Master's thesis

NTNU
Norwegian University of Science and Technology
Faculty of Natural Sciences
Department of Chemistry

Mathilde K. Syvertsen

Long-range transport of pollutants to arctic areas by seabirds

Master's thesis in Environmental toxicology and chemistry
Supervisor: Øyvind Mikkelsen
June 2022

Nicola Messinger

NTNU
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Abstract

The aim of this project was to identify pollution in the arctic and to link this pollution to birds in the area. Soil samples were taken from different locations in Kongsfjorden: Ossian Sars, Botnfjell, Storholmen, Innerholmen, Irgensfjell and Leirholmen. All locations are known nesting sites for different species of migratory birds. Additionally, guano samples were taken from Innerholmen and Storholmen. The locations were divided into two groups: high bird-influence and low bird-influence. This separation was based on the phosphorus concentration in the soil from the different locations. Ossian Sars and Botnfjell in the high bird-influenced group, and Storholmen, Innerholmen, Irgensfjell and Leirholmen in the low bird-influenced group. The element concentration of Cd, Cu, Sb, Sr and Zn were found to be significantly higher in the high bird-influenced group than the low. This is a clear indication that the elements Cd, Cu, Sb, Sr and Zn are being enriched in soil influenced by birds. Seven different PCBs were also analysed for in the soil and guano, but all detected analytes were under LOD. Of the 31 PFAS also analysed for, only three were detected and only in a few of the samples. There is no indication from this project that PCBs or PFAS are being long-range transported to the arctic by seabirds.

Sammendrag

Målet i denne oppgaven er å identifisere miljøgifter i arktisk og se om disse har noen sammenheng med fugler i området. Det ble tatt jordprøver fra forskjellige lokasjoner i Kongsfjorden: Ossian Sars, Botnfjell, Storholmen, Innerholmen, Irgensfjell og Leiholmen. Alle disse lokasjonene er kjente hekkeplasser for forskjellige fuglearter. I tillegg ble det tatt guano prøver fra fugleholmene Innerholmen og Storholmen. Lokasjonene ble oppdelt i to grupper: høy fuglepåvirkning og lav fuglepåvirkning. Denne separasjoner er gjort basert på fosfor konsentrasjonen i jordprøvene fra de forskjellige lokasjonene. Ossian Sars og Botnfjell ble plassert i grupppa med høy fuglepåvirkning, mens Storholmen, Innerholmen, Irgensfjell og Leirholmen ble plassert i gruppa med lav fuglepåvirkning. Konsentrasjonen av elementene Cd, Cu, Sb, Sr og Zn var signifikant høyere i gruppa med høy fuglepåvirkning i forhold til gruppa med lav fuglepåvirkning. Dette er en klar indikasjon på at elementene Cd, Cu, Sb, Sr og Zn er beriket i jord som er påvirket av fugl. Syv forskjellige PCBer ble også analysert for i jord og guano, men alle detekterte analytter var under LOD. Av de 31 PFASene som det ble analysert for ble tre av de detektert, og kun i noen av prøvene. I denne oppgaven er det ingen indikasjon på at verken PCBer eller PFASer blir langtransportert til arktiske områder av sjøfugl.

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I also appreciate the financial support from Arctic Field Grant for my fieldwork at Ny-Ålesund.

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Glossary

4:2FTS 1H,2H-Perfluorohexansulfonate. 45, 62

Al Aluminium. 58

As Arsenic. 6, 17, 18, 53, 65

ASE accelerated solvent extraction. 31, 32

B Boron. 58

Ba Barium. 40, 53, 58

Ca Calcium. 14

Cd Cadmium. 1, 2, 6, 17, 18, 50, 65

Co Cobolt. 17, 53, 58, 65

Cr Chromium. 58

Cu Copper. 6, 12, 17, 18, 31, 51, 65

DDE Dichlorodiphenyltrichloroethane. 9

DDT dichlorodiphenyltrichloroethane. 6, 9

EI electron impact ionization. 35

EPA U.S. Environmental Protection Agency. 10

Fe Iron. 6, 58

GC Gas Chromatography. 19–21

HCB hexachlorobenzene. 17

Hg Mercury. 6, 11, 18, 40, 58

HPLC high-performance liquid chromatography. 20

ICP-MS Inductively coupled plasma mass spectrometry. 18, 30

IS internal standard. 21–23

K Potassium. 14, 18, 53, 65

LC liquid chromatography. 20

Li Lithium. 17, 65

LOD limit of detection. 18, 22, 45, 58, 62, 65

LOQ limit of quantification. 22, 45

MeFOSAA 2-(N-methyl)Perfluoro-1-octansulfonamido. 45, 62

Mg Mangnesium. 58

Mn Manganese. 6, 12, 17, 53, 65

Mo Molybdenum. 17, 65

MS Mass Spectrometry. 19, 20

N nitrogen. 1, 14, 17

Na Sodium. 58

Ni Nickel. 6, 17, 18, 53, 65

P phosphorus. 1, 14, 17, 18, 47, 49, 65

PAHs Polycyclic aromatic hydrocarbons. 6

Pb Lead. 40, 90

PCA principle component analysis. 58, 65

PCBs Polychlorinated biphenyls. 2, 9–11, 13, 17, 62

PFAS Per- and polyfluoroalkyl substances. 2, 11, 12, 39, 45, 62, 65

PFHpA Perfluoroheptanoic acid. 45, 62

PFOA Perfluorooctanoic acid. 11

PFOS perfluorooctane sulfonic acid. 11, 12, 62

POPs Peristent organic pollutants. 8–10, 13, 16, 17

S Sulfur. 58

Sb Antimony. 17, 51, 53, 65

Se Selenium. 12

Si Silicon. 54

SIM selected ion monitor. 35

Sr Strontium. 18, 53, 65

TOC total organic carbon. 58

UNEP United Nations Environment Programme. 9

UPLC Ultra high-performance chromatography. 20, 21

Zn zinc. 12, 18, 51, 65

1 Introduction

The Arctic is known to be a remote area with little or no anthropogenic activity, and therefore less polluted than areas in more populated or central areas. However, arctic areas can be polluted as well, due to long-range transport of pollutants. Long-range transport of pollutants through the atmosphere and the ocean currents are well known mechanisms for long-range transport and are considered the greatest form for long-range transport globally. [1] It is however also known that biovectors, like, fish, whales and seabirds, can contribute to long-range transport of pollutants. Fish which travel up rivers to freshwater to breed after feeding in the ocean will transport both nutrients and pollution from the ocean to the freshwater system [2]. The transport of pollutants through biovectors are generally considered to be smaller than through the atmosphere and the ocean, but in small areas where there is an accumulation of deposits from fish or birds this can be a considerable pollution source. [2, 3]

Seabirds are an important biovector of nutrients from the marine environment to the terrestrial environment. [4–7] The birds transfer inorganic and organic matter by feeding in the ocean before they travel back to the terrestrial environment and excrete guano and deposit feathers, eggshell, carcasses and other materials. This biovector is even more important in the arctic environment which is generally low in nutrients like phosphorus (P) and nitrogen (N) which are needed for vegetation to grow. Unfortunately, the seabird does not only transport nutrients, but they also take with them different pollutants as well. In areas influenced by seabirds an enrichment has been observed of the toxic element Cd and organic pollutants like the PCBs. [4–8]

Arctic seabirds are top predators and will therefore be a good indicator for bioaccumulation and biomagnification in the environment. [7] It also means that they have the potential to give away a greater portion of nutrients and pollutants to the terrestrial environment during breeding. Most birds at Svalbard are also migratory birds. They feed at lower latitudes in the winter, and breed in the arctic during summer. Areas in lower latitudes, closer to anthropogenic sources are usually more polluted than the arctic areas. [1, 3, 9–11]

It is hypothesised that the terrestrial environment around breeding sites for migratory seabirds in Kongsfjorden, Ny-Ålesund, are influenced by the birds. The influence is

believed to be shown in increased concentration in nutrients, organic material and pollutants like PCBs, PFAS and some potential toxic elements. The aim of this project is to identify pollutants like Cd, PCBs and PFAS, and to link this pollution to birds.

2 Theoretical background

2.1 Soil

Soil is a mixture of water, minerals, gases, organisms, organic and inorganic matter. The combination of different substances in a soil varies largely with the type of soil. Typical solids in soils contain mostly inorganic substances, and that is because soil is mainly a product of weathering of rocks. However, some types of soil contain more organic matter. Soil will therefore exhibit large differences in characteristics due to large differences in composition. The organic matter in soil, even if it is a small fraction of the soil, plays a large role in the physical, chemical and biological characteristics of the soil. For example, most of the water is held by the organic matter in the soil, and different organic substances like some pesticides will have strong affinity to the organic matter. Therefore, it is important to know the soil composition when investigating soil. [12].

