds in the sediment core, followed by 4-MBC ($8 \pm 20\%$), and HMS and EHS ($3 \pm 6\%$ and $4 \pm 6\%$). Spearman rank correlation analysis indicated that 4-MBC ($r = 0.34$, $p < 0.05$), EHS ($r = 0.75$, $p < 0.001$) and HMS ($r = 0.69$, $p < 0.001$) were all correlated with EHMC, pointing out a possible common source of contamination.

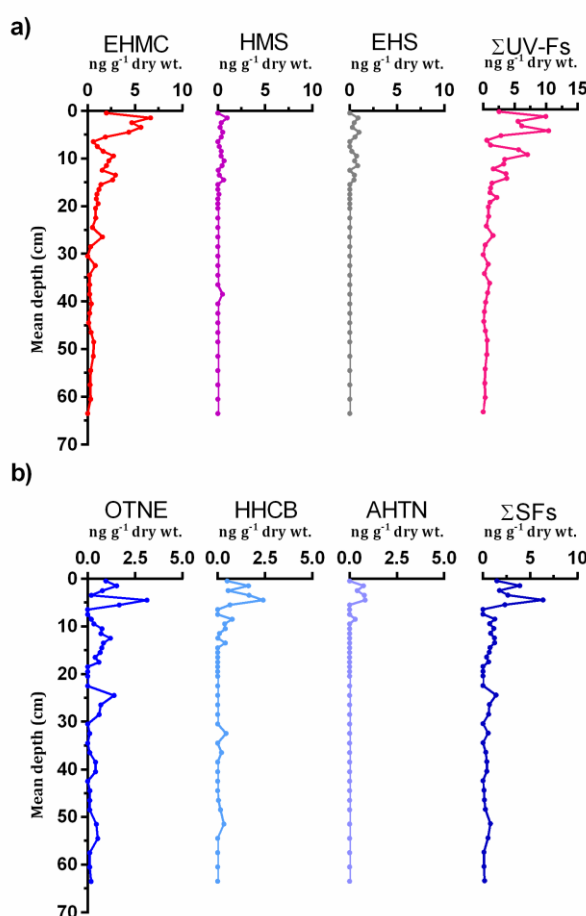


Figure 20 - Concentrations ($\text{ng g}^{-1} \text{ dry wt.}$) and composition profiles of (a) individual and total UV-Fs, (b) individual and total SFs in the sediment core NYA11_09.

As for individual SFs, OTNE, HHCB and AHTN were detected in 78%, 43% and 13% of the samples, respectively, and their concentrations increased in the following order: OTNE ($< \text{LOD} - 3.1 \text{ ng g}^{-1}$) $>$ HHCB ($< \text{LOD} - 2.4 \text{ ng g}^{-1}$) $>$ AHTN ($< \text{LOD} - 0.82 \text{ ng g}^{-1}$). On average, OTNE was the predominant synthetic fragrance contributing to $78 \pm 28\%$ of the total concentrations of SFs in the sediment core, followed by AHTN and HHCB ($19 \pm 22\%$ and

4 ± 8%, respectively). In addition, OTNE displayed a significant correlation with both HHCB ($r = 0.46$, $p < 0.01$) and EHMC ($r = 0.41$, $p < 0.01$), whereas AHTN was correlated with HHCB ($r = 0.63$, $p < 0.001$).

Since organic carbon is an important factor influencing the absorption and distribution of organic contaminants in sediments, correlations between the concentrations of UV-Fs, SFs, and OC content were explored. Spearman correlation analysis indicated a strong association between OC content and Σ UV-F ($r = 0.60$, $p < 0.001$), EHMC ($r = 0.62$, $p < 0.001$), and HMS ($r = 0.35$, $p < 0.001$) (Tab. 12).

Table 12 - Spearman correlation coefficients (r) matrices among UV-Fs, SFs and total organic carbon (TOC) (*= p -value < 0.05; **= p -value < 0.01; ***= p -value < 0.001).

	4MBC	EHMC	EHS	HMS	HHCB	AHTN	OTNE	Σ UV-Fs	Σ SFs	TOC
4MBC										
EHMC	0.34*									
EHS	0.39*	0.75***								
HMS	0.28	0.68***	0.84***							
HHCB	0.49**	0.63***	0.70***	0.55***						
AHTN	0.47**	0.53***	0.59***	0.54***	0.63***					
OTNE	0.12	0.41**	0.43**	0.39*	0.46**	0.22				
Σ UV-Fs	0.51**	0.95***	0.77***	0.74***	0.66***	0.55***	0.36*			
Σ SFs	0.32	0.57***	0.62***	0.52**	0.79***	0.55***	0.85***	0.56***		
TOC	0.29	0.62***	0.28	0.36*	0.20	0.29	0.19	0.60***	0.23	

4.2.2 Occurrence and patterns of PBDEs

Concentrations of PBDEs in the sediment cores NYA21-01, NYA21-03 and NYA21-04 are presented in Table 13. Tri-BDEs congeners -17, -25, -30, Tetra-BDEs congeners -66, -74, -75, Penta-BDEs congeners -85, -97+118, -101, Hexa-BDEs congeners -138, -139, -153, -154, -155, -156, Hepta-BDEs congeners -182, -181, -185, -191, Octa-BDEs congeners -196, -204, -198, -203 and Nona-BDEs congeners -206, -208 were never detected, thus they are not included in the following discussion. Overall, 11 out of 38 target PBDE congeners were detected in all three sediment cores.

The total concentrations of 11 PBDEs (Σ PBDEs), including BDE-28, BDE-47, BDE-49, BDE-71, BDE-99, BDE-100, BDE-119, BDE-116, BDE-173+190 and BDE-183, ranged from <LOD to 15.33, <LOD to 3.30 and 0.12 to 6.01 ng g⁻¹ in the sediment core NYA21_01, NYA21_03 and NYA21_04, respectively. Total PBDEs concentrations and individual congeners depth profiles are shown in Figure 21.

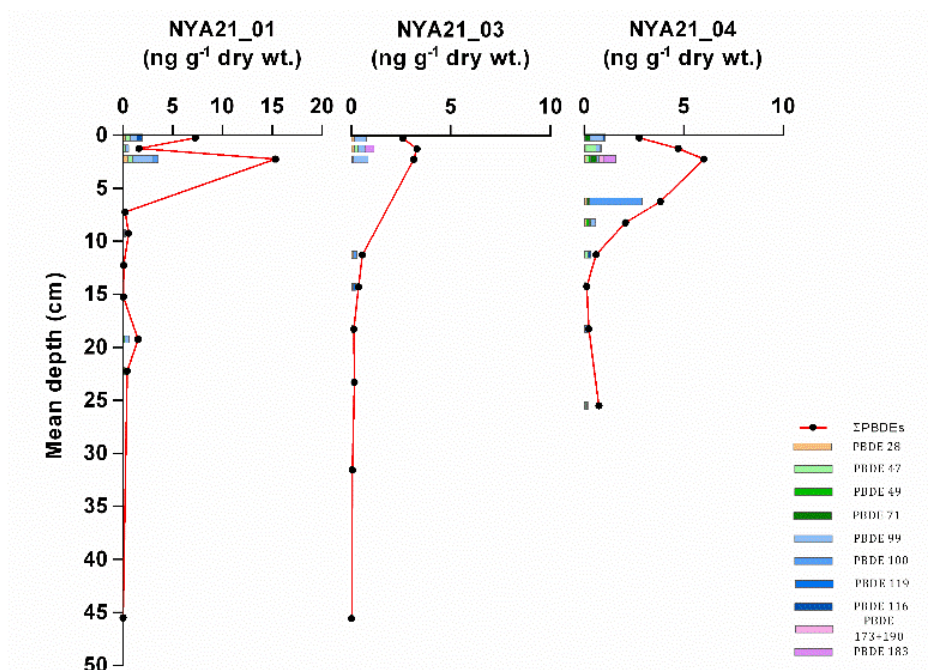


Figure 21 - Concentrations (ng g^{-1} dry wt.) and composition profiles of total and individual PBDE congeners in the sediment cores NYA21_01, NYA21_03 and NYA21_04.

Regarding the sediment core NYA21_01, the PBDE homologues distribution is as follows: penta- > tetra- > hepta- > tri- (Fig. 22a). Among penta-BDEs, BDE-99 is the most abundant congener (mean value $0.59 \pm 0.95 \text{ ng g}^{-1}$) contributing to 22 % of the total PBDEs, followed by BDE-116 (17 %), BDE-100 (14 %) and BDE-119 (7 %). Spearman rank correlation analysis indicated strong correlations between BDE-116 and BDE-28 ($r = 0.9$, $p < 0.001$), and between BDE-99 and BDE-49 ($r = 0.9$, $p < 0.001$), pointing out a possible common source of contamination (Tab 14a).

Regarding the sediment core NYA21_03, the PBDE homologues distribution is as follows: penta- > hepta- > tetra- > tri- (Fig. 22b). Among penta-BDEs, BDE-99 is the most abundant congener (mean value $0.26 \pm 0.37 \text{ ng g}^{-1}$) contributing to 23% of the total PBDEs, followed by BDE-116 (14%) BDE-100 (11) and BDE-119 (9%). Spearman rank correlation analysis indicated that BDE-116 was correlated with BDE-28 ($r = 0.9$, $p < 0.01$) and BDE-99 ($r = 0.9$, $p < 0.01$) (Tab 14b).

Regarding the sediment core NYA21_04, the PBDE homologues distribution is as follows: penta- > hepta- > tetra- > tri- (Fig. 22c). Among penta-BDEs, BDE-100 is the most abundant congener (mean value $0.26 \pm 0.37 \text{ ng g}^{-1}$) contributing to 22 ± 20 % of the total PBDEs, followed by BDE-116 (18%), BDE-99 (15 %) and BDE-119 (6 ± 13 %). Spearman rank correlation analysis indicated that BDE-119 was correlated with BDE-71 ($r = 0.8$, $p < 0.01$) (Tab 14c).

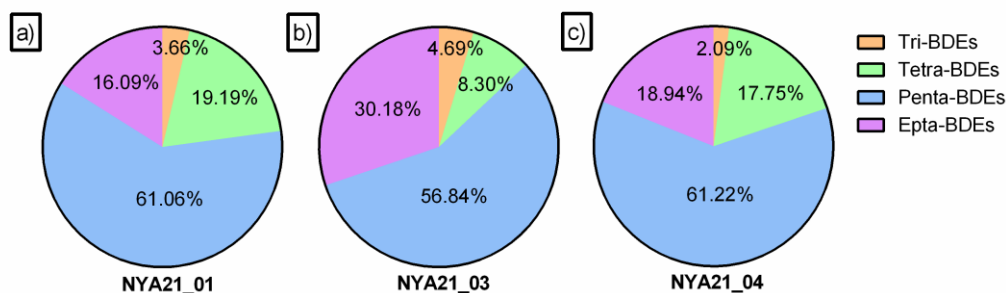


Figure 22 – PBDEs distribution pattern in the sediment cores a) NYA21_01, b) NYA21_03 and c) NYA21_04.

Besides the penta-BDEs, among the most abundant PBDE homologues in all three sediment cores are the hepta-BDEs, represented in this case by the congeners BDE 183 and BDE 173+190. Indeed, in the sediment core NYA21_01, BDE-183 accounted for 16% of the total PBDEs. BDE-183 and BDE 173+190 accounted for 17% and 13% in the sediment core NYA21_03 respectively, and 11% and 8% in the sediment core NYA21_04, respectively. In the sediment core NYA21_01, Spearman correlation analysis indicated that BDE-183 was correlated with BDE-28 ($r = 0.8$, $p < 0.01$), BDE-47 ($r = 0.9$, $p < 0.01$), BDE-49 ($r = 0.9$, $p < 0.01$), BDE-71 ($r = 0.8$, $p < 0.01$) and BDE-99 ($r = 0.8$, $p < 0.01$). Whereas, in the sediment core NYA21_03, BDE-183 was strongly correlated with BDE-47 ($r = 1.0$, $p < 0.001$) and in the sediment core NYA21_04, with BDE-49 ($r = 0.8$, $p < 0.01$), BDE-99 ($r = 0.8$, $p < 0.01$), BDE-119 ($r = 0.9$, $p < 0.01$) and BDE-173+190 ($r = 0.9$, $p < 0.01$); BDE-173+190 was correlated with BDE-99 ($r = 0.8$, $p < 0.01$).

Since organic carbon (OC) plays an important role in the absorption and distribution of organic contaminants within sediments, the concentrations of PBDEs were correlated with OC content (Tab 14). For sediment core NYA21_01, Spearman correlation analysis showed significant positive correlations between TOC and seven of the eleven detected congeners: BDE-28 ($r = 0.8$, $p < 0.01$), BDE-47 ($r = 0.7$, $p < 0.05$), BDE-49 ($r = 0.7$, $p < 0.05$), BDE-71 ($r = 0.7$, $p < 0.05$), BDE-99 ($r = 0.8$, $p < 0.01$), BDE-116 ($r = 0.7$, $p < 0.05$), and BDE-183 ($r = 0.8$, $p < 0.05$).

For sediment core NYA21_03, three of the eleven detected congeners correlated positively with TOC: BDE-28 ($r = 0.8$, $p < 0.05$), BDE-99 ($r = 0.8$, $p < 0.01$), and BDE-116 ($r = 0.9$, $p < 0.01$).

For sediment core NYA21_04, positive correlations were observed for TOC and five of the eleven detected congeners: BDE-71 ($r = 0.7$, $p < 0.05$), BDE-99 ($r = 0.8$, $p < 0.05$), BDE-119 ($r = 0.7$, $p < 0.05$), BDE-116 ($r = 0.7$, $p < 0.05$), and BDE-173+190 ($r = 0.7$, $p < 0.05$).

The total PBDE concentrations (Σ_{11} PBDEs) were strongly correlated with TOC across all three sediment cores: NYA21_01 ($r = 0.9$, $p < 0.001$), NYA21_03 ($r = 0.9$, $p < 0.001$), and NYA21_04 ($r = 0.8$, $p < 0.01$).

Tabella 14 - Spearman correlation coefficients (*r*) matrices among PBDEs and total organic carbon (TOC) (*= *p* < 0.05; **= *p* < 0.01; ***= *p* < 0.001) in the sediment core: a) NYA21_01; b) NYA21_03 and c) NYA21_04.

a)	BDE-28	BDE-47	BDE-49	BDE-71	BDE-99	BDE-100	BDE-119	BDE-116	BDE-173+190	BDE-183	ΣPBDEs	TOC
BDE-28												
BDE-47	0.70*											
BDE-49	0.82**	0.85*										
BDE-71	0.88**	0.70*	0.88**									
BDE-99	0.77*	0.75*	0.89***	0.67*								
BDE-100	0.79**	0.71*	0.61	0.64	0.64							
BDE-119	0.71*	0.86*	0.79*	0.71*	0.70*	0.86*						
BDE-116	0.94***	0.63	0.66*	0.85**	0.59	0.81**	0.69*					
BDE-173+190												
BDE-183	0.80**	0.92**	0.98**	0.82**	0.87**	0.61	0.79*	0.65				
ΣPBDEs												0.93***
TOC	0.79**	0.75*	0.73*	0.68*	0.81**	0.57	0.51	0.70*		0.78*	0.93***	

b)	BDE-28	BDE-47	BDE-49	BDE-71	BDE-99	BDE-100	BDE-119	BDE-116	BDE-173+190	BDE-183	ΣPBDEs	TOC
BDE-28												
BDE-47	0.67											
BDE-49	0.72	0.70										
BDE-71	0.72	0.70	1.00*									
BDE-99	0.82*	0.76*	0.55	0.55								
BDE-100	0.59	0.07	0.60	0.60	0.35							
BDE-119	0.32	0.46	0.11	0.11	0.43	-0.28						
BDE-116	0.88**	0.75*	0.67	0.67	0.90**	0.40	0.63					
BDE-173+190	0.49	0.57	0.22	0.22	0.80*	0.02	0.38	0.55				
BDE-183	0.67	1.00***	0.70	0.70	0.76*	0.07	0.47	0.75*	0.57*			
ΣPBDEs												0.95***
TOC	0.71*	0.60	0.43	0.43	0.86**	0.44	0.55	0.88**	0.55	0.60	0.95***	

c)	BDE-28	BDE-47	BDE-49	BDE-71	BDE-99	BDE-100	BDE-119	BDE-116	BDE-173+190	BDE-183	ΣPBDEs	TOC
BDE-28												
BDE-47	0.07											
BDE-49	0.40	0.64										
BDE-71	0.83*	0.18	0.65									
BDE-99	0.30	0.64	0.74*	0.64								
BDE-100	0.69*	0.17	0.05	0.39	0.05							
BDE-119	0.68	0.48	0.71*	0.85**	0.77*	0.47						
BDE-116	0.42	0.46	0.46	0.56	0.68	0.23	0.81*					
BDE-173+190	0.43	0.72*	0.72*	0.67	0.85**	0.33	0.78*	0.47				
BDE-183	0.54	0.59	0.85**	0.78*	0.85**	0.31	0.87**	0.50	0.94**			
ΣPBDEs												0.85**
TOC	0.59	0.47	0.39	0.69*	0.78*	0.54	0.81*	0.75*	0.75*	0.68	0.85**	

4.3 Chronology

4.3.1 Dating in sediment core of 2011

The age of the individual core sections has been estimated from the unsupported ^{210}Pb activity using the rPlum age-depth model (Fig. 23). The age-depth model was anchored using the coring date, and the time markers obtained from ^{137}Cs activity (Miseroocchi et al., 2016) indicating that the signal of nuclear bomb tests occurred at 21 and 31 cm depth (1964 and 1954) with the Chernobyl accident recorded at 10 cm (1986). A further chronological marker (Ca/Ti) (Fig.15) indicative of the last Kongsvegen glacier surge (1948) (Kehrl et al., 2011) was used to constrain the ^{210}Pb age-depth model.

The unsupported activities occurred in the first 40 cm reaching the age of 1932 AD. The Bayesian rplum model returned a modeled sedimentation accumulation rate (SAR) between 0.3 and 0.9 cm yr^{-1} over a time span < 100 yr. SAR was constant before the mid-20th century ($\sim 0.5 \text{ cm yr}^{-1}$), and then nearly doubled between the mid- and late 1950s ($\sim 0.8\text{-}0.9 \text{ cm yr}^{-1}$).

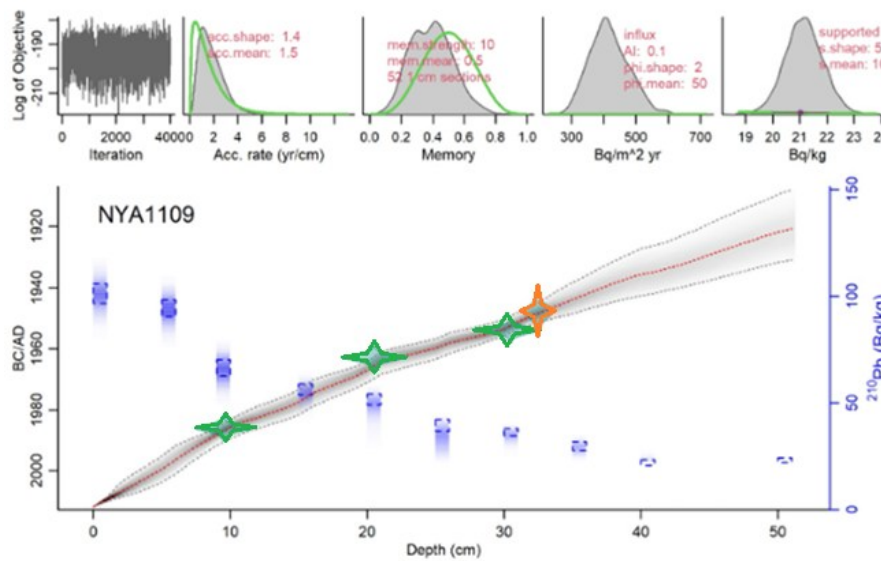


Figure 23 - Age-depth model for sediment core NYA11_09 (green outline symbols represent ^{137}Cs time marker, orange outline symbol represents the discontinuity detected by Ca/Ti ratio at 32-33 cm used as time marker of the last Kongsvegan glacier surge in 1948).