2.1.1 Pedogenesis

Pedogenesis or soil formation is a continuous process which gradually breaks down rocks to soil through weathering. There are three main types of weathering: physical, chemical and biological. Physical weathering is a result of mechanical action like temperature changes, earth quakes, wind erosion or colliding rocks. Chemical weathering is when minerals in rock react with and break down the rock. This can for example happen when rocks are in contact with water or air. Biological weathering is the breakdown of rocks by living organisms. Plants can for example grow roots into cracks of rocks which breaks the rock into pieces. There are five main interactions affecting soil formation: parent material, living organisms, climate, topography and time. Different interactions between these five factors can make an infinite variety of soils. [13–15]

2.1.2 Soil horizons

Soils typically are composed of different layers, known as horizons. These horizons are made from different processes in the soil such as weathering, soil formation and different biological processes. The different layers have different composition and characteristics. [12, 13] The different layers are:

- O: This horizon is typically exposed to the land surface. It contains organic decaying and decayed organic materials [12, 13].
- A: Topsoil which has a high humus content which is rich in nutrients. The biological activity is highest in this layer and is often darker because of the high organic material content [12, 13, 16].
- E: This horizon has lower levels of clay, minerals and organic matter. The layer consists mostly of sand and silt [12, 16].
- B: Have high content of clay and minerals which have leached from horizon A and E. This horizon has more moisture than the A horizon but has less biological activity [14, 16].
- C: This horizon is the weathered parent rock. Contains little or no soil [12, 13].
- R: Also known as Bedrock, the R horizon is located under the C horizon and is not soil [16].

All the soil horizons together make the soil profile. All types of soil do not necessarily have all the soil horizons, but most soils exhibit the horizons A, B and C. [14]

2.2 Svalbard

The archipelago of Svalbard is in the Arctic Ocean at $74 - 81^{\circ}$ north. Spitsbergen is the largest island and all the settlements Longyearbyen, Ny-Ålesund, Barentsburg and Pyramiden are located on Spitsbergen. The population at Svalbard is 2940, and most of Svalbard's area is covered in glaciers and mountains. The average temperature during a year in Longyearbyen is between $-8^{\circ}C$ and $-2^{\circ}C$, and the precipitation is low. However, the climate on Svalbard is changing to become warmer and more humid, which is made visible by thawing permafrost and decreasing glaciers. [17, 18]

2.2.1 Ny-Ålesund

Ny-Ålesund is the world's northernmost settlement and is situated on Svalbard at 79° north. The settlement is located in Kongsfjorden, on the north-west coast of Spitsbergen. From 1917 to 1962 Ny-Ålesund was a coal mining settlement driven by Kings Bay Coal Company. In 1962 there was an explosion in one of the mines which killed 21 persons. This was the end of the mining industry at Ny-Ålesund. However, there are still remaining buildings and other constructions present after the mining. Today Ny-Ålesund is the centre for natural science research and environmental monitoring on Svalbard. The international research station infrastructure is driven by Kings Bay AS, and during the whole year there are about 30 people living at the settlement to serve the station. In summer during fieldwork season more than 100 scientists visit the settlement. [19, 20] In Figure 1 a map of Svalbard can be seen. The location of Ny-Ålesund is indicated with a red rectangle.

Figure 1: Map of Svalbard, Bjørnøya is not included. The red rectangle shows where at Svalbard Ny-Ålesund and Kongsfjorden are located. Illustration made in TopoSvalbard [21], Norwegian Polar institute.

2.2.2 Characteristics of arctic soil

Arctic soil profile differs from soil in the southerly parts of the world. As mentioned in Section 2.1.1, climate is one of the main factors affecting soil formation. The physical and biological processes are generally slow in the arctic because of the low temperatures. The arctic soil horizons are poorly differentiated, the soil profiles are shallow, and the organic carbon content is usually between 0 to 10 %. [22]

Plant growth is very slow in the terrestrial arctic environment due to the low temperature, low moisture, a short growing season, low nutrient availability and cryoturbation (disturbance by the processes in the soil due to permafrost) [23]. This is a contrast to the high production in the marine environment due to the vertical mixing in the ocean. The terrestrial environment can benefit from the nutrient-rich sea, given that there is a vector for transporting the nutrients from sea to land. Seabirds are an important biovector from sea to land, because they feed at sea and breed at land. In the summer, during their reproductive period, seabirds deposit guano, feathers, eggshell, dead birds and chicks. An accumulation of deposits from seabirds underneath bird cliffs will happen, and the soil is often more productive in these areas because of the increase in nutrients. [24, 25] Unfortunately the seabirds do not just bring nutrients, but also contaminants [25]. Studies have shown that surface sediments of high arctic lakes and arctic lake ecosystems influenced by seabirds have increased amounts of contaminants like DDT and Hg [6, 25].

Long-range transport of pollutants, described in Section 2.3 is not the only source for pollution in the arctic. There are some local sources, for example from the old mining areas, settlements, abandoned settlements and airports in the arctic. The mining areas can have increased concentrations of elements Fe, Mn, Cu, Cd, As, Ni and Hg, and from both unburnt and burnt coal there can be large amounts of PAHs which can be transferred to soil by coal dust. [26] Most settlements on Svalbard does not have any sewage treatment plant, and release of untreated sewage is one of the largest unregulated sources for pollution in the arctic. [26]

2.3 Long-range transport of pollutants

There are many sources of pollutants, both anthropogenic sources and natural sources. There are different routes for the pollution to the ecosystem and some of these have

the potential for long-range transport. [1] Pollution present in surface water either in a solution or in suspension can travel with the river for several miles, if it does not get precipitated and fall to the bottom of the lake. The pollution can enter the ocean currents and be transported from continent to continent through the deep water circulation. The density of the surface water can increase due to decrease in temperature or increase in salinity. When this happens the surface water will move towards the bottom of the ocean and become a part of the deep water circulation. [1] The transport of pollutants is illustrated in Figure 2.

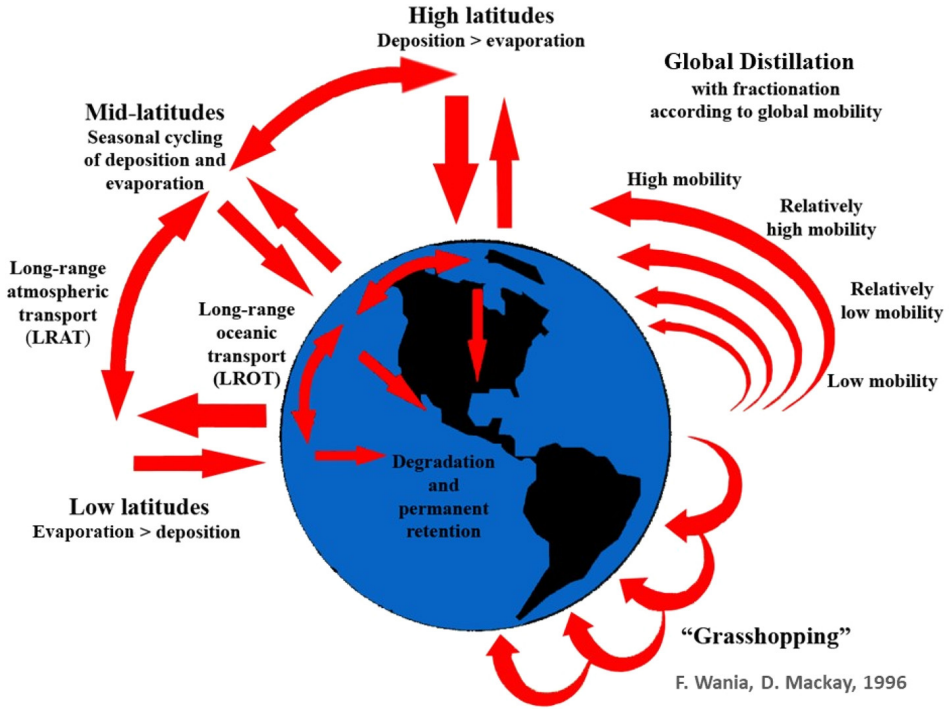

Figure 2: Illustration of how pollutant can be transported from low latitudes to mid- and high latitudes with global distillation or "grasshopping". How far the pollutants travel depends on the mobility of the specific compound which depend on the volatility of the compound. The arrows in the ocean also illustrate the long-range transport of pollutants with the ocean. Reprinted with permission from [27] American Chemical Society.

Pollution can also be transported through the air. Air pollutants in gaseous form can be transported through diffusion. They can also be associated with droplets or particles in the air. Atmospheric deposition of these droplets or particles is considered to be an important removal process of pollutants in the atmosphere. Atmospheric deposition can be divided into wet and dry deposition, where wet deposition is associated with droplets

and dry deposition is associated with particles. Soluble gases like SO_2 and NO_x can be dissolved in the rain droplets and transported long distance with the clouds. Raindrops may also bring with them dust particles that are present in the air. [1] Metals and metalloids are usually transported with the atmosphere as particles. There are many different anthropogenic sources for metals in the atmosphere, such as motor vehicles, coal burning, bonfires or industrial emissions. Deposition of metals and metalloids to the soil is low since the emission in the air is diluted in the large air masses, but the deposition process continues for a long time. Therefore, contamination of surface soil by atmospheric deposition can be significant. [28]

Semi-volatile compounds can be vaporised in warm regions and travel in the atmosphere to colder regions where they condensate. This process is called global distillation and describes how semi-volatile compounds can be transported from lower latitudes to higher latitudes. The global distillation is illustrated in Figure 2. Compounds with higher volatilities can be transported to higher latitudes. That is why there can be found high concentrations of, for example, organochlorine compounds, far away from any source. [29]

This way of long-range transport of pollutants are greatly influenced by the distribution of the pollutants in the environmental compartments. The distribution of the pollutants in the environment are important to predict the fate of the specific pollutant. K_{OA} describes the distribution between octanol and air in an equilibrium and are useful to predict the distribution of organic compounds between air and environmental matrixes like soil and vegetation. [30] K_{OW} is another distribution coefficient describing the distribution between octanol and water. This coefficient has a high value for chemicals of low polarity, and low value for chemicals of high polarity. The K_{OW} is used to predict hydrophobicity, the distribution in the environment and the bioconcentration potential of a chemical. [1]

2.4 Persistent organic pollutants

Peristent organic pollutants also called POPs are organic pollutants which have toxic properties. POPs persistent against degradation, bioaccumulates and are long-range transported [31]. The qualities that POPs have, together with releases to the environment mainly from human activities, have allowed them to be distributed all over the globe [32]. The POPs are persistent and can therefore be transported over long

distances without being degraded. These organic pollutants are also semi-volatile and have great ability to be long-range transported through the atmosphere, as described more in Section 2.3. Many of the POPs can for this reason be found all over the globe, including Arctic and Antarctic. [33]

POPs have a long half-life in substances as soil, sediment and biota, and this makes them persistent in the environment [33]. Typically, the POPs are hydrophobic and lipophilic. Which means that they get attracted to organic matter like soil and sediment. They will also be taken up with the lipids in the biota and be stored in the fatty tissue. Since the POPs do not metabolise easily, they will bioaccumulate in the organism, and have the potential to biomagnify up the food chain. [33] Which means that organisms in a higher trophic level often have a higher concentration of POPs than organisms in a lower trophic level.

There are many different POPs, and both individually and in mixtures they can do harm to the environment. The effects of POPs on the top predators are of most concern since they are the species with the highest concentration. [33] POPs have shown the potential to affect the neurological, reproductive, developmental, endocrine and immunologic system of humans and other animals [11]. Dichlorodiphenyltrichloroethane (DDE) induced eggshell thinning is a well-studied harmful effect on several different bird species, and affects the reproduction of for example the American kestrel [34, 35].

The physical and chemical properties that the POPs possess makes them available almost everywhere on the globe and very hard to get rid of [33]. In top predators the POPs can be found in such high concentration that the animals can exhibit a harmful effect [36]. Even though POPs like dichlorodiphenyltrichloroethane (DDT) and Polychlorinated biphenyls (PCBs) have been studied for many years, their harmful effect on every species is not yet fully understood. The mixture effect of new and old POPs is also unknown, and new POPs released to the environment can be a huge stress for the biota. There is a need for further studies on mixture effects of the POPs. [37,38]

The Stockholm convention is a global treaty to protect the environment and humans from the POPs. The potential for long-range transport of these chemicals makes it impossible for one government to protect their own citizens and environment alone. That is why the Stockholm convention on Peristent organic pollutants was made. All participants in the convention are required to eliminate or reduce the release of POPs to the environment. [39] The convention was adopted in 2001 by the United Nations Environment Programme (UNEP) and entered into force in 2004 [40]. Originally there

were 12 POPs which were regulated by the Stockholm convention. Polychlorinated biphenyls are one of these 12 POPs [41]. As POPs get restricted there are always coming new chemicals to take over, and some of them fit the POP category. Therefore, new POPs have been added to the Stockholm convention after the 12 original, and new are proposed to be added. [42, 43]

2.4.1 Polychlorinated biphenyls

Polychlorinated biphenyls are a group of organic chlorinated compounds and are one of the original 12 POPs in the Stockholm convention [44]. In total there are 209 possible congeners of the PCBs with different degrees of chlorination and different position of the chlorine atoms. They are stable, unreactive, non-flammable, have low volatility and low solubility in water. PCBs have been used for many purposes because of their useful properties. They have been used for insulation fluids, coolants, plasticizers in paints and much more. [1] The PCBs were first commercially manufactured in 1929. In 1966 the first mention of PCBs in the environment was published in New Scientist which is a British science magazine. After this there have been many published articles about the problems with PCBs. In 1979 the production of PCBs was banned by EPA in the USA, but it was still produced in Europe and Asia. [45] In 2004 the Stockholm convention entered into force and PCBs was banned. Participants in the convention must also stop using all equipment that contain or are contaminated with PCBs by 2025. [39, 44]

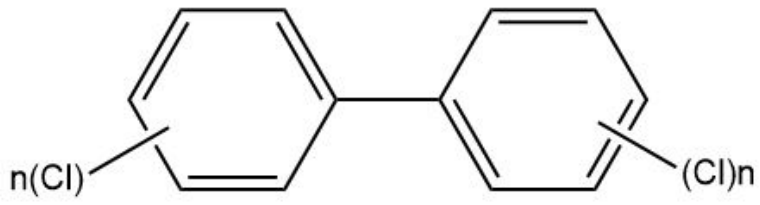

Figure 3: The general structure of PCB. The properties of the PCB is dependant on the number of Cl atoms replacing the H atoms on the benzene ring, and the location of the Cl atoms.

PCBs was mostly produced in the middle latitudes, but because of global distillation

(explained in Section 2.3) high concentrations can be found in high latitudes, for example in the Arctic. [46] The PCBs have the potential to biomagnify up the food chain, and top predators like the polar bears can have significantly high concentrations of this contaminant. PCBs, together with Hg, are suspected to be the main contributor to the immunological, reproductive and carcinogenic effects of polar bears during the years 1983-2013 [36].

The mixture of different PCBs has shown to affect the environment in different ways. American kestrels exposed to PCBs in their diet have shown to have a lower baseline level and corticosterone response than birds without this dietary intake of PCBs [47] Even low "background" levels of PCBs have been shown to affect humans. [48, 49] Prenatal exposure of PCBs have shown to affect the immunology and give a higher susceptibility to diseases like middle-ear infection to children [49].

2.4.2 Per- and polyfluoroalkyl substanses

Per- and polyfluoroalkyl substances (PFAS) is a large group of aliphatic fluorinated compounds. The C-F bond is very strong and stable which makes the PFAS persistent. [50] The fluorinated tail is hydrophobic while the functional group is hydrophilic, and these properties make them very useful as protective coating for paper and textiles [51]. Because of their practical functionalities the PFAS have been used a lot in industrial and commercial products, and these compounds are therefore to be found everywhere in the global environment. [50] The two most known PFASs are the Perfluorooctanoic acid (PFOA) and the perfluorooctane sulfonic acid (PFOS) and they are both listed under the Stockholm convention together with their salts. The chemical structure of PFOS can be seen in Figure 4.

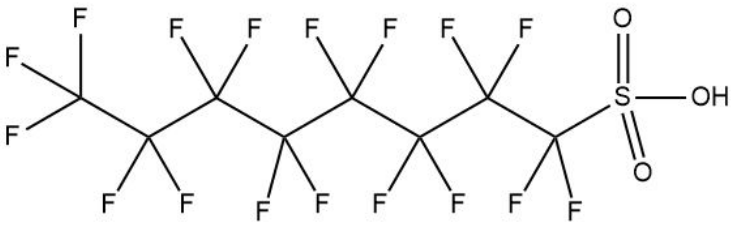

Figure 4: The chemical structure of PFOS.