4.3.2 Dating in sediment cores of 2021

An age-depth model was developed for each sediment core to exploit the dating results obtained from the ^{14}C analyses (Fig.24). These results have been compared with retene depth profiles (Fig. 25). Retene (1-methyl-7-isopropyl phenanthrene) is a pyrogenic polycyclic aromatic hydrocarbon (PAH) used as a biomarker for biomass burning (Kim et al., 2011). Since retene is a marker of terrestrial organic matter and is associated with coal particles, it has become a particularly useful tool for dating sediments in the proximity of coal mining, an activity that flourished at Ny-Ålesund in the 20th century. Retene was previously applied by (Tesi et al., 2021) as an external time marker in the same area, so the same method there reported was applied in this study.

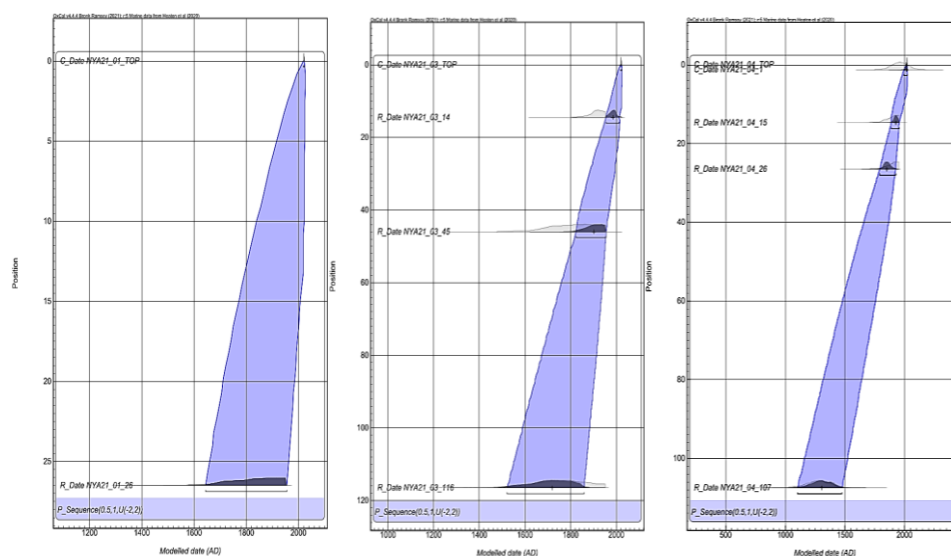


Figure 24 - Age-depth models for sediment cores NYA21_01, NYA21_03 and NYA21_04.

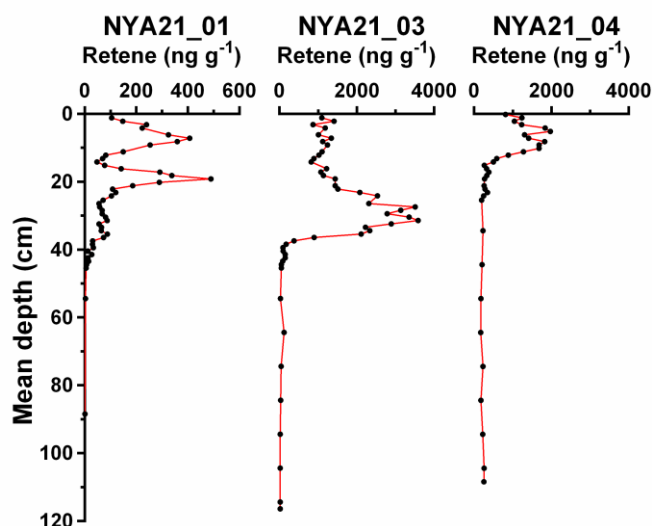


Figure 25 – Retene depth profiles (ng g^{-1}) in the sediment cores NYA21_01, NYA21_03 and NYA21_04.

Depth levels used for the construction of the age-depth models are different for each sediment core, based on the quantity of forams detected for that layer and the resulting radiocarbon dating. Only the top (0 cm) corresponded to 2021 AD for each core.

For the sediment core NYA21_01, two depth levels (0 cm and 26.5 cm) were used for the construction of the age-depth model. The median calibrated age (year AD) obtained for the depth level 26.5 cm corresponded to 1835 ± 153 AD. In this case, the dating error is very large considering that only two depth levels were used, and so this makes it more difficult to compare this result with the retene profile. However, from the retene profile it is possible to notice that from depth 26.5 the trend increases, revealing a possible onset of the coal mining activity that took place in Ny-Ålesund from 1916 to 1962. This date falls within the temporal range obtained by the age-depth model, so it can be considered congruent. The sediment accumulation rate (SAR) obtained from the age-depth model was 0.13 cm yr^{-1} .

For the sediment core NYA21_03, four depth levels (0 cm, 14.5 cm, 46 cm and 116.5 cm) were used for the construction of the age-depth model. The median calibrated age (year AD) obtained for the depth level 116.5 cm corresponded to 1719 ± 168 AD, defining the bottom age of the core. The median calibrated age (year AD) obtained for the depth level 46 cm corresponded to 1902 ± 65 AD, consistent with the retene profile that, at the same depth, showed a first increase in the trend, which might indicate the year 1916. The median calibrated age (year AD) obtained for the depth level 14.5 cm corresponded to 1984 ± 31 AD, consistent with the retene profile that revealed a drop of the trend, which might indicate the abrupt end of the mining activity in 1962. The sediment accumulation rate (SAR) obtained from the age-depth model was 0.40 cm yr^{-1} from the top to 14 cm

depth, then 0.36 cm yr^{-1} from 15 to 45 cm depth, and 0.38 cm yr^{-1} from 46 to the bottom of the core.

For the sediment core NYA21_04, five depth levels (0 cm, 1.25 cm, 14.75 cm, 26.5 cm and 107.5 cm) were used for the construction of the age-depth model. The median calibrated age (year AD) obtained for the depth level 107.5 cm corresponded to $1306 \pm 150 \text{ AD}$, defining the bottom age of the core. The median calibrated age (year AD) obtained for the depth level 26.5 cm corresponded to $1849 \pm 67 \text{ AD}$, consistent with the retene profile that, at the same depth, showed a first increase in the trend. The median calibrated age (year AD) obtained for the depth level 14.75 cm corresponded to $1923 \pm 35 \text{ AD}$, consistent with the retene profile that revealed a rapidly increasing trend which might indicate the beginning of coal mining activity in 1916. The median calibrated age (year AD) obtained for the depth level 1.25 cm corresponded to $2015 \pm 14 \text{ AD}$, consistent with retene profile that revealed a clearly declining trend. The sediment accumulation rate (SAR) obtained from the age-depth model was 0.15 cm yr^{-1} from the top to 14 cm depth, then 0.17 cm yr^{-1} from 15 to 26 cm depth, and 0.15 cm yr^{-1} from 27 to the bottom of the core.

Table 11 - Synthetic fragrances (SFs) and organic UV-Filters (UV-Fs in the sediment core NYA11-09 (n=40). Mean concentration (ng g⁻¹ dry wt.), standard deviation (SD), minimum value (Min), maximum value (Max), Detection rate (%DR); samples not detected are indicated as <LOD= below limit of detection.

Class	Compound	Mean	SD	Min	Max	%DR
SFs	AHTN	0.08	0.21	<LOD	0.82	13
	HHCB	0.27	0.53	<LOD	2.41	43
	ATII	-	-	<LOD	<LOD	0
	ADBI	-	-	<LOD	<LOD	0
	AHMI	-	-	<LOD	<LOD	0
	OTNE	0.60	0.61	<LOD	3.13	78
	ΣSFs	0.94	1.19	<LOD	6.37	-
UV-Fs	HMS	0.15	0.24	<LOD	0.99	38
	BP-3	-	-	<LOD	<LOD	0
	OC	-	-	<LOD	<LOD	0
	OD-PABA	-	-	<LOD	<LOD	0
	4-MBC	0.38	1.03	<LOD	4.52	18
	EHS	0.16	0.29	<LOD	0.98	28
	EHMC	1.43	1.56	<LOD	6.65	95
	ΣUV-Fs	2.12	2.60	<LOD	10.38	-

Table 13 - PBDEs concentration (ng g⁻¹ dry wt.) in the sediment cores NYA21_01 (n=10), NYA21_03 (n=9) and NYA21_04 (n=9). Mean ± Standard Deviation (Mean ± SD), Range (minimum value-maximum value), Detection Rate % (DR %); congeners not detected are indicated as <LOD= below the limit of detection.

	NYA21_01			NYA21_03			NYA21_04		
Tri-BDEs	Mean ± SD	Range	DR (%)	Mean ± SD	Range	DR (%)	Mean ± SD	Range	DR (%)
PBDE 28	0.10 ± 0.16	<LOD-0.52	70	0.05 ± 0.07	<LOD-0.16	67	0.05 ± 0.05	<LOD-0.12	67
Tetra-BDEs									
PBDE 47	0.19 ± 0.36	<LOD-0.99	30	0.06 ± 0.11	<LOD-0.34	44	0.13 ± 0.19	<LOD-0.59	55
PBDE 49	0.14 ± 0.28	<LOD-0.88	40	0.02 ± 0.04	<LOD-0.10	22	0.09 ± 0.12	<LOD-0.32	67
PBDE 71	0.18 ± 0.27	<LOD-0.81	70	0.02 ± 0.03	<LOD-0.09	22	0.20 ± 0.20	<LOD-0.61	67
Penta-BDEs									
PBDE 99	0.59 ± 0.95	<LOD-2.99	80	0.26 ± 0.37	<LOD-0.85	44	0.36 ± 0.40	<LOD-0.94	67
PBDE 100	0.39 ± 1.11	<LOD-3.55	30	0.13 ± 0.12	<LOD-0.35	66	0.53 ± 0.93	<LOD-2.89	78
PBDE 119	0.20 ± 0.62	<LOD-1.96	20	0.10 ± 0.21	<LOD-0.64	33	0.13 ± 0.16	<LOD-0.43	55
PBDE 116	0.47 ± 0.75	<LOD-1.98	70	0.16 ± 0.23	<LOD-0.61	44	0.41 ± 0.36	<LOD-1.05	89
Hepta-BDEs									
PBDE 173 +190	-	-	-	0.15 ± 0.30	<LOD-0.72	22	0.19 ± 0.35	<LOD-0.95	55
PBDE 183	0.43 ± 0.74	<LOD-1.88	40	0.19 ± 0.38	<LOD-1.15	44	0.25 ± 0.51	<LOD-1.59	55
ΣPBDEs									
	-	<LOD-15.33	-	-	<LOD-3.30	-		0.12-6.01	

CHAPTER 5 – Discussion

5.1 Sedimentary evolution of the study area

Dating obtained for the four sediment cores analyzed in this study represents a necessary tool to interpret both past and present sedimentation processes in this area. Indeed, periods of glacier advances and retreat, and shoreline evolution are responsible for fluctuations in sediment fluxes in the fjord and changes in the geomorphological regime (Husum et al., 2019, Svendsen et al., 2002). Sedimentation accumulation rate (SAR) values obtained in this study are consistent with those obtained in this area in previous studies (Streuff et al., 2015, Pouch et al., 2017, Elverhøi et al., 1983, Tesi et al., 2021). In this context, the contribution of tidewater glaciers Kronebreen and Kongsbreen is particularly relevant. Indeed, these two glaciers are among the fastest-flowing glaciers on Svalbard and, therefore, important contributors to the total dynamic mass loss in the Svalbard archipelago (Schellenberger et al., 2015). These two tidewater glaciers are located in the inner part of Kongsfjorden and are among the main suppliers of freshwater and sediments in the fjord (Pramanik (Pramanik et al., 2018, Kehrl et al., 2011, Svendsen et al., 2002). The last Kronebreen surge dates back to 1869, since then it retreated 10-11km until 1995 (Schellenberger et al., 2015). In 1948, Kongsvegen surged, with a major advance of 4km (Kehrl et al., 2011). At that time both glaciers shared the same calving front, and successively the Kronebreen-Kongsvegen complex retreated afterwards. In this study, the SAR variation observed in the sediment core NYA11_09 around 1950s matches the last surge event of 1948. Retreat of the Kronebreen-Kongsvegen glacier complex has significantly slowed since the late 1980s, due to post-surge quiescent-phase conditions (Trusel et al., 2010). This might explain the constant SAR values since the late 1980s, in relation to the steady state of glaciers.

Higher OC content was observed in the sedimentary sequences collected in the outer KKS (NYA21_01 and NYA21_04) compared to those collected in the inner part (NYA21_03 and NYA11_09). The inner part of the fjord is more influenced by glaciers activity, resulting in higher sedimentation rates and lower organic matter content, which is consistent with previous results obtained by (Miserocchi et al., 2016, Howe et al., 2003, Svendsen et al., 2002).

In this study, the marine contribution was higher in sediment cores from the outer part of the fjord, reflecting the dominant influence of nutrient-rich Atlantic water inflow on the depositional environment (Winkelmann and Knies, 2005) and the terrestrial contribution was higher in the cores collected in the inner part of the fjord. The OC spatial gradient might be related to decreasing biological productivity from the open ocean towards the inner fjord, also related to the marine vs. terrestrial organic matter contribution (Kim et al., 2011). An explanation for the decreasing OC content could be due to the dilution from increasing detritic material discharged from glacier melting (Miserocchi et al., 2016).

This contribution showed an increasing trend in the upper part of the cores as reported by (Wu et al., 2023), revealing an ever-increasing release of terrigenous materials in recent years. Indeed, the analysis of a 6-year time series of particle fluxes collected by an oceanographic mooring in Kongsfjorden, already reported a progressive increase in the glacier-derived fluxes of lithogenic material and watershed run-off, also revealing the land-derived input will remarkably increase over time in a warming scenario (D'Angelo et al., 2018).

5.2 *Historical deposition of selected contaminants*

5.2.1 UV-Fs and SFs in sediment core of 2011

The modern (last century) sediment chronology estimated from the ^{210}Pb rplum age-depth model was paired to the concentration profiles of target UV-Fs and SFs, and to the period of production and consumption at global and regional scale (1950 – to the early 2010s), as well as human presence in the Kongsfjorden. On the basis of the age-depth model and historical UV-Fs and SFs concentrations, three time periods were selected in the sediment record:

- A) the top section, dated from the end of the 1980s to the early 2010s, corresponding to peak concentrations and growing human presence in the fjord;
- B) the intermediate section, dated between the 1950 and the end of the 1980s, corresponding to industrial production and consumption global and regional trends;
- C) the deeper section, deposited before the 1950s, prior to industrial production of the target compounds.

Temporal trends in concentrations of the individual UV filters (EHMC, HMS, EHS) and synthetic fragrances (OTNE, HHCB, AHTN) with estimated age of sediment layers are shown in Figure 26. Among the UV-Fs, the only compound showing an erratic trend was 4-MBC, for this reason it will not be discussed. EHS and HMS were undetected until the early 1970s, and then increased until a peak concentration around late 1990s-early 2000s, declining thereafter. EHMC has been detected as early as the 1950s, with the highest concentrations and a trend increasing to around late 1990s-early 2000s, as previously described for the other UV-Fs (EHS and HMS). These results are in accordance with those obtained by (Langford et al., 2015, Mizukawa et al., 2017, Pintado-Herrera et al., 2017, Tsui et al., 2015) that confirmed EHMC as predominant in sediments. There is a lack of data regarding UV-Fs in sediments from polar regions, thus it is difficult to compare the results in this study with UV-Fs levels in the Arctic. However, a recent study (Costa et al., 2024) detected UV-Fs (including EHMC, 4-MBC and HMS) in surface sediments from Admiralty Bay (Antarctica Peninsula). Moreover, several studies have been carried out, especially in the last decade, to assess the occurrence and concentration of organic UV-Fs and SFs in different matrices from polar and high-altitude areas (Tab.15).

Among synthetic fragrances, HHCB and AHTN were undetected until the early 1980s, and then increased until a peak concentration around late 1990s-early 2000s, declining thereafter. OTNE showed a peak concentration around late 1990s-early 2000s too, however displaying a variable concentration trend from the 1950s. OTNE was predominant and, along with HHCB and AHTN, it was always detected in marine surface sediment samples (Pintado-Herrera et al., 2017) and wastewater and sludge samples collected in a SW Spain coastal area (Combi et al., 2016).

Principal Component Analysis (PCA) was performed to compare individual UV-Fs and SFs profiles and highlight differences in the sediment sections in the three time periods.

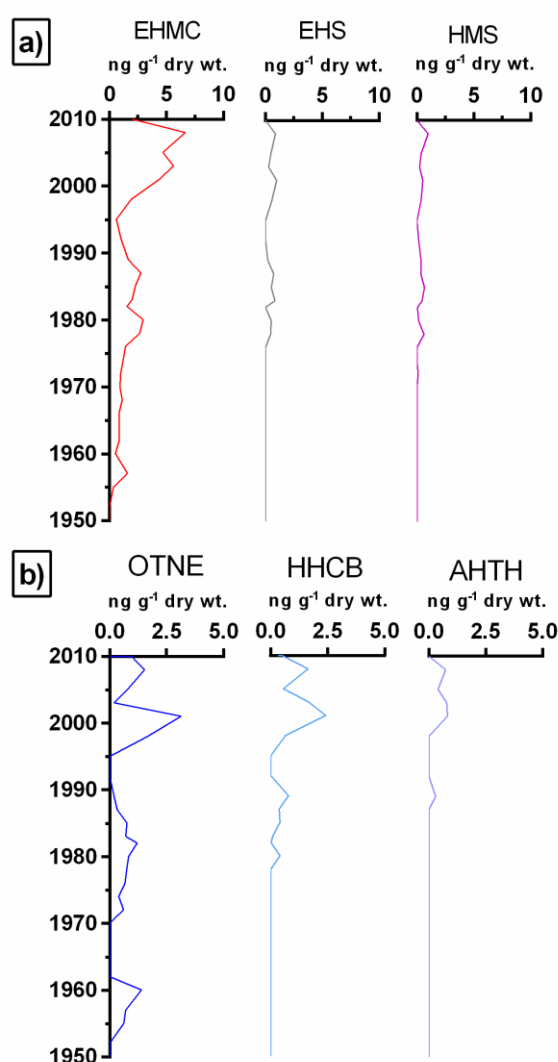


Figure 26 - Temporal trends of a) UV-Fs and b) SFs concentrations (ng g^{-1} dry wt.) in sediment core NYA11_09.

PCA results are shown in Fig. 27 and Table 16. Regarding UV-Fs, the first principal component (PC1) accounted for 72% of total variation and has large association with EHMC, while the second principal component (PC2) accounted for 23% of total variation

and has large association with 4-MBC, accounting for a total cumulative variation of 95%. The results of PCA based on SFs, show that PC1 and PC2 explained a variation of 72 and 26% respectively, accounting for a total cumulative variation of 98%. PC1 has a large association with OTNE and HHCB, while PC2 has large association with OTNE. For both UV-Fs and SFs, PCA scores for the intermediate time period (1950 - end of the 1980s) are overlapped with those of the deep section (before 1950), while the top section (end of 1980s to present) was clearly separated from the intermediate and older time periods. These results were confirmed by Permanova statistical analysis, carried out according to the division into the three time periods described above (Table 17). Regarding UV-Fs, Permanova results showed that individual UV-Fs concentrations found in the top ($1.3 \pm 1.7 \text{ ng g}^{-1}$), the intermediate ($0.4 \pm 0.7 \text{ ng g}^{-1}$) and the deep ($0.1 \pm 0.2 \text{ ng g}^{-1}$) sections of the sediment core differ significantly from each other ($0.001 < p < 0.01$). Regarding SFs, the results showed that individual SFs concentrations are significantly different between the top section ($0.7 \pm 0.8 \text{ ng g}^{-1}$) and intermediate section ($0.2 \pm 0.4 \text{ ng g}^{-1}$) ($p = 0.001$), and between top and bottom section of the sediment core ($0.2 \pm 0.3 \text{ ng g}^{-1}$) ($p = 0.002$). This suggests that concentrations of UV-Fs deposited in early 2010s – end of 1980s are significantly higher than levels measured in the intermediate and deeper sediments.

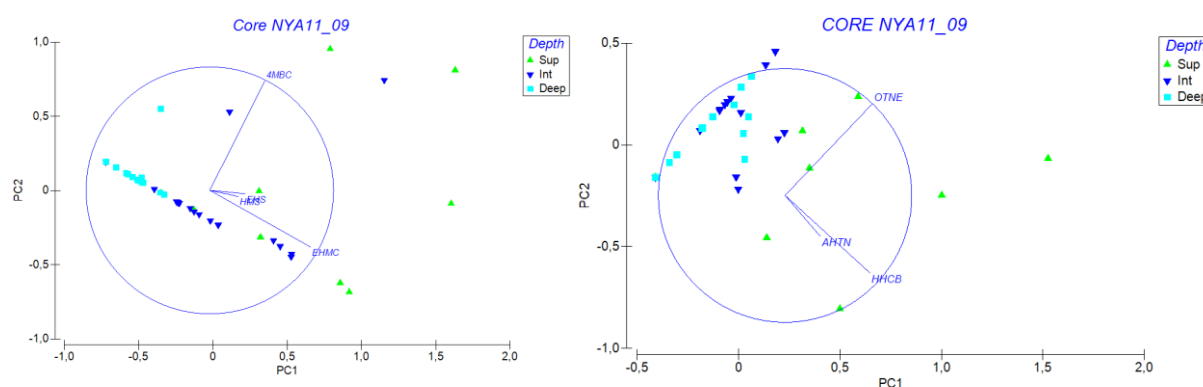


Figure 27 - PCA of individual UV-Fs (left) and SFs (right) in the sediment core NYA11_09.

Table 16 - UV-Fs and SFs PCA coefficients in the sediment core NYA11_09.

<i>Eigenvectors</i>				
<i>SFs</i>				
	PC1	PC2	PC3	
HHCB	0.669	-0.611	0.422	
AHTN	0.277	-0.322	-0.905	
OTNE	0.689	0.723	-0.046	
<i>UV-Fs</i>				
	PC1	PC2	PC3	PC4
4MBC	0.445	0.886	0.122	-0.04
EHMC	0.816	-0.46	0.347	-0.047
EHS	0.287	-0.028	-0.611	0.737
HMS	0.231	-0.05	-0.701	-0.673

Table 17 - PERMANOVA table of results and pair-wise tests for target a) UV-Fs and b) SFs ($p < 0.05$, with a confidence interval of 95%).

a) UV-Fs							b) SFs						
Source	df	SS	MS	Pseudo-F	P(perm)	Unique perms	Source	df	SS	MS	Pseudo-F	P(perm)	Unique perms
De	2	7.5618	3.7809	10.908	0.001	999	De	2	2.3005	1.1503	6.8398	0.001	999
Res	37	12.825	0.34662				Res	37	6.2223	0.16817			
Total	39	20.387					Total	39	8.5229				
Groups	t	P(perm)	Unique perms					Groups	t	P(perm)	Unique perms		
A, B	2.2219	0.017	999					A, B	2.9155	0.001	994		
A, C	4.4961	0.001	998					A, C	2.86	0.002	993		
B, C	3.4006	0.001	999					B, C	0.35934	0.848	999		

The manufacturing of HHCB (Galaxolide®) started in late 1962 (David, 2020, Gautschi et al., 2001), with large scale production beginning in 1963 reaching 35 tons in 1966 (David, 2020). Prior to 1962, it was detected in some samples at low concentrations, but this could be attributed to downcore diffusion. AHTN (Tonalide®) was patented in 1954, but it was not detected until the late 1980s/early 1990s. From there, it followed the same trend as previously described for HHCB, but at lower concentrations. Presumably, this is related to HHCB being used globally in much larger quantities than AHTN. Indeed, in 2003, HHCB was defined a high production volume (HPV) chemical by the U.S. EPA (Peck and Hornbuckle, 2004). However, AHTN was considered the most employed polycyclic musk after HHCB due to its hydrophobicity, one of the factors accounting for musk odorants deposit on the fabric during the washing process (David, 2020; Gautschi et al., 2001). Among the synthetic fragrances analyzed in this study, OTNE is the one that showed the most erratic trend, as well as higher concentrations than HHCB and AHTN. OTNE belongs to the category of synthetic ionone and woody smelling compounds. Its “predecessor” compound was created in 1893, although it was patented as Iso E Super® in 1972 (Gautschi et al., 2001). Earlier detection of this compound is likely due to diffusion into the deeper layers bioturbation-induced down-core diffusion or vertical transport through interstitial waters.

This is the first study analyzing the compound OTNE in the Arctic. On the contrary, few studies have been conducted in Arctic environmental matrices to investigate the occurrence of HHCB, AHTN and other synthetic fragrances. For example, (McDonough et al., 2016) analyzed HHCB and AHTN in dissolved water and gaseous phase in Great Lakes (Canada) revealing elevated concentrations ($< \text{LOD} - 2.6 \text{ ng L}^{-1}$) at many shoreline sites nearby urban centers and WWTPs.

Until the early 2000s, HHCB and OTNE were among the most widely used perfumery ingredients in detergents and homecare products, accounting for an annual production of 7,000-8,000 and 2,500-3,000 tonn/yr, respectively (Gautschi et al., 2001). Approximately 63% of the European production volume of HHCB is exported outside the EU (including also Norway and Switzerland) (TNO, 2008). Moreover, OTNE, AHTN and HHCB have been widely used in luxury perfumery, above all in the most famous perfumes

of the 80s (David, 2020). Thus, their wide manufacturing and use in many different products may explain why these compounds have been detected over others. However, according to surveys carried out in Europe in the early 1990s and early 2000s, the second half of the 1990s saw a significant decrease in the use volumes of polycyclic musks, which also included HHCB and AHTN (HERA, 2004). As a result of negative publicity due to the detection of these substances in the environment and in breast milk, brands across Europe have abstained from using products containing polycyclic musks. In fact, on the European market, Polycyclic Musks-free products have increasingly started to replace those containing polycyclic musks (HERA, 2004). Today, OTNE still represents one of the largest compounds used in a variety of perfumery products, with a volume percentage in some top fragrances ranging from 18 to 100% (Stepanyuk and Kirschning, 2019).

Regarding the organic UV-filters, the highest concentrations were recorded for EHMC. EHMC was always detected also in other Arctic matrices, like snow samples from north-west Spitsbergen (D'Amico et al., 2024) and the Arctic char from Svalbard Archipelago (Magali et al., 2013). Indeed, EHMC is considered a High Production Volume (HPV) Chemical (supply in EU > 1,000 ton/year) (OECD, 2004) and it is widely used in European personal care products, with concentration up to 10% in cosmetic formulations (other UV-Fs concentrations in cosmetics: 4-MBC 4%, EHS 5 %, HMS 10%) (EC, 2009). This, in combination with its continuous release in the environment could explain its high detection frequency in all different matrices. However, there is still a lack of knowledge about the occurrence of UV-Fs in the Arctic environment and biota.

UV filters analyzed in this study were mostly synthesized around the 1950s (Christensen (Christensen and Giese, 1950), although they were marketed in sun screening mixtures around late 60s-early 70s, when formulators began to develop water-resistant sunscreens (Torosian and Lemberger, 1972, U.S., 1967, U.S., 1973, Watanabe Toshio et al., 1971). As for OTNE, the earlier detection of EHMC in the deepest layers of the core could be explained by considering its physico-chemical properties in association with the organic carbon content, that may have facilitated post-depositional transport to deeper sediments through down-core diffusion over time. EHMC is the one that showed the highest concentrations, probably because in the 1990s it was the most common ingredient in sunscreens for UV-B protection (Drissi et al., 2022, Svarc, 2015). Thus, greater production and use of this compound might explain the higher concentrations found in the sediment core compared to the UV filters EHS and HMS.

These results are in accordance with production and use of these compounds, but also with their physico-chemical properties, determining a greater or lower affinity for organic matter in sediments. Evidence thereof is given by (Domínguez-Morueco et al., 2021) that measured organic UV-Fs in water and suspended particulate matter samples from the Antarctic peninsula, showing higher concentrations of the less polar compounds (e.g. EHMC) in the suspended particulate matter than in water samples.

In the early 2000s, new regulations and monitoring tools came into force to assess the potential environmental risk posed by chemicals. EHMC was included in the first European Watch List under the Environmental Quality Standards Directive (EQSD - Directive 2008/105/EC as amended by Directive 2013/39/EU) for monitoring data on potential water pollutants (EQSD, 2008). The list was first updated in June 2018 and was concluded that EHMC should be removed from the Watch List since the monitoring data quality was good enough to perform the risk assessment. EHMC has also been included into the European Chemicals Agency (ECHA) CoRAP list 2014 for further evaluation as suspected persistent, bioaccumulative, toxic (PBT) (ECHA, 2013). These EU-wide decisions have had an impact on the detection of EHMCs in the environment. As a result, a study (Nagorka and Duffek, 2021) conducted on suspended particulate matter (SPM) samples from major German rivers revealed a decreasing discharge of EHMC into German waters from 2005 to 2017. This could be attributed to a strongly decreasing frequency use of EHMC as an ingredient in sunscreens in Germany, from about 65% in 1994 to 15% in 2014 (Nagorka & Duffek, 2021).

Generally, this common decreasing trend for both selected UV-Fs and SFs compounds from the early 2000s onwards could probably result from a combination of different factors. The implementation of new regulations and monitoring tools probably had some influence, however it must also be considered that Ny-Ålesund experienced the gradual reduction of cruise ships operating in Kongsfjorden, with a large number of tourists walking around the village during the summer months (Fride Eeg-Henriksen and Sjørmæling, 2016); and changes to the sewage pipe system in 2006 (Sanders et al., 2006). This latter aspect could be relevant since, initially, the sewage effluent from the central settlement of Ny-Ålesund was discharged via an underwater sea outfall located below the beach beside the old boathouse (Shears et al., 1998). This effluent was untreated and contained sewage, grey water from showers and sinks, detergents and cleaning agents from the kitchen and laundry, as well as small quantities of waste hazardous chemicals produced because of scientific experiments (Shears et al., 1998). Indeed, among the investigations conducted for the Environmental Impact Assessment (EIA) drafting, local contamination of marine sediments emerged, also due to the release of untreated sewage directly into the beach in Ny-Ålesund. For this reason, in 2006 Kings Bay company planned to extend the sewage pipeline at Palm Beach so that the sewage can be discharged further out in the fjord (Sanders et al., 2006).

5.2.2 PBDEs in sediment cores of 2021

Temporal trends in total PBDE congener concentrations relative to the estimated age of sediment layers in sediment cores NYA21_01, NYA21_03, and NYA21_04 are presented in Figure 28. The chronology of modern sediments (last century) was estimated using a radiocarbon age-depth model and compared with retene trend profiles. This chronology

was then correlated with PBDE concentration profiles and the periods of global and regional production and consumption of PBDEs (from the late 1970s to 2021).

Based on the age-depth model and historical PBDE concentration data, two distinct time periods were identified in the sediment cores:

- S1 (late 1970s–2021), that corresponds to peak PBDE concentrations and the era of increasing consumption;
- S2 (pre-1970s), that predates industrial PBDE production.

Principal Component Analysis (PCA) was conducted to compare PBDE congener profiles across the three sediment cores and to highlight differences between these two time periods. PCA results are shown in Fig. 29 and Table 18. The first principal component (PC1) accounted for 69% of the total variation and was strongly negatively associated with BDE-99, BDE-183 and BDE-116. The second principal component (PC2) accounted for 15% of total variation and was positively associated with BDE-100, resulting in a cumulative explained variation of 84%.

Table 18- PBDEs PCA coefficients in the three sediment cores collected in 2021.

<i>Eigenvectors</i>	<i>PBDEs</i>				
	PC1	PC2	PC3	PC4	PC5
PBDE 28	-0.122	0.033	0.077	0.016	0.084
PBDE 47	-0.241	-0.066	0.14	0.088	0.014
PBDE 49	-0.185	-0.016	0.064	0.013	0.284
PBDE 71	-0.217	-0.005	0.096	0.068	-0.057
PBDE 99	-0.487	-0.31	-0.12	-0.435	0.121
PBDE 100	-0.401	0.859	-0.018	0.169	-0.092
PBDE 119	-0.282	0.122	-0.356	-0.382	0.485
PBDE 116	-0.41	-0.129	0.29	-0.283	-0.668
PBDE 173+190	-0.096	-0.126	-0.849	0.244	-0.39
PBDE 183	-0.437	-0.335	0.119	0.696	0.226

PCA scores revealed similarities among the three cores in the contribution of individual PBDE congeners but demonstrated marked differences between the two temporal sections. PERMANOVA statistical analysis, based on the temporal division described above (Table 19), confirmed no significant differences ($p>0.05$) among the three sediment cores. However, a significant difference was observed between the S1 and S2 periods ($p=0.003$), indicating a clear distinction between the era of high PBDE consumption (late 1970s–2021) and the period before industrial production (pre-1970s).

Table 19 - PERMANOVA table of results for PBDE congeners in the three sediment cores collected in 2021 ($p < 0.05$, with a confidence interval of 95%) (Factors: CO=CORE; DE=DEPTH; COxDE=interaction between CORE and DEPTH).

PBDEs						
Source	df	SS	MS	Pseudo-F	P(perm)	Unique perms
CO	2	1.5528	0.7764	1.5712	0.146	999
DE	1	4.3897	4.3897	8.8831	0.003	999
COxDE	2	0.92705	0.46353	0.938	0.476	999
Res	22	10.872	0.49416			
Total	27	17.34				

In cores NYA21_01 and NYA21_04, some layers dated before 1900 AD exhibited low but detectable concentrations above the limit of detection (LOD). Similar findings have been reported in other studies (Nipen et al., 2022, Da et al., 2019, Yang et al., 2016, Evenset et al., 2007, Muir et al., 2003), attributing the early detection of PBDE congeners to mechanisms such as bioturbation-induced down-core diffusion or vertical transport through interstitial waters. In all three sediment cores, the total PBDE concentrations began to increase noticeably from the late 1970s to early 1980s, aligning with the production, usage, and disposal of technical PBDEs mixtures.

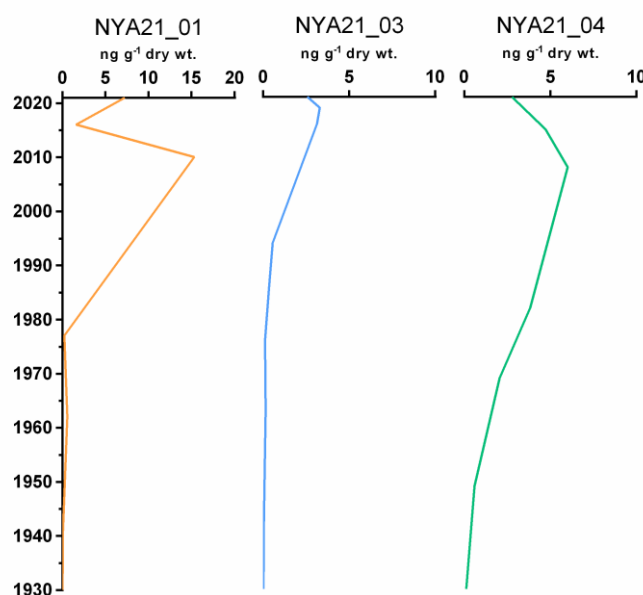


Figure 28 - Temporal trends of total PBDE concentrations (ng g^{-1} dry wt.) in the sediment cores NYA21_01, NYA21_03 and NYA21_04.

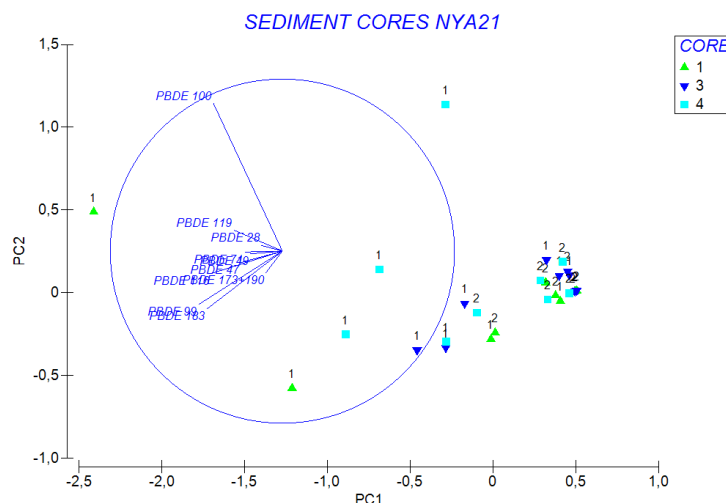


Figure 29 - PCA of PBDE congeners in the three sediment cores collected in 2021 (the numbers 1 and 2 above each core symbol - 1, 3 and 4 as shown in the legend - indicate time sections 1 and 2).

In sediment core NYA21_01, a distinct trend was observed for tri- to hepta-BDEs, with the highest concentrations detected within the top 5 cm, corresponding to a period of approximately 30 years (1990–2021). The concentrations of the ten PBDE congeners peaked at a depth of 2.5 cm, followed by a sharp decline and a subsequent increase in the uppermost layer of the core.

In sediment core NYA21_03, tri- and tetra-BDEs were present at very low concentrations, preventing the identification of a clear trend. However, penta- and hepta-BDE congeners exhibited their highest concentrations within the top 5 cm, spanning approximately 20 years (2000–2021). Unlike most other penta-BDE congeners, BDE-100 and BDE-99 displayed increasing concentrations up to the surface layer, a trend also observed for the hepta-BDE congener BDE-173+190.

In sediment core NYA21_04, tri-BDE 28 was detected at very low concentrations, while a clear trend emerged for tetra- to hepta-BDEs. The highest concentrations were found within the top 7 cm, representing a period of approximately 40 years (1980–2021). In contrast to other penta-BDE congeners, BDE-116 and BDE-99 showed progressively increasing concentrations up to the surface. For the remaining congeners, concentrations peaked at around 2.5 cm depth, corresponding to the early 2000s, and subsequently decreased gradually.

Only one previous study (Hermanson et al., 2010) investigated PBDE deposition in this region, analyzing an ice core from Holtedahlfonna (~40 km NE of Ny-Ålesund) covering the period 1953–2005. Unlike the present study, Hermanson did not detect BDE-47, BDE-99, or BDE-100 above background levels but identified BDE-49, BDE-71, BDE-190, and BDE-209. These congeners exhibited increasing trends from the late 1970s, consistent with the findings of this study. BDE-49 and BDE-71 showed temporal trends similar to

those in sediment core NYA21_04, with peaks in the late 1970s, declines during the mid-1980s, and subsequent increases.

(Evenset et al., 2007) also reported PBDEs, including BDE-28, BDE-47, BDE-99, and BDE-100, in lacustrine sediments from Bjørnøya. Among these, only BDE-47 and BDE-99 displayed clear increasing trends starting in the 1950s, aligning with the rise of BDE-47 and BDE-99 observed in this study from the late 1970s. Similar increases in PBDEs from the late 1970s to early 1980s have been documented globally in sediment cores from environments such as the Great Lakes (Zhu and Hites, 2005), Germany (Zegers et al., 2003), Canada (Muir et al., 2003), and Mexico (Ontiveros-Cuadras et al., 2019). These trends reflect the widespread adoption of technical PBDE mixtures following the phase-out of PCBs.