The persistence of PFAS has led to their ubiquitous presence in the environment all over

the world. The length of the PFAS, and which functional group they possess decides the physical characteristics of the specific PFAS. Several of the PFAS have been shown to be long-range transported by the ocean currents or the atmosphere. [52] They have also been shown to accumulate up the food chain and to bind to phospholipids and proteins. Most top predators in the arctic has therefore detectable concentrations of different PFAS in their liver, kidney and blood. [52, 53]

It has been shown that different PFAS can disrupt the homeostatic processes in the body which affects every system in the body. [54] In a laboratory study they found that in utero exposure of PFOS, decreased the survival of neonatal rats and mice [55]. However, it is indicated that the reported effects of PFAS are unlikely to occur in the environment. Lack of knowledge of new PFAS and their mixture toxicity are still incomplete, and the risk of chronic effects must be investigated further. [56]

2.5 Toxic elements

Several of the elements are essential, like Zn, Cu, Mn and Se. They can be deficient in agricultural soil, which can affect productivity in agricultural soil and be deficient in crops which can affect human health. In high concentration on the other hand can they act as toxic elements. [28] Selenium (Se) for example is an essential micronutrient but are also toxic at relatively low intakes. Se toxicity in humans can be shown as hair and nail loss or dental, skin or nervous system disorder. Se toxicity is however less usual than Se deficiency in humans. [28] Hg, Cd and Pb are three elements which do not have any known biological function, and are called non-essential elements. All three elements are toxic at relatively low concentrations. [28]

Toxic elements both have natural and anthropogenic sources to the environment. Wind erosion, volcanoes, wild forest fires and sea salt spray are some natural sources of trace elements to the atmosphere. Some anthropogenic sources to the environment are fuel combustion, waste incineration, fertilizer production and mining and smelting activities. [28,57] The parent material is a great contributor to the toxic element concentration in soil, but the contribution from anthropogenic sources are still large. Anthropogenic affected soil has shown 32 times higher Cd concentration, and 10 times higher concentration for Cu and Pb. [28]

Toxic elements such as Pb, Hg and As are elements and can not be destroyed or bro-

ken down any further in the environment. They are therefore persistent. [58] Not all elements are known to have the potential to bioaccumulate, and the potential for elements to bioaccumulate is highly dependent on the speciation of the element. For an element to bioaccumulate it must be bioavailable. [28, 59] MeHg is an example of an Hg species which have a high potential to bioaccumulate, while Me_2Hg does not have this potential [60].

2.6 Biovectors

A biovector is usually referred to as substances, like contaminants and nutrients, carried by organisms, transported and then released as a part of a distribution process [3]. Pacific salmon for example accumulate more than 95 % of their biomass in the ocean before they go up to fresh waters where they spawn and die. The salmon is one of the top predators in their food web and accumulates POPs. When the salmon dies, they release the biomass gathered in the ocean containing the nutrients, but also the contaminants that the ocean has given them. It has been shown that freshwater lakes where the pacific spawn and die have an increased concentration of PCBs. [2] Whales as a biovector is not studied broadly, but one single whale has such a large biomass so when one individual dies the local system can be widely affected. The humpback whale, *Megaptera novaeangliae*, for example migrates over long distances each year between their feeding and breeding grounds, and they can therefore gather a lot of different contaminants over this large distance [2, 61]. Arctic seabirds are a group of animals which migrate over long distances and can work as a biovector. This biovector will be discussed further later on. An illustration of how both the biota and the atmosphere can transport materials and deposit them in different compartments of the environment are shown in Figure 5.

The long-range transport from biovectors is generally considered to be smaller than the abiotic pathways like atmospheric transport and ocean currents, described in Section 2.3. At a global scale the mass per day transported by biota will be less significant than the mass transport by the abiotic pathways. However, for specific areas where migratory species concentrate after a period of dispersal, mass transport by biovectors will be more significant. [2,3] A contaminant has to be lipid soluble and bioaccumulate in an organism for the biovector pathway to be significantly larger than the abiotic pathways [2, 62].

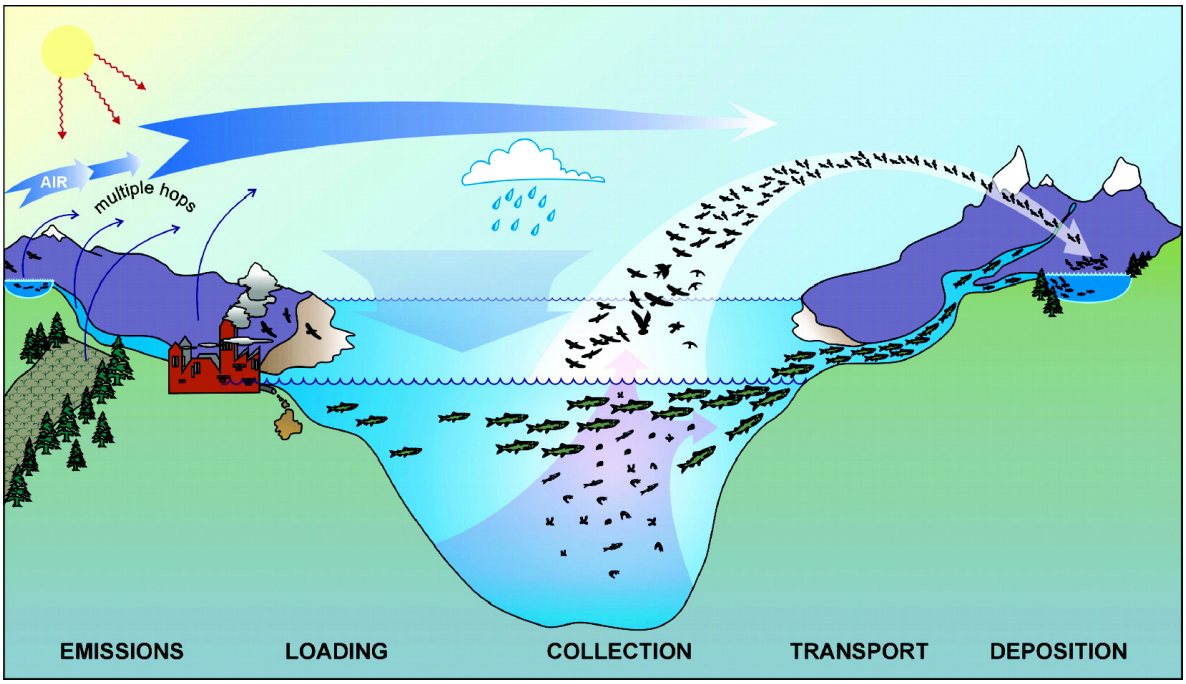

Figure 5: Illustration of how anthropogenic pollutants can be loaded in the air and water. The pollutants can be collected by fish and birds and be transported long distances. The fish can travel up rivers and by that way transport the pollutants from the ocean to fresh waters. While the birds can feed on the fish in the ocean and bioaccumulate the pollutants in their body. Migratory birds can transport these pollutants over great distances before they deposit them in the form of guano, eggshell or similar. Printed with permission from [2] American Chemical Society.

2.6.1 Seabirds as a biovector

Several studies have shown that the bio transport of nutrients by seabirds is an important factor for the productivity and diversity of the soil nearby seabird colonies in the Arctic and Antartica [4–7]. The transportation of both organic and inorganic matter from ocean to terrestrial areas are crucial in areas like the arctic, which usually has a deficiency in nutrients like phosphorus (P), nitrogen (N), Potassium (K) and Calcium (Ca). [4] The impact seabirds have on the terrestrial environment depends on the size of the colony, the body size of the bird, the diet of the bird and the behaviour of the bird. Piscivore birds, which feed on fish, will be in a higher trophic level than planktivorous birds which feed on plankton. Birds feeding on fish will have a higher concentration of nutrients than planktivory, but they will also have a higher content of pollution. [4–6]

The diets of the different species of birds are an important factor in which amounts of pollution they transfer to the soil through their excrement. Black-legged kittiwakes, *Rissa tridactyla*, feed mainly on invertebrates and small fish (15-20cm in length) like capelin and polar cod. Brünnich guillemots, *Uria lomvia*, feeds mainly on fish and crustaceans like capelin, polar cod and blennies. Common Eiders, *Somateria mollissima*, feed mainly on small benthic organisms such as mussels, clams and amphipods. Barnacle goose, *Branta leucopsis*, feeds on a wide variety of plants like roots, mosses, grasses and sedges. [9, 63] These bird species can be organised from highest to lowest trophic level as following: Black-legged kittiwake, Brünnich guillemots, Common Eiders and Barnacle Geese [8, 9, 64]. All the bird species mentioned above are abundant at Svalbard and are breeding in Kongsfjorden at the location studied in this project. Pictures of the Barnacle goose, Black-legged kittiwake, Common eider and Brünnich guillemots are found in Found in Figure 6, 7 and 8.

Figure 6: The Barnacle goose. Credit: Christina Moen Larsen

Most of the birds at Svalbard are migratory birds and are only present at Svalbard from spring to autumn. These birds take advantage of the large food supply present in the arctic ocean at this time of year by breeding in the Arctic. [9] Migratory birds does not only reflect the pollution input from the area they breed, but also from their

Figure 7: The Black-legged kittiwake. Credit: Christina Moen Larsen

migratory routes [65]. Arctic areas are generally less polluted than areas at lower latitudes, where migratory birds feed during winter. During breeding some seabirds stop feeding, and they can decrease the concentration of contaminants stored in their fat storage by converting the stored lipid into energy in the blood. [9, 10] When lipids are converted to energy, POPs which are associated with lipids will be released to the blood. POPs in the blood can possibly also be excreted through guano. When birds stop feeding, they will also excrete less guano as well. However, this might be a way of accumulating pollution from lower latitudes to the Arctic by long-range transport by migratory seabirds. [1, 3, 9, 10]

The migratory seabirds might also be a source of food for some of the animals which live in the Arctic for the whole year [2]. For example: eggs and small chicks from the Common Eider are subject to strong predation, mainly from glaucous gulls and arctic foxes [63]. In that way the pollutants can enter the food chain and bioaccumulate in the top predators. The arctic ecosystem is possibly also more vulnerable for stress caused by increased contamination because of less diversity and more extreme climatic variations than temperate and tropical ecosystems [2].