PBDE production peaked after the 1970s, coinciding with a sharp decline in global PCB emissions following their ban due to environmental and health concerns (Johannessen et al., 2008). Between 1970 and 2001, PBDE production reached approximately 420,000 tons, with Deca- and Penta-BDE mixtures dominating the market (Salvadó et al., 2016). The prevalence of penta- and hepta-BDE congeners (e.g., BDE-99, BDE-47, and BDE-183) in this study aligns with commercial mixtures such as Bromkal 70-5DE and DE-71, widely used worldwide. Air, soil, and biological samples from Ny-Ålesund also confirm these congeners as dominant (Xiong et al., 2022, Zhu et al., 2015).

Interestingly, this study detected congeners typically absent from commercial mixtures, such as BDE-116, BDE-119, BDE-49, and BDE-173+190. Notably, BDE-116 and BDE-173+190 were among the most abundant, potentially resulting from the degradation of highly brominated congeners like deca-BDEs (Ghimire et al., 2019).

Decreasing PBDE concentrations in cores NYA21_03 and NYA21_04 during 2010–2020 likely reflect the impact of restrictions on penta- and octa-BDE mixtures implemented under the Stockholm Convention (2009), consistent with global trends (Xiong et al., 2022, Hung et al., 2016). However, the sharp rise in PBDE concentrations in the uppermost layers of core NYA21_01 and certain layers of NYA21_03 and NYA21_04 suggests the influence of secondary sources, including re-volatilization, glacial meltwater, and sediment runoff from permafrost. Similar increases in recent deposition were reported for PCBs and PAHs in Kongsfjorden sediments by (Pouch et al., 2017).

Comparing the results of this study with previous research is challenging due to variations in the congeners analyzed and the limited availability of PBDE concentration data in Arctic sediments. Studies on Arctic seawater generally report lower PBDE concentrations compared to sediments, reflecting the compounds' lipophilicity and tendency to adsorb onto particulate matter. (McDonough et al., 2018) analyzed deep-water moorings in the Fram Strait and surface waters in the Canada Basin, reporting Σ PBDE concentrations of <LOD–0.9 pg/L and <LOD–21.4 pg/L, respectively. The higher concentrations in the Canada Basin were attributed to local human activities.

Seawater samples from East Greenland showed Σ PBDEs concentrations ranging from 0.03 to 0.64 pg/L, with elevated levels near Greenland's eastern coast, likely influenced by glacial meltwater (Möller et al., 2011b). These values were lower than those observed in Kongsfjorden, Svalbard (2.9–4.7 pg/L; (Sun et al., 2020)), the pan-Arctic shelf seas and interior basin (0.3–11.2 pg/L; (Salvadó et al., 2016)), and the Kara Sea shelf (2.4–10.8 pg/L; (Carroll et al., 2008)).

The PBDE concentrations in sediments from this study exceeded those reported in other Arctic marine sediments, such as the Bering Sea, Chukchi Sea, and Canada Basin (Σ PBDEs: 3.54–148.95 pg/g dw; (Cai et al., 2012)). Concentrations were also higher than those recorded in Svalbard fjords, including Adventfjorden (BDE-99: 26.7–30.8 pg/g dw), Grønfjorden (BDE-99: <LOD–22.8 pg/g dw; (Evenset et al., 2018)), and Kongsfjorden (0.04–0.19 ng/g dw, (Jiao et al., 2009); Σ PBDEs: 2.8–15 pg/g dw, (Sun et al., 2020)).

However, PBDE concentrations in this study were comparable to those reported by (Carlsson et al., 2018) (Σ PBDEs: 5520–21,000 pg/g dw) in surface sediments from Adventfjorden, near a small boat harbor identified as a local pollution source. Similarly, (Ma et al., 2015) found BDE-209 concentrations in Kongsfjorden sediments to be lower in the inner fjord (n.d.–104.1 pg/g dw) but significantly higher near the Ny-Ålesund harbor (233.8 pg/g dw), suggesting harbor activities as a contaminant source.

5.3 Sources of contamination: Local vs. Long-Range Environmental Transport (LRET)

5.3.1 Potential sources of UV-Fs and SFs in 2011 sediment core

Several sources contribute to the presence of CECs in the sampling area of the sediment core NYA11_09. Hence, it is not possible to discriminate a single source of contamination as prevalent, but rather a combination of both local sources (e.g. human activities, local-medium range transport) and long-range transport. However, other local sources gaining increasingly relevance in recent decades are the so-called 'secondary sources' resulting from climate change impacts in the Arctic, due to their significant contribution to the re-introduction of contaminants into the environment (Hung et al., 2022, Xie et al., 2022).

Figure 30 shows the temporal trends of OTNE and EHMC (ng g⁻¹ dry wt.) in comparison with the researchers' days in Ny-Ålesund, in the time period 1989–2010, showing a very similar increasing trend from late 1990s to 2010.

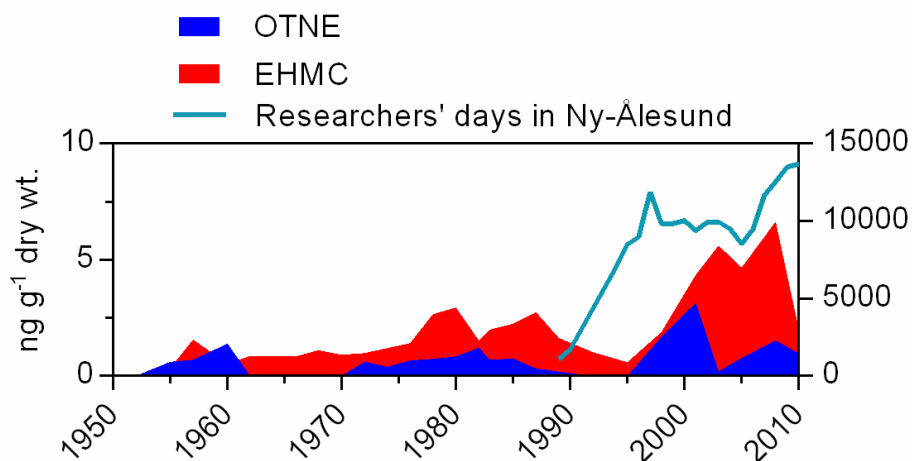


Figure 30 - Time series of OTNE and EHMC (ng g⁻¹ dry. wt.) in comparison with the number of researchers' days in Ny-Ålesund (1989-2010) (Source: Kristiansen, 2014).

This might reveal the anthropogenic influence in PCPs contamination in the study area. Also (Domínguez-Morueco et al., 2021, Emnet et al., 2015) investigated PCPs in different Antarctic matrices, suggesting the research stations sewage effluents as the major source of these loads in the environment. Another study conducted in the Svalbard archipelago (Warner et al., 2010), assessed the presence of siloxanes, that are mainly used in personal care products, in sediment and biota samples taken in the Adventfjorden and Kongsfjorden with concentrations decreasing further away from the effluent discharging points, revealing the impact of sewage on the surrounding marine environment. Untreated sewage as well as domestic and municipal wastes constitute the main sources of PCPs contamination in the Arctic, mainly the receiving aquatic environment (Kallenborn et al., 2018). Sewage discharge is one of the sources included among the local polluting activities in Svalbard (Granberg et al., 2019). Thus, the observed decreasing trend of the selected UV-Fs and SFs in the early 2000s, could probably be related to changes to the sewage pipe system in 2006, resulting in the effluents being discharged further out into the fjord and no longer in proximity of the village of Ny-Ålesund.

Over the past decade, several studies investigated the occurrence of UV-Fs and SFs in samples collected in remote and high-altitude areas to evaluate their potential for long-range atmospheric transport (LRAT) in addition to local contamination. As evidence, target CECs have been found in snow samples collected on glaciers in Svalbard (D'Amico et al., 2024, Vecchiato et al., 2018), in lacustrine sediments near a glacier from Switzerland (Bogdal et al., 2009), in an ice core from Russia's Mount Elbrus (Vecchiato et al., 2020), in snow samples from Alpine glaciers (Ferrario et al., 2017, Villa et al., 2014) and Antarctica (D'Amico et al., 2022). As already reported by (Xie et al., 2007), these studies also confirmed the LRAT potential of these compounds, with snow deposition

acting as the main removal mechanism of volatile compounds from the atmosphere in the Arctic (Xie et al., 2022).

For example, regarding the synthetic fragrances HHCB and AHTN, when analyzing different matrices, the HHCB/AHTN ratio has been used as a valuable tool to better understand the sources and behavior of these two compounds in the environment. In this study, HHCB/AHTN ratio was calculated when both compounds were above the detection limit in the same sample. The median (range) of HHCB/AHTN ratio was 2.2 (1.4-2.9), that is lower than ~ 4.0 estimated from the market volumes for these two compounds in the European Union (OSPAR, 2004). This could be due to the degradation processes (e.g. photodegradation) these substances undergo as they are released into the environment. However, it is comparable to the median value of 2.0 measured in the seawater dissolved phase samples from the North Sea (Xie et al., 2007) where the major rivers were considered a significant input of HHCB and AHTN to the North Sea; and with the value of 2.2 from water samples of a sewage plant in Germany (Gatermann et al., 2002).

The HHCB/AHTN ratio determined in the dissolved fraction and in air from two Canadian lakes (McDonough et al., 2016) and from air and seawater dissolved phase samples from the North Sea and the Arctic region (Xie et al., 2007) was higher in water than in air samples. This is related to the half-life of these compounds in the different matrices (i.e. air and water). Indeed, the half-life of HHCB, with respect to photolysis in water, is about 25 times longer than for AHTN; whereas, HHCB may degrade more rapidly in the atmosphere during transport than AHTN (McDonough et al., 2016; Xie et al., 2007). Therefore, it can be assumed that as a result of atmospheric transport over short-medium distances (as the ratio value found in this study of 2.2 is much higher than the ratio in Arctic air of 0.2 reported by (Xie et al., 2007)), these substances were deposited and reached the marine compartment (e.g. meltwater from the cryosphere, sewage effluents), then accumulating in the sediments, where the ratio will be higher due to the photolytic degradation processes AHTN was mainly exposed to.

However, besides LRAT and direct release from human activities on site, there are other local sources of CECs contamination as a consequence of the effects of climate change in the Arctic environment. In this regard, remobilization and re-volatilization from the so called 'reservoirs' (e.g. soil, sediments or oceans, glaciers) in which organic pollutants have been trapped for a long time, represent important secondary environmental sources of local contamination (Hung et al., 2022, Ma et al., 2011, Xie et al., 2022). For example, (McDonough et al., 2016) confirmed that volatilization from surface waters was a significant loss process for dissolved SFs in the lower Great Lakes (Canada), at many locations near urbanized shorelines. Furthermore, the remobilization of CECs that were deposited on the snow also constitutes another source of local contamination. On this point, (Vecchiato et al., 2018) analyzed snow and seawater samples from Ny-Ålesund (Svalbard), detecting SFs concentrations below 5.8 ng L^{-1} in the seawater and up to 72 ng L^{-1} in the surface snow near the settlement of Ny-Ålesund and at increasing distances.

They suggested a short- and long-range transport of these pollutants, since back trajectories analysis revealed most air masses to have a polar origin and about one third of the trajectories were starting or passing above anthropized areas of Europe and Russia in the previous five days (Vecchiato et al., 2018). This highlights another process that could contribute to local contamination, i.e. the local-medium range atmospheric transport of pollutants. In this regard, (Villa et al., 2014) showed that the presence of the synthetic fragrances HHCB and AHTN in fresh snow samples and meltwater from an Alpine glacier was due to medium-range transport, supported by the fact that the back trajectories analysis revealed air masses of local origin as the main source of contamination in the sampling area. This would suggest the hypothesis that these substances may derive not only from human activities in Ny-Ålesund, but likely also from other nearby settlements, e.g. Longyearbyen.

Nevertheless, many elements of the cryosphere, including glaciers, snow, sea ice and frozen ground, are considered a repository for pollutants. In fact, by atmospheric transport, pollutants can be 'trapped' in the cryosphere through dry and wet deposition (Beard et al., 2022a). In particular, in the Arctic and partly in the Alpine regions, wind-packed snow has a greater capacity to accumulate semi-volatile organic chemicals, with the potential to release relatively high amounts of these substances into aquatic and terrestrial ecosystems (Meyer and Wania, 2008). Increasing meltwater discharges, shorter periods of ice-coverage, increased particle loads and higher flows in rivers are some of the effects of climate change occurring in the Arctic Ocean (Hung et al., 2022). As a result, the annual runoff in Svalbard has increased more than 35% since 1980, mainly due to enhanced glacial melt (McGovern et al., 2022b). In the Kongsfjorden, the largest source of freshwater discharge comes from the tidewater glacier Kronebreen, which is equivalent to around 40% of the total freshwater flux to the fjord (McGovern et al., 2022b). However, other few rivers and streams originating from the land-terminating glaciers drain into the fjord. Among these, Bayelva is the major river, receiving runoff contributions from the two land-terminating glaciers Austre and Vestre Brøggerbreen, then flowing into the fjord near the village of Ny-Ålesund (Pramanik et al., 2020). As evidenced by (Spataro et al., 2022) and (Rauseo et al., 2024) in studies conducted on marine sediment samples collected in Kongsfjorden, Bayelva plays an important role as a secondary source of pollution load, especially in the summer season. Thereby, large quantities of both POPs and CECs that were trapped in ice or snow are remobilized, constituting an important source of these compounds for the receiving marine environment (Ademollo et al., 2021, Pouch et al., 2021, Balmer et al., 2019, Kallenborn et al., 2018, Pouch et al., 2017, Szczybelski et al., 2016, Vecchiato et al., 2018).

5.3.2 Potential sources of PBDEs in 2021 sediment cores

Pollutants are transported to the Arctic primarily through atmospheric and oceanic currents, river inflow, and sea ice movement (Macdonald et al., 2005). Transport efficiency depends on the route: atmospheric transport occurs over days to weeks (Kallenborn et al., 2015), whereas sea currents may take 30–40 years (Polkowska et al., 2011).

Studies on Arctic seawater have shown a general decrease in PBDE concentrations with increasing latitude, from the Barents Sea to the Amundsen Basin. This pattern reflects the Barents Sea's stronger influence from northern Norway (Salvadó et al., 2016). Surface samples were dominated by BDE-209, whereas deeper water samples contained higher proportions of tri- to hepta-BDE congeners. These findings suggest that while BDE-209 has significant long-range transport (LRT) potential, oceanic circulation supports latitudinal and vertical degradation into less brominated congeners (Salvadò et al., 2016).

Spatial distribution of BDE-209 in Kongsfjorden sediments reveals slightly higher concentrations in the outer fjord compared to the inner fjord, attributed to the influence of Atlantic Water via the West Spitsbergen Current (WSC) (Ma et al., 2015). However, analysis of PBDE fluxes in this study highlights an additional mechanism. The Σ PBDE concentrations showed the following pattern: NYA21_01 (<LOD–15.33 ng g⁻¹) (Krossfjorden) > NYA21_04 (0.12–6.01 ng g⁻¹) (outer Kongsfjorden) > NYA21_03 (<LOD–3.30 ng g⁻¹) (inner Kongsfjorden). Despite being closer to Ny-Ålesund, a likely local contamination source, NYA21_03 exhibited the lowest concentrations but the highest Σ PBDE fluxes (0.13 ± 0.16 ng cm⁻² yr⁻¹), compared to NYA21_04 (0.06 ± 0.05 ng cm⁻² yr⁻¹) and NYA21_01 (0.05 ± 0.09 ng cm⁻² yr⁻¹). This suggests a higher sediment and meltwater supply in the inner fjord, diluting contaminant concentrations.

The increased sediment influx aligns with accelerated glacier melting in Kongsfjorden since the mid-1990s, which led to: i) increased glacial meltwater containing debris; ii) an increase in suspended particulate matter (SPM) transported by the Bayelva River from 7,697 t/yr (1990–1995) to 10,374 t/yr (1996–2000); iii) glacial retreat and frontal ablation in the inner fjord (Wu et al., 2023).

The Ca/Ti vertical profiles in the three sediment cores corroborate these findings. Mineralogical analysis can trace sediment provenance (Miserocchi et al., 2016; Streuff et al., 2013; Howe et al., 2003), with the Ca/Ti ratio serving as a proxy for glacial sediment supply. Ca-rich sediments, primarily from the Kronebreen and Kongsvegen glaciers, dominate the inner fjord (Streuff et al., 2013). In this study, the Ca/Ti ratio was highest in NYA21_03, decreasing progressively in NYA21_04 and NYA21_01, indicating a stronger glacial influence in the inner fjord compared to the outer regions. This terrigenous-to-marine gradient in the Kongsfjorden-Krossfjorden system (KKS) was also observed by (Winkelmann and Knies, 2005). Additionally, (Wu et al., 2023) noted an increasing contribution of terrestrial organic matter (OM) since the mid-1990s based on $\delta^{13}\text{C}$ values.

Consistent with Wu's findings, in this study the terrestrial OM contribution (F_{terr}) for fjord sediments was calculated, revealing an increasing detrital contribution in recent years in all three cores.

The presence of legacy contaminants in the Arctic is largely attributed to long-range transport (LRT) (AMAP, 2021). Early studies confirmed PBDEs' LRT potential from source regions to remote areas (Breivik et al., 2006, de Wit et al., 2006, Wang et al., 2005, Wania and Dugani, 2003). More recently, (Möller et al., 2011a, Möller et al., 2011b) identified BDE-47, -99, and -100 as the dominant congeners in air and seawater samples from East Greenland and a polar expedition from East Asia to the Arctic, indicating Western Europe and East Asia as key sources. Similarly, (Hermanson et al., 2010) analyzed PBDEs in Svalbard ice cores, suggesting that the "Arctic haze" season enhances transport of particle-bound PBDEs from Eurasian sources.

Long-term monitoring at the Zeppelin Observatory (Ny-Ålesund) since 2006 and through passive air samplers (2011–2019) revealed declining trends for most PBDEs, with concentrations significantly higher in the 2000s than the 2010s, except for BDE-209 (Xiong et al., 2022, Wong et al., 2021, Hung et al., 2016). The decline corresponds with the ban on penta- and octa-BDE mixtures in Europe and North America in the mid-2000s, although deca-BDE mixtures gained wider use subsequently (Wong et al., 2021). Higher brominated PBDEs, like BDE-183 and -209, exhibit limited LRT potential due to their low volatility and association with particulates (de Wit et al., 2010, Wang et al., 2005).

Despite declining trends, persistent detection of banned PBDEs suggests secondary emissions, such as re-volatilization from soil and oceans. Detection of higher-brominated PBDEs in Arctic air highlights the potential contribution of local sources, including settlements, shipping, and historical coal mining (Granberg et al., 2019). Other local inputs include emissions from power generation, vehicle exhaust, and waste management practices. Tourism, particularly cruise ships, has also increased emissions, as reflected in high BDE-209 concentrations near Ny-Ålesund (Ma et al., 2015).

Early environmental assessments identified significant pollution sources, including landfill sites, untreated sewage, and improper disposal of mining waste (Shears et al., 1998; Granberg et al., 2019). Open burning and landfill leachates continue to impact local ecosystems (Sanders et al., 2006). Electronic waste (e-waste) recycling and disposal are notable sources of PBDEs, with thermal recycling producing stable, debrominated congeners such as BDE-71, BDE-116, and BDE-190 (Ghimire et al., 2019, Ohajinwa et al., 2019).

BDE-209, though not analyzed in this study, degrades into lower-brominated congeners via photolysis and microbial debromination in sediments and soils (Zhao et al., 2018, Lee and He, 2010). This process, where bromine atoms are replaced by hydrogen, explains the presence of uncommon PBDE congeners (e.g., BDE-71, -116, -190) found in deep-sea

sediments (Cheng et al., 2015, Söderström et al., 2004). Observed degradation pathways, such as BDE-190 → BDE-119 → BDE-71, indicate environmental debromination during transport (Tokarz et al., 2008, Ghimire et al., 2019).