Figure 8: The Common eider. Credit: Christina Moen Larsen

2.7 Compounds accumulated by seabirds

Many studies show that migratory seabirds enrich the terrestrial environment with nutrients [4,7,24,66,67]. Ziołek et al found that P concentrations were highest underneath bird cliffs in soil from Bellsund coast in western Spitsbergen. Indicating that seabirds have a crucial role in the P content in arctic soil. [68] Both nitrogen (N) and phosphorus (P) will be enriched in ornithogenic soil. However, N will often be lost through leaching or volatilisation in the form of ammonia. P on the other hand is not as mobile and will not be lost through leaching. P will often stay in the soil where it was deposited and can persist in the soil for many years. [68, 69] That is why P can be a good indicator for bird-influence in the soil.

The ornithogenic soil will not only be enriched with nutrients [6,8,25]. Kristiansen et al found that the POPs chlordanes, PCBs and HCB were enriched in seabird-influenced soil [8]. Brimble et al (2009) found a close association between nutrients and trace element enrichment in ponds nearby a northern fulmar colony. The trace elements correlating with the ornithogenic gradient was As, Cd, Co, Cu, Li, Mn, Mo, Ni, Sb

and Sr. [70] However, Brimble and al (2010) identified P, Cd, K, Zn and As as seabird-derived elements [71]. Furthermore Ziołek et al found that Cd, Zn and Cu positively correlated with the P concentration in bird-influenced soil [72]. Enrichment of Mercury from seabirds have shown inconsistent results [64, 73, 74]

2.8 Analytical methods

2.8.1 ICP-MS analysis

Inductively coupled plasma mass spectrometry (ICP-MS) was first developed over 30 years ago, but it is just the last decade that the technique has become widely used. Soil analysis with ICP-MS is now widely used. The largest advantages with ICP-MS compared to other atomic spectrometry techniques is the ability to analyse for multiple elements in one analysis and to get LOD up to parts per trillion level. Together with simple sample preparation and short analyse time, this technique can go through a lot of samples in a short amount of time. The disadvantages with ICP-MS are the high cost and the need for staff with a high level of expertise. [28, 75]

ICP-MS has six fundamental compartments: the sample introduction system, inductively coupled plasma (ICP), interface, ion optics, mass analyzer and detector. Firstly, the samples are aerosolized by a nebuliser then the aerosols enter a spray chamber. In the spray chamber the larger aerosols droplets are filtered out before entering the plasma. This is important because the dissociation by the plasma is inefficient with larger droplets. The filtered droplets are transported in a stream of argon gas through the injector and into the plasma. The plasma holds a temperature of 7000-10 000 K and has the energy to ionise most elements. [28, 75] Then the plasma reaches the interface. One of the major challenges while developing ICP-MS was getting the hot, dense plasma into the mass analyzer with a high vacuum environment. The interface solves this challenge. The interface consists of two water-cooled Ni cones, one sample cone and one skimmer cone. The two cones apply vacuum and focus the ions with electrostatic lenses. Located behind the skimmer cone there is a set of electrostatic lenses which is called the ion optics. The purpose of the ion optics is to guide the ion beam towards the mass analyzer and to prevent photons and neutral species from reaching the detector. The mass analyzer is basically a mass filter which separates the ions based on the mass to charge ratio (m/z). One of the most common mass analyzers is the quadruple.

When the appropriate m/z ratio ions reach the detector, the ions are converted into an electrical signal and the electrical signal is detected. [75, 76]

Interference in ICP-MS can happen and can be classified in either spectroscopic interference or non-spectroscopic interference. Spectroscopic interference are when non-analyte ions have the same m/z ratio as the analyte and will therefore interfere with the analyte signal. This can happen in several ways, for example with isobaric elements which are when two elements can form ions with the same mass, or the formation of polyatomic ions which also can have the same m/z ratio as the analyte. Tailing is also a spectroscopic interference and can happen if two analytes have approximately the same m/z ratio and can result in an overlap in the spectrum. A non-spectroscopic interference is matrix effect which can lead to an enhancement or suppression of the analyte signal due to the composition of the matrix. [75]

2.8.2 Accelerated solvent extraction

Accelerated solvent extraction is an automated extraction method that uses organic solvents at temperatures above the boiling point and high pressure. The method are used on solid and semi-solid samples and have the advantages of short extraction time, and less solvent volume compared to several other extraction techniques. [77] Applying pressure, around 1500psi, to the extraction makes it possible for the temperature to be above the boiling point of the solvent [77, 78]. Increased temperature helps the solvent to get in contact with the analytes by disrupting the strong solute-matrix interactions, hydrogen-bonding and by decreasing the viscosity of the solvent and the surface tension. More contact between the solvent and analyte does so that the extraction time can be decreased. [77] The extraction cell, usually in stainless steel, are packed with different layers of resins to retain inferences and to provide a clean extract. Cu powder is usually added to remove sulphur, and alumina is usually added to remove nonpolar lipids and coloured compounds. One of the advantages with ASE is that the clean-up step can be done at the same time as the extraction. [78]

2.8.3 GC-MS analysis

Gas Chromatography (GC) coupled with Mass Spectrometry (MS) is an analytical technique which is very useful to analyse several compounds at low concentrations

in a complex mixture. GC is a separation technique where there is a mobile and a stationary phase. The separation is obtained if the analytes have different distributions between the mobile and the stationary phase. Analytes which are more connected to the stationary phase than the mobile phase will use more time to go through the column and will be separated from the analytes which are more connected to the mobile phase. The mobile phase, also called the carrier gas, is an inert gas often helium, hydrogen or nitrogen. Before the separation can happen, the sample must be introduced to the carrier gas. This can happen through split or splitless injection. The splitless injection introduces the entire sample to the column and is used to analyse for analytes in trace amounts. The samples are vapourised in the column entrance and are separated in the column which is coated with a layer of stationary phase. The column is in a heated compartment, or column oven, to provide a controlled temperature for the separation. It is possible to do the separation with constant temperature, but a temperature gradient separation is the most effective for a sample with a mixture of analytes with large differences in volatility. [79, 80]

The mass spectrometer is an important detector for GC. The principles of MS have been described above, in Section 2.8.1. To use MS as a detector in GC is relatively simple because the mobile phases usually do not interfere, and the samples are already in the gas phase when getting out of the GC. The main problem is the difference in pressure. This has been fixed by putting an interface between the GC and MS. The GC-MS has the advantage that large amounts of compounds can be detected simultaneously in complex mixtures. The MS can also detect non-target compounds in samples. [79, 80]

2.8.4 UPLC-MS/MS analysis

Ultra high-performance chromatography (UPLC) are developed from HPLC which again is developed from the classical column liquid chromatography (LC). The difference between HPLC and LC is mainly smaller particles of the stationary phase in the column and higher pressure on the mobile phase. This makes the HPLC analysis more efficient than the LC. The difference between HPLC and UPLC is basically higher pressure and smaller particles in the stationary phase in UPLC than HPLC. [79, 81, 82] UPLC have pressure up to 1000 bars compared to HPLC with pressure around 300/400 bar. The UPLC is more accurate, faster and have better resolution and sensitivity than the HPLC. [81]

To benefit from the advantages of UPLC it is important to have an appropriate detection method. Tandem mass spectrometry (MS/MS) is one of the spectrometric techniques which is used together with UPLC. [81] The MS/MS is two mass spectrometers combined in series. The MS/MS can be described as "taking the mass spectrum of an ion in a mass spectrum" [83]. This is done to get more information about the molecular structure of the compound. [81]

The largest interference problem in chromatography is compounds coeluting. This happen when two eluting compounds have similar chemical properties and will therefore elute closely in the chromatogram. The resolution of the peak will then be small, and separating the signals will be hard. The easiest way of increasing resolution is to increase the retention. In liquid chromatography this is done by reducing the solvent strength of the mobile phase. However, in GC the retention is easily increased by reducing the temperature. [79]

2.8.5 Analysis of TOC,TIC and ROC

Total organic carbon (TOC), residual organic carbon (ROC) and toal inorganic carbon (TIC) can be quantified by combustion at $400°C$, $600°C$ and $900°C$ in oxygen gas. TOC will be detected with combustion at $400°C$, ROC at $600°C$ and TIC at $900°C$. Carbon dioksid generated by the combustion is led by the oxygen carrier gas through the IR detector. The detector measures the carbon dioksid concentration continuously, and from these concentrations the TOC, ROC and TIC contents of the sample are calculated. [84]