Climate change further influences PBDE behavior by accelerating contaminant decomposition and redistribution. Rising temperatures, glacier melting and changes in snow deposition dynamics alter transport and degradation pathways (AMAP, 2021). Snow acts as a scavenger of atmospheric pollutants and a source of meltwater-borne contaminants during seasonal thaw (Pawlak et al., 2021).

Continued research is essential to elucidate the interplay between climate change, contaminant dynamics, and the Arctic ecosystem. Historical trends and meteorological variability must be considered to fully understand PBDE behavior in this sensitive environment (Hung et al., 2022).

Tab. 15 - UV-Fs and SFs concentrations in different environmental matrices from polar and high-altitude areas.

Sampling location	Matrix	Compound	Concentration	Reference
Italy				
Alpine glaciers (Lys, Forni, Gioco Alto)	Ice (ng/L)	HHCB	1.25 (0.99– 1.57)	Ferrario et al., 2017
		AHTN	1.27 (0.86–1.79)	
Forni glacier	Snow (ng/L)	HHCB	3.14 (2.13– 5.07)	Villa et al., 2014
		AHTN	3.88 (2.28– 9.83)	
Norway				
Oslofjord	Sediments (ng/g dry wt.)	EHMC	8.5-16.4	Langford et al., 2015
Mjøsa	Sediments (ng/g dry wt.)	EHMC	9.9-19.8	Langford et al., 2015
Arctic				
Kongsfjorden-Krossfjorden system (Svalbard)	Marine sed. (ng/g dry wt.)	4-MBC	<LOD-4.5	This study
		EHMC	<LOD-6.6	
		HMS	<LOD-1.0	
		EHS	<LOD-1.0	
Arctic Ocean and Chukchi Sea	Surface seawater (ng/L)	4-MBC	<LOD	Tsui et al., 2014
		EHMC	25-66	
		HMS	<LOD	
		EHS	<LOD	
Antarctic				

Antarctic Peninsula	Inlet surface sediments (ng/g)	EHMC 4-MBC HMS	<LOD-26.6 <LOD-5.5 <LOD-251.0	Costa et al., 2024
Terra Nova Bay	Snow (ng/L)	EHMC	0.4-3.1	D'Amico et al., 2022
Erebus Bay	Seawater (ng/L)	4-MBC EHMC	<LOD-45.1 <LOD-32.3	Emnet et al., 2015
Antarctic Peninsula	Stream Freshwater (ng/L)	4-MBC	18-45	Domínguez-Morueco et al., 2021
Antarctic Peninsula	Glacier drain Freshwater (ng/L)	4-MBC	<14	Domínguez-Morueco et al., 2021
Antarctic Peninsula	Glacier drain Suspended particulate matter (ng g ⁻¹ dry wt.)	EHMC	69	Domínguez-Morueco et al., 2021
Antarctic Peninsula	Freshwater Suspended particulate matter (ng/g dry wt.)	EHMC	250-1900	Domínguez-Morueco et al., 2021
Erebus Bay	Sea ice (ng/L)	4-MBC EHMC	<LOD-4.3 <LOD-4.8	Emnet et al., 2015
Erebus Bay	Wastewater (ng/L)	4-MBC EHMC	173-11,700 <LOD	Emnet et al., 2015
Antarctic Peninsula	Wastewater Suspended particulate matter (ng/g dry wt.)	EHMC	7300	Domínguez-Morueco et al., 2021

CHAPTER 6 – Conclusions

This study evaluates the occurrence, concentrations and historical deposition of selected legacy and emerging contaminants in four marine sediment cores collected from the Kongsfjorden-Krossfjorden system (KKS). The specific objectives of this PhD project were to: i) assess the presence and concentration profiles of selected contaminants of anthropogenic origin; ii) reconstruct the introduction of these contaminants into the fjord system and define temporal trends highlighting distinct periods of deposition, and iii) identify potential sources of contamination in the region.

The period of glaciers advances and retreat, along with shoreline evolution, are key drivers of sediment flux distribution and accumulation in the fjord. In The tidewater glaciers Kronebreen and Kongsbreen contribute significantly to the sedimentation dynamics, resulting in higher sedimentation rates and lower organic matter content in the inner fjord. Conversely, sediment cores from the outer fjord indicate a stronger marine influence, driven by the inflow of nutrient-rich Atlantic water, while terrestrial contributions dominate in cores from the inner fjord, revealing an increasing release of terrigenous materials from continental runoff mainly in the last decade.

Emerging contaminants, including organic UV-filters (UV-Fs) and synthetic fragrances (SFs), were analyzed in a sediment core collected from the Kongsfjorden in 2011. Legacy contaminants, specifically polybrominated diphenyl ethers (PBDEs), were analyzed in three sediment cores collected from the KKS in 2021. To reconstruct the historical accumulation trends, radiocarbon (^{14}C) and ^{210}Pb age-depth models were constructed. Notably, this is the first study to investigate the historical trends of UV-Fs, SFs and PBDEs in sediment cores from the KKS and, more generally, from the Arctic marine sedimentary environment.

For the emerging contaminants, total and individual UV-F and SF concentrations exhibited a general increasing trend from the early 1970s and early 1980s, peaking around the late 1990s to early 2000s before declining. This decline likely reflects the changes in the sewage disposal system implemented in 2006, which relocated effluents discharge farther from the village of Ny-Ålesund, reducing contamination in the fjord.

For legacy contaminants, temporal trends revealed that PBDE concentrations in the KKS increased significantly from the late 1970s to early 1980s, peaked in the mid-2000s and subsequently declined. This pattern corresponds to the phase-out of certain PBDE technical mixtures in the global market during the early 2000s. These findings align with production and usage trends of the studied contaminants, reaffirming the role of sediment cores as valuable natural archives for reconstructing historical environmental contamination.

Determining a dominant contamination source is challenging, necessitating consideration of both local sources (e.g., human activities and short- to medium-range transport) and long-range atmospheric and oceanic transport.

Local sources include historical and ongoing human activities, including untreated sewage, landfill leachate, open burning, improper waste disposal, and mining, that significantly contribute to contamination in the fjord system. Temporal trends showed a parallelism between the increasing human activity in Ny-Ålesund since the late 1980s/early 1990s and the concentration profiles of UV-Fs and SFs. These contaminants likely enter the marine environment through direct release during use or sewage effluents discharged into the fjord. The establishment of multiple research stations in Ny-Ålesund has further amplified human presence in recent decades.

The detection of PBDEs in the Arctic is predominantly attributed to long-range atmospheric and oceanic transport. However, the higher concentrations of heavily brominated PBDEs - compounds with limited potential for long-range transport - suggest a significant contribution from local sources in this area.

Climate change exacerbates contamination through 'secondary sources', such as increased meltwater discharge, rivers runoff and remobilization or re-volatilization of pollutants from environmental reservoirs. These processes particularly affect local contamination in aquatic environments, which act as major sinks for organic contaminants due to their association with settling organic matter. Rising temperatures and enhanced meltwater discharge from the cryosphere have significantly altered contaminant transport mechanisms, fate, and distribution in the Arctic.

The scarcity of data on these contaminants in Arctic marine sediment cores underscores the need for further studies. However, temporal trends analysis in sediment cores has proven invaluable for identifying sources and reconstructing the historical deposition of these anthropogenic chemicals.

Future research should prioritize high-resolution sampling transects within the fjord to better quantify the contributions of local sources and their impacts on marine sediments, using source-oriented models (SMs). Additionally, analyzing the selected legacy and emerging contaminants in water samples could further elucidate the role of oceanic currents in contaminant transport and deposition within the study area.

References

- ABBASI, G., LI, L. & BREIVIK, K. 2019. Global Historical Stocks and Emissions of PBDEs. *Environmental Science & Technology*, 53, 6330-6340.
- ADEMOLLO, N., SPATARO, F., RAUSEO, J., PESCATORE, T., FATTORINI, N., VALSECCHI, S., POLESELLO, S. & PATROLECCO, L. 2021. Occurrence, distribution and pollution pattern of legacy and emerging organic pollutants in surface water of the Kongsfjorden (Svalbard, Norway): Environmental contamination, seasonal trend and climate change. *Marine Pollution Bulletin*, 163, 111900.
- ALAE, M., ARIAS, P., SJÖDIN, A. & BERGMAN, Å. 2003. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environment International*, 29, 683-689.
- AMAP 2021. POPs and Chemicals of Emerging Arctic Concern: Influence of Climate Change. Summary for Policy-makers. Arctic Monitoring and Assessment Programme (AMAP), Tromsø, Norway. . 16.
- ANDREASSEN IVAR, KRISTIANSEN JAN ERIK & CAMILLA, M. 2009. This is Svalbard. What the figures say. *Statistics Norway*.
- AQUINO-LÓPEZ, M. A., BLAAUW, M., CHRISTEN, J. A. & SANDERSON, K. N. 2018. Bayesian Analysis of 210Pb Dating. *Journal of Agricultural, Biological and Environmental Statistics*, 23.
- AVANGO, D., HACQUEBORD, L., AALDERS, Y., HAAS, H., GUSTAFSSON, U. & KRUSE, F. 2010. "Between Markets and Geopolitics: Natural Resource Exploitation on Spitsbergen from 1600 to the Present Day,". *Polar Record - POLAR REC*, 46, 1-11.
- AWAD, A. M., SHAIKH, S. M. R., JALAB, R., GULIED, M. H., NASSER, M. S., BENAMOR, A. & ADHAM, S. 2019. Adsorption of organic pollutants by natural and modified clays: A comprehensive review. *Separation and Purification Technology*, 228, 115719.
- BALDÉ, C. P., FORTI, V., GRAY, V., KUEHR, R. & STEGMANN, P. 2017. The Global E-waste Monitor 2017. Quantities, Flows, and Resources. *United Nations University (UNU), International Telecommunication Union (ITU) & International Solid Waste Association (ISWA), Bonn/Geneva/Vienna*.
- BALMER, J. E., HUNG, H., YU, Y., LETCHER, R. J. & MUIR, D. C. G. 2019. Sources and environmental fate of pyrogenic polycyclic aromatic hydrocarbons (PAHs) in the Arctic. *Emerging Contaminants*, 5, 128-142.
- BALMER, M. E., BUSER, H.-R., MÜLLER, M. D. & POIGER, T. 2005. Occurrence of Some Organic UV Filters in Wastewater, in Surface Waters, and in Fish from Swiss Lakes. *Environmental Science & Technology*, 39, 953-962.
- BARÓN, E., GAGO-FERRERO, P., GORGA, M., RUDOLPH, I., MENDOZA, G., ZAPATA, A. M., DÍAZ-CRUZ, S., BARRA, R., OCAMPO-DUQUE, W., PÁEZ, M., DARBRA, R. M., ELJARRAT, E. & BARCELÓ, D. 2013. Occurrence of hydrophobic organic pollutants (BFRs and UV-filters) in sediments from South America. *Chemosphere*, 92, 309-316.
- BEARD, D. B., CLASON, C. C., RANGE-CROFT, S., PONIECKA, E., WARD, K. J. & BLAKE, W. H. 2022a. Anthropogenic contaminants in glacial environments I: Inputs and accumulation. *Progress in Physical Geography: Earth and Environment*, 46, 630-648.
- BEARD, D. B., CLASON, C. C., RANGE-CROFT, S., PONIECKA, E., WARD, K. J. & BLAKE, W. H. 2022b. Anthropogenic contaminants in glacial environments II: Release and downstream consequences. *Progress in Physical Geography: Earth and Environment*, 46, 790-808.
- BESTER, K. 2009. Analysis of musk fragrances in environmental samples. *Journal of Chromatography A*, 1216, 470-480.
- BESZCZYNSKA-MÖLLER, A., FAHRBACH, E., SCHAUER, U. & HANSEN, E. 2012. Variability in Atlantic water temperature and transport at the entrance to the Arctic Ocean, 1997–2010. *ICES Journal of Marine Science*, 69, 852-863.
- BLAAUW, M. & CHRISTEN, J. 2011. Flexible Paleoclimate Age-Depth Models Using an Autoregressive Gamma Process. *Bayesian Analysis*, 6, 457-474.

- BLAAUW, M., CHRISTEN, J. A. & AQUINO-LÓPEZ, M. A. 2020. A Review of Statistics in Palaeoenvironmental Research. *Journal of Agricultural, Biological and Environmental Statistics*, 25, 17-31.
- BLAIS, J. M., ROSEN, M. R. & SMOL, J. P. 2015. Environmental contaminants. Using natural archives to track sources and long-term trends of pollution. *Developments in Paleoenvironmental Research*, 18.
- BOGDAL, C., SCHMID, P., ZENNEGG, M., ANSELMETTI, F. S., SCHERINGER, M. & HUNGERBÜHLER, K. 2009. Blast from the Past: Melting Glaciers as a Relevant Source for Persistent Organic Pollutants. *Environmental Science & Technology*, 43, 8173-8177.
- BOSSI, R., VORKAMP, K. & SKOV, H. 2016. Concentrations of organochlorine pesticides, polybrominated diphenyl ethers and perfluorinated compounds in the atmosphere of North Greenland. *Environmental Pollution*, 217, 4-10.
- BOX, J. E., COLGAN, W. T., CHRISTENSEN, T. R., SCHMIDT, N. M., LUND, M., PARMENTIER, F.-J. W., BROWN, R., BHATT, U. S., EUSKIRCHEN, E. S., ROMANOVSKY, V. E., WALSH, J. E., OVERLAND, J. E., WANG, M., CORELL, R. W., MEIER, W. N., WOUTERS, B., MERNILD, S., MÅRD, J., PAWLAK, J. & OLSEN, M. S. 2019. Key indicators of Arctic climate change: 1971–2017. *Environmental Research Letters*, 14, 045010.
- BRAUSCH, J. M. & RAND, G. M. 2011. A review of personal care products in the aquatic environment: Environmental concentrations and toxicity. *Chemosphere*, 82, 1518-1532.
- BREIVIK, K., ARMITAGE, J. M., WANIA, F., SWEETMAN, A. J. & JONES, K. C. 2016. Tracking the Global Distribution of Persistent Organic Pollutants Accounting for E-Waste Exports to Developing Regions. *Environmental Science & Technology*, 50, 798-805.
- BREIVIK, K., WANIA, F., MUIR, D. C. G., ALAEE, M., BACKUS, S. & PACEPAVICIUS, G. 2006. Empirical and Modeling Evidence of the Long-Range Atmospheric Transport of Decabromodiphenyl Ether. *Environmental Science & Technology*, 40, 4612-4618.
- CAI, K., SONG, Q., YUAN, W., RUAN, J., DUAN, H., LI, Y. & LI, J. 2020. Human exposure to PBDEs in e-waste areas: A review. *Environmental Pollution*, 267, 115634.
- CAI, M. G., HONG, Q. Q., WANG, Y., LUO, X. J., CHEN, S. J., CAI, M. H., QIU, C. R., HUANG, S. Y. & MAI, B. X. 2012. Distribution of polybrominated diphenyl ethers and decabromodiphenylethane in surface sediments from the Bering Sea, Chukchi Sea, and Canada Basin. *Deep Sea Research Part II: Topical Studies in Oceanography*, 81-84, 95-101.
- CARLSSON, P., VRANA, B., SOBOTKA, J., BORGÅ, K., BOHLIN NIZZETTO, P. & VARPE, Ø. 2018. New brominated flame retardants and dechlorane plus in the Arctic: Local sources and bioaccumulation potential in marine benthos. *Chemosphere*, 211, 1193-1202.
- CARROLL, J., SAVINOV, V., SAVINOVA, T., DAHLE, S., MCCREA, R. & MUIR, D. C. G. 2008. PCBs, PBDEs and pesticides released to the Arctic Ocean by the Russian Rivers Ob and Yenisei. *Environmental Science & Technology*, 42, 69-74.
- CHANG, W.-H., LU, Q.-O., CHEN, H.-L., HSU, N.-S. & LEE, C.-C. 2022. Insights into the long-term fates and impacts of polybrominated diphenyl ethers in sediment samples in Taiwan: The national project for background monitoring of the environmental distribution of chemical substances (BMECs). *Environmental Pollution*, 306, 119417.
- CHENG, Z., LIN, T., XU, W., XU, Y., LI, J., LUO, C. & ZHANG, G. 2015. A preliminary assessment of polychlorinated biphenyls and polybrominated diphenyl ethers in deep-sea sediments from the Indian Ocean. *Marine Pollution Bulletin*, 94, 323-328.
- CHISVERT, A. & SALVADOR, A. 2018. Chapter 5 - Ultraviolet Filters in Cosmetics: Regulatory Aspects and Analytical Methods. In: SALVADOR, A. & CHISVERT, A. (eds.) *Analysis of Cosmetic Products (Second Edition)*. Boston: Elsevier.
- CHRISTENSEN, E. & GIESE, A. C. 1950. Photosensitivity of sunscreens. *Journal of the American Pharmaceutical Association*, 39, 223-226.
- COMBI, T., PINTADO-HERRERA, M. G., LARA-MARTIN, P. A., MISEROCCHI, S., LANGONE, L. & GUERRA, R. 2016. Distribution and fate of legacy and emerging contaminants along the Adriatic Sea: A comparative study. *Environmental Pollution*, 218, 1055-1064.

- COSTA, L. R., TOVAR SALVADOR, M. D. L. L., PINTADO-HERRERA, M. G., ALBERGARIA-BARBOSA, A. C. R., MARTINS, C. C., LOURENÇO, R. A. & COMBI, T. 2024. Legacy and novel contaminants in surface sediments of Admiralty Bay, Antarctica Peninsula. *Science of The Total Environment*, 951, 175551.
- COTTIER, F., TVERBERG, V., INALL, M., SVENDSEN, H., NILSEN, F. & GRIFFITHS, C. 2005. Water mass modification in an Arctic fjord through cross-shelf exchange: The seasonal hydrography of Kongsfjorden, Svalbard. *Journal of Geophysical Research: Oceans*, 110.
- COTTIER, F. R., NILSEN, F., INALL, M. E., GERLAND, S., TVERBERG, V. & SVENDSEN, H. 2007. Wintertime warming of an Arctic shelf in response to large-scale atmospheric circulation. *Geophysical Research Letters*, 34.
- COTTIER, F. R., NILSEN, F., SKOGSETH, R., TVERBERG, V., SKARÐHAMAR, J. & SVENDSEN, H. 2010. Arctic fjords: a review of the oceanographic environment and dominant physical processes. In: HOWE, J. A., AUSTIN, W. E. N., FORWICK, M. & PAETZEL, M. (eds.) *Fjord Systems and Archives*. Geological Society of London.
- CROUDACE, I., RINDBY, A. & ROTHWELL, R. 2006. ITRAX: Description and Evaluation of a New Multi-Function X-ray Core Scanner. *Geological Society, London, Special Publications*, 267, 51-63.
- CROUDACE, I. W. & ROTHWELL, G. R. 2015. Micro-XRF Studies Of Sediment Cores. Applications of a non-destructive Tool for the Environmental Sciences.
- D'AMICO, M., GAMBARO, A., BARBANTE, C., BARBARO, E., CAIAZZO, L. & VECCHIATO, M. 2022. Occurrence of the UV-filter 2-Ethylhexyl 4-methoxycinnamate (EHMC) in Antarctic snow: First results. *Microchemical Journal*, 183, 108060.
- D'AMICO, M., KALLENBORN, R., SCOTO, F., GAMBARO, A., GALLET, J. C., SPOLAOR, A. & VECCHIATO, M. 2024. Chemicals of Emerging Arctic Concern in north-western Spitsbergen snow: Distribution and sources. *Science of The Total Environment*, 908, 168401.
- D'ANGELO, A., GIGLIO, F., MISEROCCHI, S., SANCHEZ-VIDAL, A., ALIANI, S., TESI, T., VIOLA, A., MAZZOLA, M. & LANGONE, L. 2018. Multi-year particle fluxes in Kongsfjorden, Svalbard. *Biogeosciences*, 15, 5343-5363.
- DA, C., WANG, R., YE, J. & YANG, S. 2019. Sediment records of polybrominated diphenyl ethers (PBDEs) in Huaihe River, China: Implications for historical production and household usage of PBDE-containing products. *Environmental Pollution*, 254, 112955.
- DACHS, J., LOHMANN, R., OCKENDEN, W. A., MÉJANELLE, L., EISENREICH, S. J. & JONES, K. C. 2002. Oceanic Biogeochemical Controls on Global Dynamics of Persistent Organic Pollutants. *Environmental Science & Technology*, 36, 4229-4237.
- DALLMANN, W. K. 2015. Geoscience Atlas of Svalbard. *Norwegian Polar Institute*.
- DAUGAARD-PETERSEN, T., LANGEBAEK, R., RIGÉT, F. F., LETCHER, R. J., HYLDSTRUP, L., JENSEN, J.-E. B., BECHSHOFT, T., WIIG, Ø., JENSSEN, B. M., PERTOLDI, C., LORENZEN, E. D., DIETZ, R. & SONNE, C. 2018. Persistent organic pollutants, skull size and bone density of polar bears (*Ursus maritimus*) from East Greenland 1892–2015 and Svalbard 1964–2004. *Environmental Research*, 162, 74-80.
- DAUGHTON, C. G. & TERNES, T. A. 1999. Pharmaceuticals and personal care products in the environment: agents of subtle change? *Environmental Health Perspectives*, 107, 907-938.
- DAVID, O. R. P. 2020. A Chemical History of Polycyclic Musks. *Chemistry – A European Journal*, 26, 7537-7555.
- DE WIT, C. A. 2002. An overview of brominated flame retardants in the environment. *Chemosphere*, 46, 583-624.
- DE WIT, C. A., ALAEE, M. & MUIR, D. C. G. 2006. Levels and trends of brominated flame retardants in the Arctic. *Chemosphere*, 64, 209-233.
- DE WIT, C. A., HERZKE, D. & VORKAMP, K. 2010. Brominated flame retardants in the Arctic environment — trends and new candidates. *Science of The Total Environment*, 408, 2885-2918.
- DE WIT, C. A., VORKAMP, K. & MUIR, D. 2022. Influence of climate change on persistent organic pollutants and chemicals of emerging concern in the Arctic: state of knowledge and

- recommendations for future research. *Environmental Science: Processes & Impacts*, 24, 1530-1543.
- DESCAMPS, S., AARS, J., FUGLEI, E., KOVACS, K. M., LYDERSEN, C., PAVLOVA, O., PEDERSEN, Å. Ø., RAVOLAINEN, V. & STRØM, H. 2017. Climate change impacts on wildlife in a High Arctic archipelago – Svalbard, Norway. *Global Change Biology*, 23, 490-502.
- DÍAZ-CRUZ M. SILVIA. & DAMIÀ, B. 2015. Personal Care Products in the Aquatic Environment. *Springer Cham*, The Handbook of Environmental Chemistry.
- DIVYA, D. T. & KRISHNAN, K. P. 2017. Recent variability in the Atlantic water intrusion and water masses in Kongsfjorden, an Arctic fjord. *Polar Science*, 11, 30-41.
- DOMÍNGUEZ-MORUECO, N., MORENO-MERINO, L., MOLINS-DELGADO, D., DÍAZ-CRUZ, M. S., AZNAR-ALEMANY, Ò., ELJARRAT, E., FARRÉ, M., LÓPEZ-MARTÍNEZ, J., LÓPEZ DE ALDA, M., SILVA, A., DURÁN VALSERO, J. J. & VALCÁRCEL, Y. 2021. Anthropogenic contaminants in freshwater from the northern Antarctic Peninsula region. *Ambio*, 50, 544-559.
- DRISSI, M., CARR, E. & HOUSEWRIGHT, C. 2022. Sunscreen: a brief walk through history. *Proc (Bayl Univ Med Cent)*, 35, 121-123.
- EC 2003. DIRECTIVE 2002/95/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment.
- EC 2009. REGULATION (EC) N.1223/2009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 30 November 2009 on cosmetic products.
- EC 2017. COMMISSION REGULATION (EU) 2017/227 of 9 February 2017 amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards bis(pentabromophenyl)ether.
- ECHA 2013. Justification for the selection of a candidate CoRAP substance – 2-Ethylhexyl 4-methoxycinnamate. <https://echa.europa.eu/documents/10162/5d8d8771-0175-130a-098e-b72d1ec8e4aa>.
- ELVERHØI, A., LØNNE, Ø. & SELAND, R. 1983. Glaciomarine sedimentation in a modern fjord environment, Spitsbergen. *Polar Research*, 1, 127-150.
- EMNET, P., GAW, S., NORTHCOTT, G., STOREY, B. & GRAHAM, L. 2015. Personal care products and steroid hormones in the Antarctic coastal environment associated with two Antarctic research stations, McMurdo Station and Scott Base. *Environmental Research*, 136, 331-342.
- EQSD 2008. DIRECTIVE 2008 105 EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council.
- EVENSET, A., CHRISTENSEN, G. N., CARROLL, J., ZABORSKA, A., BERGER, U., HERZKE, D. & GREGOR, D. 2007. Historical trends in persistent organic pollutants and metals recorded in sediment from Lake Ellasjøen, Bjørnøya, Norwegian Arctic. *Environmental Pollution*, 146, 196-205.
- EVENSET, A., OLSSON, A., HARJU, M. & GABRIELSEN, G. 2018. Settlements on Svalbard as sources for emerging contaminants. *Akvaplan-niva report*, 7874-1, 56.
- FENT, K., KUNZ, P. Y. & GOMEZ, E. 2008. UV Filters in the Aquatic Environment Induce Hormonal Effects and Affect Fertility and Reproduction in Fish. *CHIMIA*, 62, 368.
- FERRARIO, C., FINIZIO, A. & VILLA, S. 2017. Legacy and emerging contaminants in meltwater of three Alpine glaciers. *Science of The Total Environment*, 574, 350-357.
- FIELD, J. A., JOHNSON, A. C. & JOAN, R. B. 2006. What is “emerging”? *Environmental Science & Technology*, 40, 7105-7105.
- FØRLAND, E., BENESTAD, R., HANSSSEN-BAUER, I., HAUGEN, J. & ENGEN-SKAUGEN, T. 2011. Temperature and Precipitation Development at Svalbard 1900–2100. *Advances in Meteorology*, 2011.
- FRIDE EEG-HENRIKSEN & SJØMÆLING, E. 2016. This is Svalbard 2016. What the figures say. *Statistics Norway*.

- FRIGNANI, M., LANGONE, L., RAVAIOLI, M., SORGENTE, D., ALVISI, F. & ALBERTAZZI, S. 2005. Fine-sediment mass balance in the western Adriatic continental shelf over a century time scale. *Marine Geology*, 222-223, 113-133.
- FRIGNANI, M., SORGENTE, D., LANGONE, L., ALBERTAZZI, S. & RAVAIOLI, M. 2004. Behavior of Chernobyl radiocesium in sediments of the Adriatic Sea off the Po River delta and the Emilia-Romagna coast. *Journal of Environmental Radioactivity*, 71, 299-312.
- GALBÁN-MALAGÓN, C., BERROJALBIZ, N., OJEDA, M.-J. & DACHS, J. 2012. The oceanic biological pump modulates the atmospheric transport of persistent organic pollutants to the Arctic. *Nature Communications*, 3, 862.
- GARRETT, T. & VERZELLA, L. 2007. AN EVOLVING HISTORY OF ARCTIC AEROSOLS.
- GATERMANN, R., BISELLI, S., HÜHNERFUSS, H., RIMKUS, G. G., HECKER, M. & KARBE, L. 2002. Synthetic Musks in the Environment. Part 1: Species-Dependent Bioaccumulation of Polycyclic and Nitro Musk Fragrances in Freshwater Fish and Mussels. *Archives of Environmental Contamination and Toxicology*, 42, 437-446.
- GAUTSCHI, M., BAJGROWICZ, J. A. & KRAFT, P. 2001. Fragrance Chemistry — Milestones and Perspectives. *CHIMIA*, 55, 379.
- GHIMIRE, A., DELA CRUZ, A. L. N., WONG, R., NAVASUMRIT, P., CORMIER, S. & LOMNICKI, S. M. 2019. Polybrominated diphenyl ethers (PBDEs) in ambient air samples at the electronic waste (e-waste) reclamation site. *Waste Disposal & Sustainable Energy*, 1, 79-89.
- GIOIA, R., LOHMANN, R., DACHS, J., TEMME, C., LAKASCHUS, S., SCHULZ-BULL, D., HAND, I. & JONES, K. C. 2008. Polychlorinated biphenyls in air and water of the North Atlantic and Arctic Ocean. *Journal of Geophysical Research: Atmospheres*, 113.
- GRANBERG, M., ASK, A. & GABRIELSEN, G. 2019. *Local contamination in Svalbard- Overview and suggestions for remediation actions*.
- GURUVAYOORAPPAN, H., MIETTINEN, A., DIVINE, D. V., MOROS, M., ORME, L. C. & MOHAN, R. 2020. Ocean surface warming in Krossfjorden, Svalbard, during the last 60 years. *arktos*, 6, 1-13.
- HAGEN, J. O., KOHLER, J., MELVOLD, K. & WINTHER, J.-G. 2003. Glaciers in Svalbard: mass balance, runoff and freshwater flux. *Polar Research*, 22, 145-159.
- HEATON, T. J., KÖHLER, P., BUTZIN, M., BARD, E., REIMER, R. W., AUSTIN, W. E. N., BRONK RAMSEY, C., GROOTES, P. M., HUGHEN, K. A., KROMER, B., REIMER, P. J., ADKINS, J., BURKE, A., COOK, M. S., OLSEN, J. & SKINNER, L. C. 2020. Marine20—The Marine Radiocarbon Age Calibration Curve (0–55,000 cal BP). *Radiocarbon*, 62, 779-820.
- HEIJNIS, H. 2001. *The principle of ²¹⁰Pb dating of sediments*.
- HEINTZENBERG, J., HANSSON, H. C. & LANNEFORS, H. 1981. The chemical composition of arctic haze at Ny-Ålesund, Spitsbergen. *Tellus*, 33, 162-171.
- HELENIAK, T. 2020. Polar Peoples in the Future: Projections of the Arctic Population.
- HELGASON, L., BARRETT, R., LIE, E., POLDER, A., SKAARE, J. & GABRIELSEN, G. 2008. Levels and temporal trends (1983–2003) of persistent organic pollutants (POPs) and mercury (Hg) in seabird eggs from Northern Norway. *Environmental pollution (Barking, Essex : 1987)*, 155, 190-8.
- HERA 2004. Human & Environmental Risk Assessment on ingredients of Household Cleaning Products. Environmental Risk Assessment Polycyclic Musks AHTN and HHCB.
- HERMANSON, M. H., ISAKSSON, E., FORSSTRÖM, S., TEIXEIRA, C., MUIR, D. C. G., POHJOLA, V. A. & VAN DE WAL, R. S. V. 2010. Deposition History of Brominated Flame Retardant Compounds in an Ice Core from Høltedahlfonna, Svalbard, Norway. *Environmental Science & Technology*, 44, 7405-7410.
- HILLAIRE-MARCEL, C., DE VERNAL, A., RONG, Y., ROBERGE, P. & SONG, T. 2022. Challenging Radiocarbon Chronostratigraphies in Central Arctic Ocean Sediment. *Geophysical Research Letters*, 49, e2022GL100446.
- HOWE, J. A., MORETON, S. G., MORRI, C. & MORRIS, P. 2003. Multibeam bathymetry and the depositional environments of Kongsfjorden and Krossfjorden, western Spitsbergen, Svalbard. *Polar Research*, 22, 301-316.

- HUANG, Y., LAW, J. C.-F., LAM, T.-K. & LEUNG, K. S.-Y. 2021. Risks of organic UV filters: a review of environmental and human health concern studies. *Science of The Total Environment*, 755, 142486.
- HUNG, H., HALSALL, C., BALL, H., BIDDLEMAN, T., DACHS, J., DE SILVA, A., HERMANSON, M., KALLENBORN, R., MUIR, D., SÜHRING, R., WANG, X. & WILSON, S. 2022. Climate change influence on the levels and trends of persistent organic pollutants (POPs) and chemicals of emerging Arctic concern (CEACs) in the Arctic physical environment – a review. *Environmental Science: Processes & Impacts*, 24, 1577-1615.
- HUNG, H., KALLENBORN, R., BREIVIK, K., SU, Y., BRORSTRÖM-LUNDÉN, E., OLAFSDOTTIR, K., THORLACIUS, J. M., LEPPÄNEN, S., BOSSI, R., SKOV, H., MANØ, S., PATTON, G. W., STERN, G., SVERKO, E. & FELLIN, P. 2010. Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993–2006. *Science of The Total Environment*, 408, 2854-2873.
- HUNG, H., KATSOYIANNIS, A. A., BRORSTRÖM-LUNDÉN, E., OLAFSDOTTIR, K., AAS, W., BREIVIK, K., BOHLIN-NIZZETTO, P., SIGURDSSON, A., HAKOLA, H., BOSSI, R., SKOV, H., SVERKO, E., BARRESI, E., FELLIN, P. & WILSON, S. 2016. Temporal trends of Persistent Organic Pollutants (POPs) in arctic air: 20 years of monitoring under the Arctic Monitoring and Assessment Programme (AMAP). *Environmental Pollution*, 217, 52-61.
- HUSUM, K., HOWE, J. A., BALTZER, A., FORWICK, M., JENSEN, M., JERNAS, P., KORSUN, S., MIETTINEN, A., MOHAN, R., MORIGI, C., MYHRE, P. I., PRINS, M. A., SKIRBEKK, K., STERNAL, B., BOOS, M., DIJKSTRA, N. & TROELSTRA, S. 2019. The marine sedimentary environments of Kongsfjorden, Svalbard: an archive of polar environmental change. *Polar Research*, 38.
- INGVALDSEN, R., REITAN, M., SVENDSEN, H. & ASPLIN, L. 2001. The upper layer circulation in Kongsfjorden and Krossfjorden - A complex fjord system on the west coast of Spitsbergen. *Memoirs of National Institute of Polar Research*, 54.
- IPCC 2023. Summary for Policymakers. In: Climate Change 2023: Synthesis Report. A Report of the Intergovernmental Panel on
- Climate Change. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on
- Climate Change [Core Writing Team, H. Lee and J. Romero (eds.)] IPCC, Geneva, Switzerland, 36 pages. (in press).
- ITO, H. & KUDOH, S. 1997. Characteristics of water in Kongsfjorden Svalbard. *Proc. NIPR Symp. Polar Meteorol. Glaciol.*, 11, 211-232.
- JESUS, A., AUGUSTO, I., DUARTE, J., SOUSA, E., CIDADE, H., CRUZ, M. T., LOBO, J. M. S. & ALMEIDA, I. F. 2022. Recent Trends on UV filters. *Applied Sciences* [Online], 12.
- JIAO, L., ZHENG, G. J., MINH, T. B., RICHARDSON, B., CHEN, L., ZHANG, Y., YEUNG, L. W., LAM, J. C. W., YANG, X., LAM, P. K. S. & WONG, M. H. 2009. Persistent toxic substances in remote lake and coastal sediments from Svalbard, Norwegian Arctic: Levels, sources and fluxes. *Environmental Pollution*, 157, 1342-1351.
- JOHANNESSEN, S. C., MACDONALD, R. W., WRIGHT, C. A., BURD, B., SHAW, D. P. & VAN ROODSELAAR, A. 2008. Joined by geochemistry, divided by history: PCBs and PBDEs in Strait of Georgia sediments. *Marine Environmental Research*, 66, S112-S120.
- JURADO, E., ZALDÍVAR, J.-M., MARINOV, D. & DACHS, J. 2007. Fate of persistent organic pollutants in the water column: Does turbulent mixing matter? *Marine Pollution Bulletin*, 54, 441-451.
- KALLENBORN, R., BRORSTRÖM-LUNDÉN, E., REIERSEN, L.-O. & WILSON, S. 2018. Pharmaceuticals and personal care products (PPCPs) in Arctic environments: indicator contaminants for assessing local and remote anthropogenic sources in a pristine ecosystem in change. *Environmental Science and Pollution Research*, 25, 33001-33013.
- KALLENBORN, R., GATERMANN, R., PLANTING, S., RIMKUS, G. G., LUND, M., SCHLABACH, M. & BURKOW, I. C. 1999. Gas chromatographic determination of synthetic musk compounds in Norwegian air samples. *Journal of Chromatography A*, 846, 295-306.

- KALLENBORN, R., HALSALL, C., DELLONG, M. & CARLSSON, P. 2012. The influence of climate change on the global distribution and fate processes of anthropogenic persistent organic pollutants. *Journal of Environmental Monitoring*, 14, 2854-2869.
- KEHRL, L. M., HAWLEY, R. L., POWELL, R. D. & BRIGHAM-GRETTE, J. 2011. Glacimarine sedimentation processes at Kronebreen and Kongsvegen, Svalbard. *Journal of Glaciology*, 57, 841-847.
- KIM, J. H., PETERSE, F., WILLMOTT, V., KRISTENSEN, D. K., BAAS, M., SCHOUTEN, S. & SINNINGHE DAMSTÉ, J. S. 2011. Large ancient organic matter contributions to Arctic marine sediments (Svalbard). *Limnology and Oceanography*, 56, 1463-1474.
- KRISTIANSEN, J. E. 2014. This is Svalbard 2014. What the figures say. *Statistics Norway*.
- LA GUARDIA, M. J., HALE, R. C. & HARVEY, E. 2006. Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDE Technical Flame-retardant Mixtures. *Environmental Science & Technology*, 40, 6247-6254.
- LANGFORD, K. H., REID, M. J., FJELD, E., ØXNEVAD, S. & THOMAS, K. V. 2015. Environmental occurrence and risk of organic UV filters and stabilizers in multiple matrices in Norway. *Environment International*, 80, 1-7.
- LARSEN, J. N. & FONDAHL, G. 2014. Arctic Human Development Report. Regional Processes and Global Linkages. *TemaNord*, 567.
- LEE, L. K. & HE, J. 2010. Reductive debromination of polybrominated diphenyl ethers by anaerobic bacteria from soils and sediments. *Applied and Environmental Microbiology*, p. 794-802.
- LOHMANN, R., BREIVIK, K., DACHS, J. & MUIR, D. 2007. Global fate of POPs: Current and future research directions. *Environmental Pollution*, 150, 150-165.
- LUCKENBACH, T. & EPEL, D. 2005. Nitromusk and Polycyclic Musk Compounds as Long-Term Inhibitors of Cellular Xenobiotic Defense Systems Mediated by Multidrug Transporters. *Environmental Health Perspectives*, 113, 17-24.
- MA, J., HUNG, H. & MACDONALD, R. W. 2016. The influence of global climate change on the environmental fate of persistent organic pollutants: A review with emphasis on the Northern Hemisphere and the Arctic as a receptor. *Global and Planetary Change*, 146, 89-108.
- MA, J., HUNG, H., TIAN, C. & KALLENBORN, R. 2011. Revolatilization of persistent organic pollutants in the Arctic induced by climate change. *Nature Climate Change*, 1, 255-260.
- MA, Y., ADELMAN, D. A., BAUERFEIND, E., CABRERIZO, A., MCDONOUGH, C. A., MUIR, D., SOLTWEDEL, T., SUN, C., WAGNER, C. C., SUNDERLAND, E. M. & LOHMANN, R. 2018. Concentrations and Water Mass Transport of Legacy POPs in the Arctic Ocean. *Geophysical Research Letters*, 45, 12,972-12,981.
- MA, Y., XIE, Z., HALSALL, C., MÖLLER, A., YANG, H., ZHONG, G., CAI, M. & EBINGHAUS, R. 2015. The spatial distribution of organochlorine pesticides and halogenated flame retardants in the surface sediments of an Arctic fjord: The influence of ocean currents vs. glacial runoff. *Chemosphere*, 119, 953-960.
- MA, Y. & YOO, J. 2021. History of sunscreen: An updated view. *Journal of Cosmetic Dermatology*, 20, 1044-1049.
- MACDONALD, R. W., HARNER, T. & FYFE, J. 2005. Recent climate change in the Arctic and its impact on contaminant pathways and interpretation of temporal trend data. *The Science of the total environment*, 342, 5-86.
- MAĆKIEWICZ, A. & RATAJCZAK, W. 1993. Principal components analysis (PCA). *Computers & Geosciences*, 19, 303-342.
- MACLACHLAN, S. E., HOWE, J. A. & VARDY, M. E. 2010. Morphodynamic evolution of Kongsfjorden–Krossfjorden, Svalbard, during the Late Weichselian and Holocene. In: HOWE, J. A., AUSTIN, W. E. N., FORWICK, M. & PAETZEL, M. (eds.) *Fjord Systems and Archives*. Geological Society of London.
- MAGALI, L., GABRIELSEN, G. W., HERZKE, D. & CHRISTENSEN, G. 2013. Screening of UV chemicals, bisphenols and siloxanes in the Arctic. *Norsk Polarinstitutt*.