2.9 Quality Control and Quality Assurance

In column chromatography methods, the quantification of the analyte is determined by using the relationship between the concentration and the response of the detector. The peak height or the peak area are used to determine the response of the detector. In this project the internal standard (IS) method was used for quantitation. The calibration standard used in this method is made by spiking blank samples with different, but known, concentrations of the standard analytes and a constant concentration of the internal standard. The calibration curve is then made by plotting the ratio between the analyte signal and the IS signal against the concentration of analyte. This is only

possible if the concentration of IS are the same in the calibration samples and the samples. [79]

Quantification

In column chromatography methods the quantification of the analyte is determined by using the relationship between the concentration and the response of the detector. The peak hight or the peak area are used to determine the response of the detector. The internal standard (IS) method is one way of quantifying the data. To use this method the calibration standards is made by spiking blank samples with different, but known, concentration of the standard analytes and a constant concentration of the internal standard. The calibration curve is then made by plotting the ratio between the analyte signal and the IS signal against the concentration of analyte. This is only possible if the concentration of IS are the same in the calibration samples and the samples. [79]

In order to obtain a reliable quantification a limit of detection (LOD) and a limit of quantification (LOQ) must be determined. The peak height or area normally must be three times higher than the noise to have a reliable detection. To ensure a reliable quantification on the other hand there is needed a peak height or area ten times higher than the noise. [79]

Recovery

During a chemical analysis the samples must go through different preparation steps, and during these steps there will most likely be some loss of analyte. That is why recovery studies are important. The definition of recovery is the relative amount of analyte measured in the final extract compared to the amount of analyte in the original sample. [85] Recovery can be calculated spike samples with known amount of analyte is added post-extraction and pre-extraction. The absolute recovery (R_{abs}) was calculated using this equation:

$$R_{abs}(\%) = \frac{Area_{A;SP} - Area_{A;MB}}{Area_{A;MM} - Area_{A;MB}} \cdot 100\% \quad (1)$$

where $Area_{A;SP}$ is the area of the pre-extraction spiked sample analyte peak, $Area_{A;MB}$ is the area of the analyte in the method blank and $Area_{A,MM}$ is the analyte in the post-extraction spiked sample analyte peak. [86]

When calculating relative recovery, losses during sample preparations and clean-up is considered. The relative recovery is calculated in the same way as the absolute recovery,

but instead of using the analyte response, the relative response is used. The relative response is the ratio between the analyte response and the IS response. [86]

Matrix effect

The matrix is the components of the sample other than the analyte. These components can have considerable effect on the response of an analyte. The change of the response of an analyte caused by coeluting compounds from the matrix is called the matrix effect. [87] The matrix factor (MF) can be calculated like this:

$$MF = \frac{Area_{A;MM} - Area_{A;MB}}{Area_{A;STD}} \tag{2}$$

where $Area_{A;STD}$ is the peak of the analyte in a standard solvent. [86] From the matrix factor it is possible to calculate the matrix effect (ME) like this:

$$ME = (MF - 1) \cdot 100\% \tag{3}$$

The matrix effect can be both positive and negative depending on if the matrix enhances the response or decreases the response of the analyte. [86]

2.10 Statistical methods

Statistical tests

Statistical test is necessary to do to check if there is a significant difference in the data or if there are only random differences. When the data are gathered several studies have to small sample number to have normally distributed data. With non-normally distribute data it can be hard to do statistical test, but there are some non-parametric tests which can test the data even though it is not normally distributed. Man-Witney U test is one non-parametric test which test if two independent groups are homogenous and have the same distribution. The null hypothesis in Man-Witney U says that the two groups are alike, while the alternative hypothesis (H_1) says that the two groups of data are distributed differently. The Man-Witney test can only be used when there is a comparison between two groups. [88] When comparing between several groups, a Kruskal Wallis test can be used. In a Kruskal Wallis test the probability of there being no difference between three or more groups are checked. [89]

Boxplot

The box in the boxplot starts with the first quartile of the data (25%) and ends with the third quartile of the data (75%). The horizontal line in the box represents the median. The whiskers on each side of the box represent the minimum and maximum of the data, excluding the outliers. [90]

Principle component analysis

Principle component analysis is a statistical technique which try to simplify large amount of data. PCA aims to lower the number of dimensions, but at the same time to preserve as much as possible of the variance in the data. PCA uses linear combination of the different variables and parameters to plot them onto principal components (PCs) of lower dimensions. The principal components do not correlate with each other. [91] The different PCs explain different amount of the variance in the data, and this is usually explained in %. Usually there will be made several 2D plots with the different PCs as x- and y-axis, and the first plot is made from PC1 and PC2. The PC1 explain the variance horizontally while the PC2 explain the variance vertically. PC1 explain more of the variance more than the PC2. Which means that the distance between two points horizontally will be a greater difference in the data then the same distance between two points vertically. Data that are similar will group together and make clusters in the plot, and groups of data that are different will cluster in different parts of the plot. [91]

3 Methods and materials

3.1 Sampling

3.1.1 Sampling sites

Soil samples from six different locations in Kongsfjorden were taken during the period between 16.08.21 and 20.08.21. The sampling sites included the bird cliffs at Irgensfjellet on Blomstrandhalvøya, Ossian Sars, and Botnfjellet, and the three islands Storholmen, Leirholmen and Innerholmen. In Figure 9, a map of all the sampling sites in Kongsfjorden is shown.

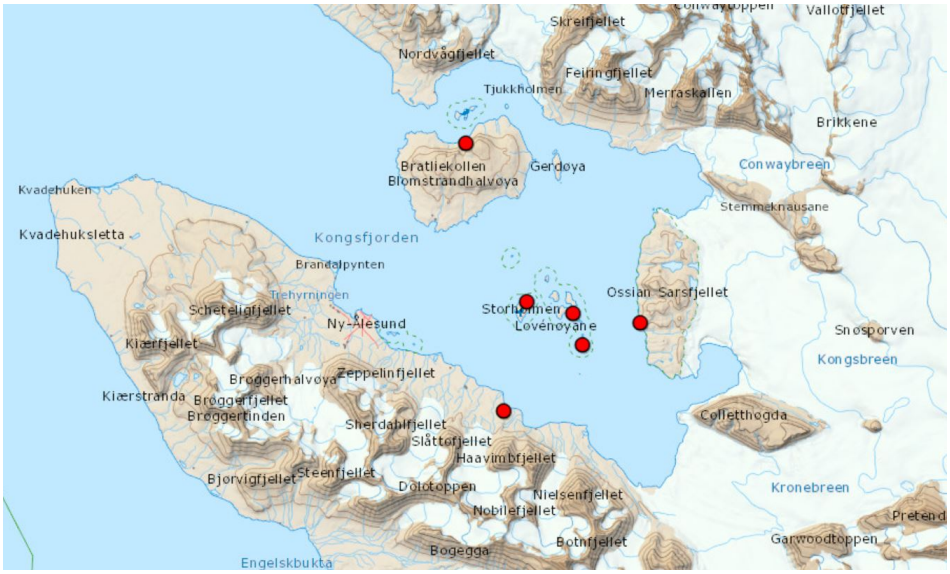

Figure 9: Map of Kongsfjorden. The red circles shows the location of the six sampling sites. Illustration made in TopoSvalbard [21], Norwegian Polar institute.

Including all samples from the six different locations, a total of 35 soil samples were collected. The coordinates for the location of each sample were noted. Coordinates for the different sampling sites are given in Table 15 in appendix. At two of the sampling sites, there were also opportunistically collected nine guano samples: five from Innerholmen, and four from Storholmen. The sampling was conducted from 16.august to 20.august in 2021.

3.1.2 Sampling method

The sampling method for this project follows the standards from ISO 18400-102 [92]. The sampling equipment consisted of a common bread knife in stainless steel, a garden trowel in plastic coated with Teflon, a GPS, nitrile gloves, aluminium boxes with aluminium-coated paper lids, paper bags and CC-cups in plastic. Nitrile gloves were used through the whole sampling procedure. The sampling equipment can be seen in Figure 10.

Figure 10: The sampling equipment used for soil and guano samples. From right to left: paper bags, aluminium boxes, nitrile gloves, GPS, CC-cups, garden trowel and common bread knife in stainless steel. Credit: Mathilde K. Syvertsen

The bread knife was used to check the depth and quality of the soil. Ideally the depth of the soil should be at least 10 cm, if it was less than 10 cm the soil was too shallow. The quality of the soil was decided by penetrating the soil with the bread knife. If the resistance of the soil was found too weak, the soil was assumed too compact to be suitable for sampling. When suitable soil was found the soil was cut in rectangles of 8-10X10-12 cm with the bread knife. The depth of each sample was all the way down to the bedrock, or as deep as the blade of the bread knife (23cm). The garden trowel was used to dig up the soil sample carefully. The void after sampling was filled with

soil and patched together to minimise the impact of the sampling.