- MALMQUIST, C., BINDLER, R., RENBERG, I., VAN BAVEL, B., KARLSSON, E., ANDERSON, N. J. & TYSKLIND, M. 2003. Time Trends of Selected Persistent Organic Pollutants in Lake Sediments from Greenland. *Environmental Science & Technology*, 37, 4319-4324.
- MCDONOUGH, C. A., DE SILVA, A. O., SUN, C., CABRERIZO, A., ADELMAN, D., SOLTWEDEL, T., BAUERFEIND, E., MUIR, D. C. G. & LOHMANN, R. 2018. Dissolved Organophosphate Esters and Polybrominated Diphenyl Ethers in Remote Marine Environments: Arctic Surface Water Distributions and Net Transport through Fram Strait. *Environmental Science & Technology*, 52, 6208-6216.
- MCDONOUGH, C. A., HELM, P. A., MUIR, D., PUGGIONI, G. & LOHMANN, R. 2016. Polycyclic Musks in the Air and Water of the Lower Great Lakes: Spatial Distribution and Volatilization from Surface Waters. *Environmental Science & Technology*, 50, 11575-11583.
- MCGOVERN, M., BORGÅ, K., HEIMSTAD, E., RUUS, A., CHRISTENSEN, G. & EVENSET, A. 2022a. Small Arctic rivers transport legacy contaminants from thawing catchments to coastal areas in Kongsfjorden, Svalbard. *Environmental Pollution*, 304, 119191.
- MCGOVERN, M., WARNER, N. A., BORGÅ, K., EVENSET, A., CARLSSON, P., SKOGSBERG, E., SØREIDE, J. E., RUUS, A., CHRISTENSEN, G. & POSTE, A. E. 2022b. Is Glacial Meltwater a Secondary Source of Legacy Contaminants to Arctic Coastal Food Webs? *Environmental Science & Technology*, 56, 6337-6348.
- MCKINNEY, M. A., LETCHER, R. J., AARS, J., BORN, E. W., BRANIGAN, M., DIETZ, R., EVANS, T. J., GABRIELSEN, G. W., PEACOCK, E. & SONNE, C. 2011. Flame retardants and legacy contaminants in polar bears from Alaska, Canada, East Greenland and Svalbard, 2005–2008. *Environment International*, 37, 365-374.
- MCKINNEY, M. A., STIRLING, I., LUNN, N. J., PEACOCK, E. & LETCHER, R. J. 2010. The role of diet on long-term concentration and pattern trends of brominated and chlorinated contaminants in western Hudson Bay polar bears, 1991–2007. *Science of The Total Environment*, 408, 6210-6222.
- MESLARD, F., BOURRIN, F., MANY, G. & KERHERVÉ, P. 2018. Suspended particle dynamics and fluxes in an Arctic fjord (Kongsfjorden, Svalbard). *Estuarine, Coastal and Shelf Science*, 204, 212-224.
- MEYER, T. & WANIA, F. 2008. Organic contaminant amplification during snowmelt. *Water Research*, 42, 1847-1865.
- MISEROCCHI, S., D'ANGELO, A., DEL BIANCO, F., GIGLIO, F., LANGONE, L., TESI, T. & ALIANI, S. 2016. Modern sediment distribution and composition within the Kongsfjorden, Svalbard Islands. *ARCA Project - Final Conference, 11 October 2016 Rome - Poster Session - Fjord system - Extended abstract*.
- MIZUKAWA, A., MOLINS-DELGADO, D., DE AZEVEDO, J. C. R., FERNANDES, C. V. S., DÍAZ-CRUZ, S. & BARCELÓ, D. 2017. Sediments as a sink for UV filters and benzotriazoles: the case study of Upper Iguaçu watershed, Curitiba (Brazil). *Environmental Science and Pollution Research*, 24, 18284-18294.
- MÖLLER, A., XIE, Z., CAI, M., ZHONG, G., HUANG, P., CAI, M., STURM, R., HE, J. & EBINGHAUS, R. 2011a. Polybrominated Diphenyl Ethers vs Alternate Brominated Flame Retardants and Dechloranes from East Asia to the Arctic. *Environmental Science & Technology*, 45, 6793-6799.
- MÖLLER, A., XIE, Z., STURM, R. & EBINGHAUS, R. 2011b. Polybrominated diphenyl ethers (PBDEs) and alternative brominated flame retardants in air and seawater of the European Arctic. *Environmental Pollution*, 159, 1577-1583.
- MUIR, D., GUNNARSDÓTTIR, M. J., KOZIOL, K., VON HIPPEL, F. A., SZUMIŃSKA, D., ADEMOLLO, N., CORSOLINI, S., DE SILVA, A., GABRIELSEN, G., KALLENBORN, R., POLKOWSKA, Ż., KRÜMMEL, E. & VORKAMP, K. 2025. Local sources versus long-range transport of organic contaminants in the Arctic: future developments related to climate change. *Environmental Science: Advances*.
- MUIR, D., TEIXEIRA, C., CHIGAK, M., YANG, F., D'SA, I., CANNON, C., PACEPAVICIUS, G. & ALAEE, M. 2003. Current deposition and historical profiles of decabromodiphenyl ether in sediment cores. *Organohalogen Compounds* 61, 77-80.

- NAGORKA, R. & DUFFEK, A. 2021. Under the influence of regulations: spatio-temporal trends of the UV filter 2-Ethylhexyl-4-methoxycinnamate (EHMC) in German rivers. *Environmental Sciences Europe*, 33, 8.
- NESJE, A., LIE, Ø. & DAHL, S. O. 2000. Is the North Atlantic Oscillation reflected in Scandinavian glacier mass balance records? *Journal of Quaternary Science*, 15, 587-601.
- NILSEN, F., SKOGSETH, R., VAARDAL-LUNDE, J. & INALL, M. 2016. A Simple Shelf Circulation Model: Intrusion of Atlantic Water on the West Spitsbergen Shelf. *Journal of Physical Oceanography*, 46, 1209-1230.
- NIPEN, M., VOGT, R. D., BOHLIN-NIZZETTO, P., BORGÅ, K., MWAKALAPA, E. B., BORGES, A. R., SCHLABACH, M., CHRISTENSEN, G., MMOCHI, A. J. & BREIVIK, K. 2022. Increasing Trends of Legacy and Emerging Organic Contaminants in a Dated Sediment Core From East-Africa. *Frontiers in Environmental Science*, 9.
- OECD 2004. HPV Chemicals List, 2004. Organisation for Economic Co-operation and Development.
- OHAIJINWA, C. M., VAN BODEGOM, P. M., XIE, Q., CHEN, J., VIJVER, M. G., OSIBANJO, O. O. & PEIJNENBURG, W. J. G. M. 2019. Hydrophobic Organic Pollutants in Soils and Dusts at Electronic Waste Recycling Sites: Occurrence and Possible Impacts of Polybrominated Diphenyl Ethers. *International Journal of Environmental Research and Public Health* [Online], 16.
- ONTIVEROS-CUADRAS, J. F., RUIZ-FERNÁNDEZ, A. C., SANCHEZ-CABEZA, J.-A., SERICANO, J., PÉREZ-BERNAL, L. H., PÁEZ-OSUNA, F., DUNBAR, R. B. & MUCCIARONE, D. A. 2019. Recent history of persistent organic pollutants (PAHs, PCBs, PBDEs) in sediments from a large tropical lake. *Journal of Hazardous Materials*, 368, 264-273.
- OSPAR, C. 2004. OSPAR background document on musk xylene and other musks.
- PAGLIA, E. 2020. A higher level of civilisation? The transformation of Ny-Ålesund from Arctic coalmining settlement in Svalbard to global environmental knowledge center at 79° North. *Polar Record*, 56, e15.
- PAWLAK, F., KOZIOL, K. & POLKOWSKA, Z. 2021. Chemical hazard in glacial melt? The glacial system as a secondary source of POPs (in the Northern Hemisphere). A systematic review. *Science of The Total Environment*, 778, 145244.
- PECK, A. M. & HORNBUCKLE, K. C. 2004. Synthetic Musk Fragrances in Lake Michigan. *Environmental Science & Technology*, 38, 367-372.
- PINTADO-HERRERA, M. G., COMBI, T., CORADA-FERNÁNDEZ, C., GONZÁLEZ-MAZO, E. & LARA-MARTÍN, P. A. 2017. Occurrence and spatial distribution of legacy and emerging organic pollutants in marine sediments from the Atlantic coast (Andalusia, SW Spain). *Science of The Total Environment*, 605-606, 980-994.
- PINTADO-HERRERA, M. G., GONZÁLEZ-MAZO, E. & LARA-MARTÍN, P. A. 2016. In-cell clean-up pressurized liquid extraction and gas chromatography–tandem mass spectrometry determination of hydrophobic persistent and emerging organic pollutants in coastal sediments. *Journal of Chromatography A*, 1429, 107-118.
- PLATT, S. M., HOV, Ø., BERG, T., BREIVIK, K., ECKHARDT, S., ELEFThERiADIS, K., EVANGELIOU, N., FIEBIG, M., FISHER, R., HANSEN, G., HANSSON, H. C., HEINTZENBERG, J., HERMANSEN, O., HESLIN-REES, D., HOLMÉN, K., HUDSON, S., KALLENBORN, R., KREJCI, R., KROGNES, T., LARSEN, S., LOWRY, D., LUND MYHRE, C., LUNDER, C., NISBET, E., NIZZETTO, P. B., PARK, K. T., PEDERSEN, C. A., ASPMO PFAFFHUBER, K., RÖCKMANN, T., SCHMIDBAUER, N., SOLBERG, S., STOHL, A., STRÖM, J., SVENDBY, T., TUNVED, P., TØRNKVIST, K., VAN DER VEEN, C., VRATOLIS, S., YOON, Y. J., YTTRI, K. E., ZIEGER, P., AAS, W. & TØRSETH, K. 2022. Atmospheric composition in the European Arctic and 30 years of the Zeppelin Observatory, Ny-Ålesund. *Atmos. Chem. Phys.*, 22, 3321-3369.
- POLKOWSKA, Ż., CICHALA-KAMROWSKA, K., RUMAN, M., KOZIOŁ, K., KRAWCZYK, W. E. & NAMIEŚNIK, J. 2011. Organic Pollution in Surface Waters from the Fuglebekken Basin in Svalbard, Norwegian Arctic. *Sensors* [Online], 11.

- POUCH, A., ZABORSKA, A., MAZURKIEWICZ, M., WINOGRADOW, A. & PAZDRO, K. 2021. PCBs, HCB and PAHs in the seawater of Arctic fjords – Distribution, sources and risk assessment. *Marine Pollution Bulletin*, 164, 111980.
- POUCH, A., ZABORSKA, A. & PAZDRO, K. 2017. Concentrations and origin of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in sediments of western Spitsbergen fjords (Kongsfjorden, Hornsund, and Adventfjorden). *Environmental Monitoring and Assessment*, 189, 175.
- PRAMANIK, A., KOHLER, J., LINDBÄCK, K., HOW, P., PELT, W., LISTON, G. & SCHULER, T. 2020. *Hydrology and runoff routing of glacierized drainage basins in the Kongsfjord area, northwest Svalbard*.
- PRAMANIK, A., VAN PELT, W., KOHLER, J. & SCHULER, T. V. 2018. Simulating climatic mass balance, seasonal snow development and associated freshwater runoff in the Kongsfjord basin, Svalbard (1980–2016). *Journal of Glaciology*, 64, 943-956.
- PREVIDI, M., SMITH, K. L. & POLVANI, L. M. 2021. Arctic amplification of climate change: a review of underlying mechanisms. *Environmental Research Letters*, 16, 093003.
- PROVENCHER, J. F., MALAISE, F., MALLORY, M. L., BRAUNE, B. M., PIRIE-DOMINIX, L. & LU, Z. 2022. 44-Year Retrospective Analysis of Ultraviolet Absorbents and Industrial Antioxidants in Seabird Eggs from the Canadian Arctic (1975 to 2019). *Environmental Science & Technology*, 56, 14562-14573.
- QIAO, L.-N., HU, P.-T., MACDONALD, R., KANNAN, K., NIKOLAEV, A. & LI, Y.-F. 2020. Modeling gas/particle partitioning of polybrominated diphenyl ethers (PBDEs) in the atmosphere: A review. *Science of The Total Environment*, 729, 138962.
- RAHMAN, F., LANGFORD, K. H., SCRIMSHAW, M. D. & LESTER, J. N. 2001. Polybrominated diphenyl ether (PBDE) flame retardants. *Science of The Total Environment*, 275, 1-17.
- RAMSEY, B. C. 2009. Bayesian Analysis of Radiocarbon Dates. *Radiocarbon*, 51, 337-360.
- RAUSEO, J., SPATARO, F., PESCATORE, T. & PATROLECCO, L. 2024. Multiresidue determination and predicted risk assessment of emerging contaminants in sediments from Kongsfjorden, Svalbard. *Science of The Total Environment*, 922, 171156.
- REIERSEN, L.-O., VORKAMP, K. & KALLENBORN, R. 2024. The role of the Arctic Monitoring and Assessment Programme (AMAP) in reducing pollution of the Arctic and around the globe. *Environmental Science and Ecotechnology*, 17, 100302.
- REIMER, P. J., BROWN, T. A. & REIMER, R. W. 2004. Discussion: Reporting and Calibration of Post-Bomb ¹⁴C Data. *Radiocarbon*, 46, 1299-1304.
- REYMERT, P. K. 2016. Ny-Ålesund. *The Governor of Svalbard and Department for Environment Protection with Kings Bay AS*.
- RICHTER, T. O., VAN DER GAAST, S., KOSTER, B., VAARS, A., GIELES, R., DE STIGTER HENKO, C., DE HAAS, H. & VAN WEERING TJEERD, C. E. 2006. The Avaatech XRF Core Scanner: technical description and applications to NE Atlantic sediments. *Geological Society, London, Special Publications*, 267, 39-50.
- RIGÉT, F., BIGNERT, A., BRAUNE, B., DAM, M., DIETZ, R., EVANS, M., GREEN, N., GUNNLAUGSDÓTTIR, H., HOYDAL, K. S., KUCKLICK, J., LETCHER, R., MUIR, D., SCHUUR, S., SONNE, C., STERN, G., TOMY, G., VORKAMP, K. & WILSON, S. 2019. Temporal trends of persistent organic pollutants in Arctic marine and freshwater biota. *Science of The Total Environment*, 649, 99-110.
- ROTANDER, A., VAN BAVEL, B., POLDER, A., RIGÉT, F., AUÐUNSSON, G. A., GABRIELSEN, G. W., VÍKINGSSON, G., BLOCH, D. & DAM, M. 2012. Polybrominated diphenyl ethers (PBDEs) in marine mammals from Arctic and North Atlantic regions, 1986–2009. *Environment International*, 40, 102-109.
- SALVADÓ, J. A., SOBEK, A., CARRIZO, D. & GUSTAFSSON, Ö. 2016. Observation-Based Assessment of PBDE Loads in Arctic Ocean Waters. *Environmental Science & Technology*, 50, 2236-2245.
- SANCHEZ-CABEZA, J. A. & RUIZ-FERNÁNDEZ, A. C. 2012. ²¹⁰Pb sediment radiochronology: An integrated formulation and classification of dating models. *Geochimica et Cosmochimica Acta*, 82, 183-200.

- SANDERS, G., HOLST, A. & SHEARS, J. 2006. Environmental impact assessment of the research activities in Ny-Ålesund 2006. *Kortrapport - Norsk Polarinstitutt*, 04.
- SHELLENBERGER, T., DUNSE, T., KÄÄB, A., KOHLER, J. & REIJMER, C. H. 2015. Surface speed and frontal ablation of Kronebreen and Kongsbreen, NW Svalbard, from SAR offset tracking. *The Cryosphere*, 9, 2339-2355.
- SCHUBERT, C. J. & CALVERT, S. E. 2001. Nitrogen and carbon isotopic composition of marine and terrestrial organic matter in Arctic Ocean sediments:: implications for nutrient utilization and organic matter composition. *Deep Sea Research Part I: Oceanographic Research Papers*, 48, 789-810.
- SERREZE, M. C. & BARRY, R. G. 2011. Processes and impacts of Arctic amplification: A research synthesis. *Global and Planetary Change*, 77, 85-96.
- SHANG, H., WANG, P., WANG, T., WANG, Y., ZHANG, H., FU, J., REN, D., CHEN, W., ZHANG, Q. & JIANG, G. 2013. Bioaccumulation of PCDD/Fs, PCBs and PBDEs by earthworms in field soils of an E-waste dismantling area in China. *Environment international*, 54, 50-58.
- SHARKEY, M., HARRAD, S., ABOU-ELWafa ABDALLAH, M., DRAGE, D. S. & BERRESHEIM, H. 2020. Phasing-out of legacy brominated flame retardants: The UNEP Stockholm Convention and other legislative action worldwide. *Environment International*, 144, 106041.
- SHAW, G. E. 1995. The Arctic Haze Phenomenon. *Bulletin of the American Meteorological Society*, 76, 2403-2414.
- SHEARS, J., THEISEN, F., BJØRDAL, A. & NORRIS, S. 1998. Environmental impact assessment - Ny-Ålesund international scientific research and monitoring station, Svalbard. *Norwegian Polar Institute, Meddelelser no. 157*.
- SHI, F., SHI, X., SU, X., FANG, X., WU, Y., CHENG, Z. & YAO, Z. 2018. Clay minerals in Arctic Kongsfjorden surface sediments and their implications on provenance and paleoenvironmental change. *Acta Oceanologica Sinica*, 37, 29-38.
- SHUNTHIRASINGHAM, C., ALEXANDROU, N., BRICE, K. A., DRYFHOUT-CLARK, H., SU, K., SHIN, C., PARK, R., PAJDA, A., NORONHA, R. & HUNG, H. 2018. Temporal trends of halogenated flame retardants in the atmosphere of the Canadian Great Lakes Basin (2005–2014). *Environmental Science: Processes & Impacts*, 20, 469-479.
- SKIRBEKK, K., KRISTENSEN DORTHE, K., RASMUSSEN TINE, L., KOÇ, N. & FORWICK, M. 2010. Holocene climate variations at the entrance to a warm Arctic fjord: evidence from Kongsfjorden trough, Svalbard. *Geological Society, London, Special Publications*, 344, 289-304.
- SÖDERSTRÖM, G., SELLSTRÖM, U., DE WIT, C. A. & TYSKLIND, M. 2004. Photolytic Debromination of Decabromodiphenyl Ether (BDE 209). *Environmental Science & Technology*, 38, 127-132.
- SONNE, C., DIETZ, R., JENSSEN, B. M., LAM, S. S. & LETCHER, R. J. 2021. Emerging contaminants and biological effects in Arctic wildlife. *Trends in Ecology & Evolution*, 36, 421-429.
- SPASOJEVIĆ, J., MALETIĆ, S., RONČEVIĆ, S., GRGIĆ, M., KRČMAR, D., VARGA, N. & DALMACIJA, B. 2017. The role of organic matter and clay content in sediments for bioavailability of pyrene. *Water Science and Technology*, 77, 439-447.
- SPATARO, F., RAUSEO, J., PESCATORE, T. & PATROLECCO, L. 2022. Priority Organic Pollutants and Endocrine-Disrupting Compounds in Arctic Marine Sediments (Svalbard Islands, Norway). *Environmental Toxicology and Chemistry*, n/a.
- STEMMLER, I. & LAMMEL, G. 2010. Pathways of PFOA to the Arctic: variabilities and contributions of oceanic currents and atmospheric transport and chemistry sources. *Atmos. Chem. Phys.*, 10, 9965-9980.
- STEPANYUK, A. & KIRSCHNING, A. 2019. Synthetic terpenoids in the world of fragrances: Iso E Super® is the showcase. *Beilstein Journal of Organic Chemistry*, 15, 2590-2602.
- STREUFF, K., FORWICK, M., SZCZUCIŃSKI, W., ANDREASSEN, K. & Ó COFAIGH, C. 2015. Submarine landform assemblages and sedimentary processes related to glacier surging in Kongsfjorden, Svalbard. *arktos*, 1, 14.
- SU, Y., HUNG, H., SVERKO, E., FELLIN, P. & LI, H. 2007. Multi-year measurements of polybrominated diphenyl ethers (PBDEs) in the Arctic atmosphere. *Atmospheric Environment*, 41, 8725-8735.