The samples for organic analysis were packed and stored in aluminium boxes, and the samples for elemental analysis were packed and stored in paper bags. After the samples were packed, they were all labelled with the name of the location, a number and coordinates. The packing and labelling method of the soil samples followed the ISO 18400-105 standards [93]. On the return trip from Ny-Ålesund, samples were grouped in plastic bags based on sample locations.

After the return, the samples were left on a flat surface at room temperature to dry. The lids of the aluminium boxes were opened a bit to let the moisture get out. All the samples were stored as described for four days before the transport from Ny-Ålesund to Trondheim. The transport and storage of the samples were based on the standards from ISO 18400-105 [93].

Before the transport from Ny-Ålesund to Trondheim the samples were prepared further. The samples in aluminium boxes were packed in aluminium foil, and the samples in paper bags were packed in another paper bag. At the arrival in Trondheim the samples were again left at room temperature on a flat surface to air dry.

The guano samples were sampled by using the CC-cups (see Table 3 for more information) to pick the guano up. They were stored in the CC-cups at room temperature until the arrival in Trondheim. Upon arrival at NTNU, the CC cups containing the guano were put in the freezer. This was done to prevent any analytes of interest to be lost.

3.2 Pretreatment of samples

3.2.1 Drying of soil

The soil samples were air dried in accordance with ISO 11464:2006 [94]. The samples for elemental analysis were kept in their paper bags and placed on a lab counter to air dry. While the samples for organic analysis were kept in their aluminium boxes, and left on a lab counter, with one corner of the lid open to make it possible for the soil to air dry at 21 °C. The soil was considered dry when the difference in weight, between weighing, was less than 10%. The soil samples air dried for a total of three weeks.

3.2.2 Maceration of soil

Elemental analysis

After the air-drying, matter such as rocks, twigs and vegetation were removed from the samples using a plastic tweezer. All the samples were also crushed by hand and put in a new paper bag. Each sample was then put in a large plastic bag and crushed further by hand. When the samples were crushed into fine particles, the soil was sieved through a 0.6 mm synthetic analysis sieve (covering: nylon sieve cloth DIN 4197, Nr: 368753). This was done to get the sample as homogenous as possible. Between handling each sample the lab counter was washed with paper and Milli-Q water. The sieve was washed between the groups of samples from different locations.

Organic analysis

After the samples in the aluminium boxes were air-dried, matter such as rocks, twigs and vegetation were removed using a metal tweezer. The soil was then crushed by hand. All the samples were then further crushed using a porcelain mortar and pestle (Haldenwanger ^{R}). When the soil was crushed into fine particles the sample was sieved through a 0.6mm synthetic sieve (covering: nylon sieve cloth DIN 4197, Nr: 368753). The whole procedure was done on a lab counter covered in aluminium foil, which was changed between each sample. The lab counter were washed with paper and water between each sample. The mortar and pestle were washed with water and soap, then with Milli-Q water and dried with paper between each sample. The sieve was washed with water, then Milli-Q water and then air dried between samples from different location.

The maceration process for both elemental analysis and organic analysis were done in accordance with ISO 11464:2006 [94].

3.2.3 Pretreatment of guano samples

The guano was freeze dried for 48 hours with a Christ ALPHA 1-4 LD plus. After the guano was dried it was transferred from the CC-cups over to a porcelain mortar (Haldenwanger ^{R}). The guano samples were then finely crushed using a porcelain pestle (Haldenwanger ^{R}). The sample was then transferred back to the same CC-cups after being crushed in the mortar.

3.3 Elemental analysis

Soil and guano samples were pre-treated as described in Section 3.2. After pretreatment the soil was stored in paper bags and the guano in CC-cups, in room temperature.

3.3.1 UltraCLAVE

Soil

A 20ml Teflon vial containing nitric acid, HNO_3, solution was emptied and washed with Milli-Q water. The 68% HNO_3 (VWR Chemicals) was purified with a Milestone subPUR sub-boiling distillation system at Trondheim, NTNU, before it was used in the digestion process. The vial was put on a precision scale, and an amount of 250-350 mg of sample was transported to the vial. Approximately 9 ml of 50% HNO_3 was added in each vial. Two vials of reference material (moss) were treated the same way as above. To use as blanks, two vials were inserted with approximately 11ml of 50% HNO_3 which are approximately the same volume as what is in the sample and reference vials.

Guano

The guano samples were prepared for the Ultraclave in the same way as the soil, but with a higher amount of sample and lower amount of nitric acid. Approximately 400mg of guano sample, measured on a precision scale, was transported to the vial containing about 5 ml of 50% nitric acid, HNO_3. There were also prepared two vials of reference material (moss) which were treated the same way as the guano samples. Three other vials were used as blanks, inserted with 5 ml of 50% HNO_3.

To digest the soil and the guano there was used a high pressure microwave digestion reactor (UltraClave, Milestone GmbH Leutkirch, Germany). The soil and guano samples were digested separately. All the vials were put in a chamber and pressurised using nitrogen gas, N_2. A microwave oven heated the chamber, following a temperature program. When the UltraClave was finished the vials with the samples were taken out of the Ultraclave. Then, the solution in each vial was diluted to 0.6M HNO_3. A Teflon bottle was used to dilute. The Teflon bottle was put on a scale, and the solution in the vials were transferred over to the Teflon bottle. The bottle was filled with Milli-Q water to a total volume of approximately 108ml (109.8g) for the soil samples, and approximately 50ml (50.7g) for the guano samples. The Teflon bottle was rinsed in Milli-Q water three times between each dilution. Throughout the whole UltraCLAVE

process, nitrile gloves were used.

3.3.2 Analysis by ICP-MS

The digested soil and guano samples were analysed for elemental composition using a 8800 Triple Quadrupole Inductively coupled plasma mass spectrometry (ICP-MS) system (Agilent, USA). This ICP-MS system was equipped with a prepFAST M5 autosampler (ESI, USA.) The parameters for the analysis done with the ICP-MS is shown in Table 1.

Table 1: ICP-MS parameters for the elemental analysis of the digested samples of soil and guano.

System parameter	**Value**
RF Power	1550W
Nebuliser Gas	0.78L/min
Makeup Gas	0.40L/min
Sample depth	8.0 mm
Ion lenses	x-lens
H_2 mode	H_2 gas flow: $4.4ml/min$
	He gas flow: $1.2ml/min$
O_2 mode	O_2 gas flow: $0.525ml/min$

3.4 Determination of TOC, TIC and ROC

Determination of total organic carbon (TOC), total inorganic carbon (TIC) and residual oxidisable carbon (ROC) was done with a Skalar Primacs SNC100 instrument according to the DIN 19539: 2015-08 method [84]. TOC, ROC and TIC were combusted with oxygen gas at $400°C$, $600°C$ and $900°C$.

The soil samples were dried and homogenised as described in Section 3.2. A premade standard B (according to Skalar) that came with the instrument was used to calibrate the instrument. The standard was made out of ammonium oxalate monohydrate (carbon content 16.90%), carbon black (carbon content to be determined before use), calcium carbonate (carbon content 12.00%) and aluminium oxide (carbon free). The standard is made with a 2% content of each form of carbon (TOC400, ROC and

TIC900). Seven reusable ceramic crucibles were filled with approximately 10mg, 25mg, 50mg, 75mg, 100mg, 125mg and 150 mg with the pre-made standard B to make a calibration curve (accuracy in weighing: 0.0001).

Approximately 75 mg of sample were weighed out, with the accuracy 0.0001, in the reusable ceramic crucibles (2SN100370) with a metal spatula. Before the crucibles were used, they were washed with dilute hydrochloric acid solution (<0.1M), then with Milli-Q water and dried on aliminum foil, before they were heated up to $900°C$ to remove any residues. An empty crucible was used as a blank test to check for any contamination. The metal spatula that was used for weighing were washed in water from the tap and dried with paper between the weighing of different samples. All 35 soil samples were analysed using this method.

3.5 Analysis of PCB

The soil and guano samples was dried and macerated as described in Section 3.2. After the maceration and until extraction the soil were stored in aluminium boxes and guano were stored in CC-cups.