- SUN, H., LI, Y., HAO, Y., ZHU, Y., YANG, R., WANG, P., ZHANG, Q. & JIANG, G. 2020. Bioaccumulation and Trophic Transfer of Polybrominated Diphenyl Ethers and Their Hydroxylated and Methoxylated Analogues in Polar Marine Food Webs. *Environmental Science & Technology*, 54, 15086-15096.
- SUNDFJORD, A., ALBRETSSEN, J., KASAJIMA, Y., SKOGSETH, R., KOHLER, J., NUTH, C., SKARDHAMAR, J., COTTIER, F., NILSEN, F., ASPLIN, L., GERLAND, S. & TORSVIK, T. 2017. Effects of glacier runoff and wind on surface layer dynamics and Atlantic Water exchange in Kongsfjorden, Svalbard; a model study. *Estuarine, Coastal and Shelf Science*, 187, 260-272.
- SVARC, F. 2015. A brief illustrated history on sunscreens and sun protection. *Pure and Applied Chemistry*, 87.
- SVENDSEN, H., BESZCZYNSKA-MØLLER, A., HAGEN, J. O., LEFAUCONNIER, B., TVERBERG, V., GERLAND, S., ØRBØK, J. B., BISCHOF, K., PAPUCCI, C., ZAJACZKOWSKI, M., AZZOLINI, R., BRULAND, O., WIENCKE, C., WINTHER, J.-G. & DALLMANN, W. 2002. The physical environment of Kongsfjorden–Krossfjorden, an Arctic fjord system in Svalbard. *Polar Research*, 21, 133-166.
- SYNAL, H.-A., STOCKER, M. & SUTER, M. 2007. MICADAS: A new compact radiocarbon AMS system. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 259, 7-13.
- SZCZYBELSKI, A. S., VAN DEN HEUVEL-GREVE, M. J., KAMPEN, T., WANG, C., VAN DEN BRINK, N. W. & KOELMANS, A. A. 2016. Bioaccumulation of polycyclic aromatic hydrocarbons, polychlorinated biphenyls and hexachlorobenzene by three Arctic benthic species from Kongsfjorden (Svalbard, Norway). *Marine Pollution Bulletin*, 112, 65-74.
- TESI, T., MUSCHITIELLO, F., MOLLENHAUER, G., MISEROCCHI, S., LANGONE, L., CECCARELLI, C., PANIERI, G., CHIGGIATO, J., NOGAROTTO, A., HEFTER, J., INGROSSO, G., GIGLIO, F., GIORDANO, P. & CAPOTONDI, L. 2021. Rapid Atlantification along the Fram Strait at the beginning of the 20th century. *Science Advances*, 7.
- THOMPSON, M., ELLISON, S. L. R. & WOOD, R. 2002. Harmonized guidelines for single-laboratory validation of methods of analysis (IUPAC Technical Report). 74, 835-855.
- TNO 2008. (1,3,4,6,7,8-HEXAHYDRO-4,6,6,7,8,8-HEXAMETHYLIN-DENO[5,6C]PYRAN - HHCB) Summary Risk Assessment Report. *European Communities*.
- TOKARZ, J. A., III, AHN, M.-Y., LENG, J., FILLEY, T. R. & NIES, L. 2008. Reductive Debromination of Polybrominated Diphenyl Ethers in Anaerobic Sediment and a Biomimetic System. *Environmental Science & Technology*, 42, 1157-1164.
- TOROSIAN, G. & LEMBERGER, M. A. 1972. O-T-C Sunscreen and Suntan Products. *Journal of the American Pharmaceutical Association (1961)*, 12, 571-575.
- TRUSEL, L. D., POWELL, R. D., CUMPSTON, R. M. & BRIGHAM-GRETTE, J. 2010. Modern glacimarine processes and potential future behaviour of Kronebreen and Kongsvegen polythermal tidewater glaciers, Kongsfjorden, Svalbard. In: HOWE, J. A., AUSTIN, W. E. N., FORWICK, M. & PAETZEL, M. (eds.) *Fjord Systems and Archives*. Geological Society of London.
- TSUI, M. M. P., LEUNG, H. W., KWAN, B. K. Y., NG, K.-Y., YAMASHITA, N., TANIYASU, S., LAM, P. K. S. & MURPHY, M. B. 2015. Occurrence, distribution and ecological risk assessment of multiple classes of UV filters in marine sediments in Hong Kong and Japan. *Journal of Hazardous Materials*, 292, 180-187.
- TSUI, M. M. P., LEUNG, H. W., WAI, T.-C., YAMASHITA, N., TANIYASU, S., LIU, W., LAM, P. K. S. & MURPHY, M. B. 2014. Occurrence, distribution and ecological risk assessment of multiple classes of UV filters in surface waters from different countries. *Water Research*, 67, 55-65.
- TURNER, A. 2022. PBDEs in the marine environment: Sources, pathways and the role of microplastics. *Environmental Pollution*, 301, 118943.
- TVERBERG, V., SKOGSETH, R., COTTIER, F., SUNDFJORD, A., WALCZOWSKI, W., INALL, M., FALCK, E., PAVLOVA, O. & NILSEN, F. 2019. The Kongsfjorden Transect: Seasonal and Inter-annual Variability in Hydrography.
- U.S., P. O. 1967. SUN SCREENING COMPOSITIONS (Patent n°3341419).
- U.S., P. O. 1973. United States Patent Office, Ethyl hexyl salicylate (3,751,563).

- UNEP 2001. Final Act of the Plenipotentiaries on the Stockholm Convention on Persistent Organic Pollutants. . *United Nations Environment Program Chemicals, Geneva, Switzerland*, 445.
- UNEP 2009. GUIDANCE on feasible flame-retardant alternatives to commercial pentabromodiphenyl ether 2009 (UNEP/POPS/COP.4/INF24).
- UNEP 2017. The 16 New POPs. An introduction to the chemicals added to the Stockholm Convention as Persistent Organic Pollutants by the Conference of the Parties.
- VECCHIATO, M., BARBARO, E., SPOLAOR, A., BURGAY, F., BARBANTE, C., PIAZZA, R. & GAMBARO, A. 2018. Fragrances and PAHs in snow and seawater of Ny-Ålesund (Svalbard): Local and long-range contamination. *Environmental Pollution*, 242, 1740-1747.
- VECCHIATO, M., GAMBARO, A., KEHRWALD, N. M., GINOT, P., KUTUZOV, S., MIKHALENKO, V. & BARBANTE, C. 2020. The Great Acceleration of fragrances and PAHs archived in an ice core from Elbrus, Caucasus. *Scientific Reports*, 10, 10661.
- VILLA, S., VIGHI, M. & FINIZIO, A. 2014. Theoretical and experimental evidences of medium range atmospheric transport processes of polycyclic musk fragrances. *Science of The Total Environment*, 481, 27-34.
- VORKAMP, K., CARLSSON, P., CORSOLINI, S., DE WIT, C. A., DIETZ, R., GRIBBLE, M. O., HOUDE, M., KALIA, V., LETCHER, R. J., MORRIS, A., RIGÉT, F. F., ROUTTI, H. & MUIR, D. C. G. 2022. Influences of climate change on long-term time series of persistent organic pollutants (POPs) in Arctic and Antarctic biota. *Environmental Science: Processes & Impacts*, 24, 1643-1660.
- VORKAMP, K., RIGÉT, F. F., GLASIUS, M., MUIR, D. C. G. & DIETZ, R. 2008. Levels and trends of persistent organic pollutants in ringed seals (*Phoca hispida*) from Central West Greenland, with particular focus on polybrominated diphenyl ethers (PBDEs). *Environment International*, 34, 499-508.
- VORKAMP, K., THOMSEN, M., FALK, K., LESLIE, H., MØLLER, S. & SØRENSEN, P. B. 2005. Temporal Development of Brominated Flame Retardants in Peregrine Falcon (*Falco peregrinus*) Eggs from South Greenland (1986–2003). *Environmental Science & Technology*, 39, 8199-8206.
- WANG, X.-M., DING, X., MAI, B.-X., XIE, Z.-Q., XIANG, C.-H., SUN, L.-G., SHENG, G.-Y., FU, J.-M. & ZENG, E. Y. 2005. Polybrominated Diphenyl Ethers in Airborne Particulates Collected during a Research Expedition from the Bohai Sea to the Arctic. *Environmental Science & Technology*, 39, 7803-7809.
- WANIA, F. & DUGANI, S. 2003. Assessing the Long-Range Transport Potential of Polybrominated Diphenyl Ethers: A Comparison of Four Multimedia Models. *Environmental toxicology and chemistry / SETAC*, 22, 1252-61.
- WANIA, F. & MACKAY, D. 1995. A global distribution model for persistent organic chemicals. *Science of The Total Environment*, 160-161, 211-232.
- WANIA, F. & MCKAY, D. 1996. Tracking the Distribution of Persistent Organic Pollutants. *Environmental Science & Technology*, 30, 390A-396A.
- WARNER, N. A., EVENSET, A., CHRISTENSEN, G., GABRIELSEN, G. W., BORGÅ, K. & LEKNES, H. 2010. Volatile Siloxanes in the European Arctic: Assessment of Sources and Spatial Distribution. *Environmental Science & Technology*, 44, 7705-7710.
- WATANABE TOSHIO, HASHIMOTO TAKEYUKI, YOSHIMATSU SHIGEKI, TAKEYAMA SHIGEYUKI, TAKASHIMA KOHKI & KIYOSHI, I. 1971. Derivatives of cinnamic acid and preparation thereof (Patent n°CA871746).
- WENTWORTH, C. K. 1922. A Scale of Grade and Class Terms for Clastic Sediments. *Journal of Geology*, 30, 377-392.
- WERTNIK, M., WACKER, L., BERNASCONI, S. M., HAGHIPOUR, N., EGLINTON, T. I. & WELTE, C. 2023. A Universal Gas Interface for Simultaneous $\delta^{14}\text{C}$ and $\delta^{13}\text{C}$ Measurements. *Radiocarbon*, 1-11.
- WINKELMANN, D. & KNIES, J. 2005. Recent distribution and accumulation of organic carbon on the continental margin west off Spitsbergen. *Geochemistry, Geophysics, Geosystems*, 6.
- WONG, F., HUNG, H., DRYFHOUT-CLARK, H., AAS, W., BOHLIN-NIZZETTO, P., BREIVIK, K., MASTROMONACO, M. N., LUNDÉN, E. B., ÓLAFSDÓTTIR, K., SIGURÐSSON, Á., VORKAMP, K., BOSSI, R., SKOV, H., HAKOLA, H., BARRESI, E., SVERKO, E., FELLIN, P., LI, H., VLASENKO, A., ZAPEVALOV, M., SAMSONOV, D. & WILSON, S. 2021. Time trends of persistent organic pollutants

- (POPs) and Chemicals of Emerging Arctic Concern (CEAC) in Arctic air from 25 years of monitoring. *Science of The Total Environment*, 775, 145109.
- WONG, F., ROBSON, M., MELMUK, L., SHUNTHIRASINGHAM, C., ALEXANDROU, N., SHOEIB, M., LUK, E., HELM, P., DIAMOND, MIRIAM L. & HUNG, H. 2019. Urban sources of synthetic musk compounds to the environment. *Environmental Science: Processes & Impacts*, 21, 74-88.
- WU, H., DENG, B., WANG, J., ZENG, S., DU, J., YU, P., BI, Q. & DU, J. 2023. Sedimentary record of climate change in a high latitude fjord—Kongsfjord. *Acta Oceanologica Sinica*, 42, 91-102.
- WU, Z., HAN, W., YANG, X., LI, Y. & WANG, Y. 2019. The occurrence of polybrominated diphenyl ether (PBDE) contamination in soil, water/sediment, and air. *Environmental Science and Pollution Research*, 26, 23219-23241.
- XIE, Z., EBINGHAUS, R., TEMME, C., HEEMKEN, O. & RUCK, W. 2007. Air–Sea Exchange Fluxes of Synthetic Polycyclic Musks in the North Sea and the Arctic. *Environmental Science & Technology*, 41, 5654-5659.
- XIE, Z., ZHANG, P., WU, Z., ZHANG, S., WEI, L., MI, L., KUESTER, A., GANDRASS, J., EBINGHAUS, R., YANG, R., WANG, Z. & MI, W. 2022. Legacy and emerging organic contaminants in the polar regions. *Science of The Total Environment*, 835, 155376.
- XIONG, S., HAO, Y., FU, J., WANG, P., YANG, R., PEI, Z., LI, Y., LI, A., ZHANG, Q. & JIANG, G. 2022. Legacy and novel brominated flame retardants in air of Ny-Ålesund, Arctic from 2011 to 2019. *Environmental Pollution*, 313, 120195.
- XU, G., ZHAO, X., ZHAO, S., CHEN, C., ROGERS, M. J., RAMASWAMY, R. & HE, J. 2021. Insights into the Occurrence, Fate, and Impacts of Halogenated Flame Retardants in Municipal Wastewater Treatment Plants. *Environmental Science & Technology*, 55, 4205-4226.
- YANG, C., ROSE, N. L., TURNER, S. D., YANG, H., GOLDSMITH, B., LOSADA, S., BARBER, J. L. & HARRAD, S. 2016. Hexabromocyclododecanes, polybrominated diphenyl ethers, and polychlorinated biphenyls in radiometrically dated sediment cores from English lakes, ~1950–present. *Science of The Total Environment*, 541, 721-728.
- ZAJĄCZKOWSKI, M. 2008. Sediment supply and fluxes in glacial and outwashed fjords, Kongsfjorden and Adventfjorden, Svalbard. *Polish Polar Research*, 29, 59-72.
- ZEGERS, B. N., LEWIS, W. E., BOOIJ, K., SMITTENBERG, R. H., BOER, W., DE BOER, J. & BOON, J. P. 2003. Levels of Polybrominated Diphenyl Ether Flame Retardants in Sediment Cores from Western Europe. *Environmental Science & Technology*, 37, 3803-3807.
- ZHAO, S., ROGERS, M. J., DING, C. & HE, J. 2018. Reductive Debromination of Polybrominated Diphenyl Ethers - Microbes, Processes and Dehalogenases. *Frontiers in Microbiology*.
- ZHOU, C., PAGANO, J., MCGOLDRICK, D. J., CHEN, D., CRIMMINS, B. S., HOPKE, P. K., MILLIGAN, M. S., MURPHY, E. W. & HOLSEN, T. M. 2019. Legacy Polybrominated Diphenyl Ethers (PBDEs) Trends in Top Predator Fish of the Laurentian Great Lakes (GL) from 1979 to 2016: Will Concentrations Continue to Decrease? *Environmental Science & Technology*, 53, 6650-6659.
- ZHU, C., LI, Y., WANG, P., CHEN, Z., REN, D., SSEBUGERE, P., ZHANG, Q. & JIANG, G. 2015. Polychlorinated biphenyls (PCBs) and polybrominated biphenyl ethers (PBDEs) in environmental samples from Ny-Ålesund and London Island, Svalbard, the Arctic. *Chemosphere*, 126, 40-46.
- ZHU, L. Y. & HITES, R. A. 2005. Brominated Flame Retardants in Sediment Cores from Lakes Michigan and Erie. *Environmental Science & Technology*, 39, 3488-3494.

Estratto per riassunto della tesi di dottorato

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Dottorato: Polar Sciences

Ciclo: 36

Titolo della tesi: Temporal dynamics of anthropogenic contaminants in sediments of the Kongsfjorden-Krossfjorden system (Svalbard, Norway)

Abstract: Four marine sediment cores have been analyzed and collected from the Kongsfjorden-Krossfjorden system (Svalbard, Norway) to assess the occurrence and temporal trends of selected legacy and emerging contaminants. Two sampling campaigns were conducted: one in 2011, yielding a single core (NYA11_09); and another in 2021, collecting three cores (NYA21_01, NYA21_03 and NYA21_04). The targeted emerging contaminants, including seven organic UV Filters (UV-Fs) and six synthetic fragrances (SFs), analyzed in the 2011 core. Additionally, thirty-eight polybrominated diphenyl ethers (PBDEs), classified as legacy contaminants, were analyzed in the 2021 cores. Radiocarbon (^{14}C) and ^{210}Pb age-depth models were constructed to evaluate the historical deposition of these contaminants. Among the UV-Fs detected were: 4-MBC (Enzacamene), EHMC (Octinoxate), EHS (Octisalate) and HMS (Homosalate). Detected SFs included: HHCB (Galaxolide), AHTN (Tonalide) and OTNE (Iso-E Super). Among emerging contaminants, EHMC and OTNE were the most abundant compounds. Among PBDEs, penta- and hepta-BDEs were the dominant PBDE homologues across all cores. Historical trends revealed patterns that align with the production and usage trends of the studied contaminants.

Sono state prelevate ed analizzate quattro carote di sedimento marino dal sistema Kongsfjorden-Krossfjorden (Svalbard, Norvegia) per valutare la presenza e le tendenze temporali di alcuni contaminanti normati ed emergenti. Sono state condotte due campagne di campionamento: una nel 2011, che ha prodotto un'unica carota (NYA11_09); e un'altra nel 2021, con il prelievo di tre carote (NYA21_01, NYA21_03 e NYA21_04). I contaminanti emergenti mirati, tra cui sette filtri UV organici (UV-F) e sei fragranze sintetiche (SF), sono stati analizzati nella carota del 2011. Mentre, nei carotaggi del 2021 sono stati analizzati trentotto polibromo difenil eteri (PBDE), classificati come contaminanti normati. Sono stati costruiti modelli di età-profondità al radiocarbonio (^{14}C) e ^{210}Pb per valutare la deposizione storica di questi contaminanti. Tra gli UV-F rilevati vi sono: 4-MBC (Enzacamene), EHMC (Octinoxate), EHS (Octisalate) e HMS (Homosalate). Gli SF rilevati comprendono: HHCB (Galaxolide), AHTN (Tonalide) e OTNE (Iso-E Super). Tra i contaminanti emergenti, EHMC e OTNE erano i composti più abbondanti. Tra i PBDE, i penta- ed epta-BDE sono stati gli omologhi PBDE dominanti in tutte le carote. Le tendenze storiche hanno rivelato pattern in linea con la produzione e l'utilizzo dei contaminanti studiati.

Firma dello studente