3.5.1 Extraction technique: Accelerated Solvent Extractor

Extraction of the samples was done as described in Sylvia Weging master thesis [95]. The ASE cell was prepared by placing two cellulose filters in the bottom of the cell before adding a layer of Cu powder (2g) and a layer of alumina (Al_2O_3). One cellulose filter between each layer was added to separate the different layers. The sample (0.5g) was weighed up in a glass beaker and spiked with 50μL of 1μg/ml F-PCB internal standard solution dissolved in ethyl acetate. The internal standard was left to dry on the soil before it was mixed with diatomaceous earth (2g) and transferred to the ASE cell. In the end Ottawa sand was added to the cell to fill the void volume as suggested in the U.S. EPA method 3545A [96]. In Figure 11 it is shown how the cell is filled. Apart from one difference the method blanks and the reference material samples were prepared in the same way. In the method blank there were not used any sample, and in the reference material there were weighed out 0.5 g of the reference material "SQC068-50G PCB Congeners in Soil" instead of sample.

The accelerated solvent extraction (ASE) was done using a Dionex^{TM} (Sunnyvale, CA,

USA) ASE 150 accelerated solvent extractor. 22 ml stainless-steel cells and 60 ml collection vials were used. The extraction conditions are shown in Table 4. Between different sample types(study samples and recovery test samples) the system was rinsed three times using a cell filled with only the resins.

All the equipment used in the ASE procedure was rinsed with soap and water, Milli-Q water and acetone. This was repeated three times for each solvent. Diatomaceous earth and Ottawa sand were activated by transferring the resin to a porcelain crucible and heating it to $400°C$ for 4 hours in an oven.

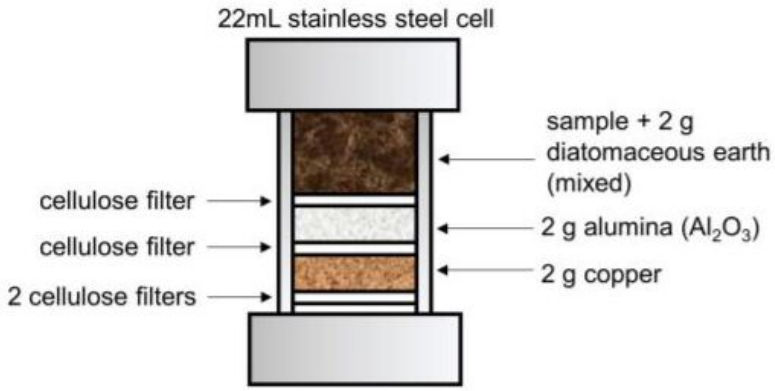

Figure 11: Figure of how resins, sample and filter are loaded in the cell before ASE is done. Adopted from Ref. [95].

After the extraction the extract was concentrated using a TurboVap Classic LV evaporator. The extract was concentrated from approximately 35 ml to 2 ml with the water bath temperature on $35°C$ and nitrogen gas stream on 5 psi. 10 ml of ethyl acetate were added to the solution through the inner wall of the vial to minimise loss of analyte. The solution was filtered through a 0.22 μm nylon syringe filter and concentrated down to the 1 ml mark on the 15ml centrifuge tube, in the same way as above. Then the solution was transferred to amber vials and put in the freezer ($-26°C$) for storage until the GC-MS analysis. All chemicals and materials used during the extraction are described in Table 3 and 2.

Table 2: Chemicals and materials purchased for PCB analysis.

Chemicals and materials	**Concentrations, specifications**	**Supplier**
Dichloromethane	GC- capillary grade	VWR Chemicals (Radnor, USA)
Ethyl acetate	ACS, Reag. Ph. Eur	VWR chemicals (Radnor, USA)
Acetone	Technical grade	VWR chemicals (Radnor, USA)
Ottawa sand	General purpose grade	Fisher Scientific (UK)
Aluminum oxide, activated	Basic, Brockmann I	Sigma-Aldrich (St.Louis, USA)
Cu powder	$< 425\mu m$, 99.5 % trace metals basis	Sigma Aldrich (St.Louis, USA)
Diatomaceous earth		Sigma Aldrich (St.Louis, USA)
Nylon syringe filter	$0.2\mu m$ pore diameter	VWR chemicals (Radnor, USA)
ASE Extraction Filter (cellulose)	for 1, 5, 10, 22 ml ASE 350/150 Cell	Thermo Scientific
15mL Centrifuge Tubes	Metal free	VWR chemicals (Radnor, USA)
50mL Centrifuge Tubes		VWR chemicals (Radnor, USA)
100Sterican kanyle	0.90 x 70mm	Braun
Syringe 10ml	not sterile	fisher scientific Germany
Kitchen foil	Aluminium foil	Snapples
Bakepose 1kg Hvit	190 X 240mm	Norwegian paper
Analysebeger, Coulter^R (CC-cups)	polysteren with polyetylen lids	VWR chemicals (Radnor, USA)

Table 3: Chemicals and materials purchased for PCB analysis.

Chemicals and materials	**Concentrations, specifications**	**Supplier**
Certified reference material - SQC068 - "PCB Congeners in Soil"		Sigma-Aldrich (St. Louis, USA)
3'F-PCB-28 (internal standard)	$0.1 mg/ml$ in isooctane	CHIRON AS (Trondheim, NO)
5'F-PCB-118 (internal standard)	10 $\mu g/ml$ in isooctane	CHIRON AS (Trondheim, NO)
"Dutch seven" PCB mixture, ISO 10382 Multicomponent Stock Solution	7 compounds (PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, PCB-180), 100 $\mu g/ml$ of each in isooctane	CHIRON AS (Trondheim, NO)

Table 4: ASE condition for extraction of PCBs in soil and guano samples.

System parameter	**Value**
Oven temperature	$100°C$
System pressure	1500 psi
Static time	5 min
Number of static cycles	3
Purge volume	60 %
Nitrogen purge time	60 s
Cell size	22 ml
Solvent	Dichloromethane
Total time per sample	24 min
Total solvent per sample	$\approx$ 35 ml

3.5.2 Analysis by GC-MS

The sample extracts from the ASE were analysed with GC-MS following the method described in Sylvia Weging master thesis [95], except Sylvia used a split injection instead of a splitless injection used in this project. The system information from the analysis is given in Table 5. The instrument used was an Agilent 7890A GC with an Agilent 5975 single quadropole MS detector. The column used was a Thermo Scientific^{TM} Trace Gold^{TM} GC column, 5% diphenyl/95% dimethyl polysiloxane. The overall analyse time for one sample with the temperature program described in Table 5 was 34.75 min. The mass detector was operated in selected ion monitor (SIM) mode using electron impact ionization (EI) at 70eV. Solutions for the calibration were prepared from the "Dutch Seven" PCB standard (specified in Table 3) in the ranging concentrations 0.5-200ng/ml. The calibration solutions were dissolved in ethyl acetate and added to the F-PCB internal standard (50ng/ml).

Table 5: System information for determination of PCB by GC-MS.

System information	**Value**
Instrument	Agilent 7890A GC
Sample introduction system	GC Pal autosampler
	(CTC Analytics, Zwingen, CH)
Detector	Agilent 5975 single quadropole MS
Column	Thermo Scientific^{TM} Trace Gold^{TM}
	GC column,5% diphenyl/95% dimethyl polysiloxane
	30m x 0,25mm inner diameter x 0.5 μm film thickness
Carrier gas	Helium
Carrier gas flow	1 ml/min
Injection port temperature	290°C
Injection method	Splitless
Injection volume	1μL
Temperature program	50°C for 2 min
	25°C/min to 250°C held for 1 min
	3°C/min to 286°C held for 3 min
	8°C/min to 308°C held for 1 min
	1°C/min to 310°C held for 3 min

A pooled sample was made from all the soil and guano samples to use for quality assurance/quality control (QA/QC). Pre-extraction matrix spiked samples (referred to as spiked) were created by using 0.5g of the pooled sample and the sample were spiked with 50 and 100 ng of PCB target analytes and they were extracted in the same way as described in Section 3.5.1. From the pooled sample there were made post-extraction matrix spiked (referred to as matrix-matched or MM samples) by extracting the same way as in Section 3.5.1. After the concentration was done, the extract was spiked with 50 and 100 ng of the target analytes. There were made three replicates of the spiked samples in each fortification level, and two replicates of the matrix-matched. Method blanks were made to check for contamination during the extraction, and solvent blanks (ethyl acetate) were run frequently to check for carry-over or cross-contamination in the GC-MS instrument.

3.6 Analysis of PFAS

The soil and guano samples were dried and macerated as described in Section 3.2. After the maceration and until extraction the soil was stored in aluminium boxes and the guano were stored in CC-cups.

3.6.1 Extraction

First 0.1 g of sample were weighed out in a 15 ml centrifuge tube. Then 20 μL of 1 $\mu g/ml$ internal standard, 300 μL of 1M ammonium acetate and 3 ml of ethyl acetate, in that order, were added to the centrifuge tubes. The content of the centrifuge tubes were mixed properly using a vortex shaker. After the content in the centrifuge tubes were mixed properly the tubes were ultrasonicated for 45 minutes in a 40 °Celsius water bath. The tubes were then centrifuged for 5 minutes at 4000 rpm. The supernatant was transferred to an empty centrifuge tube and the original sample was left in the original centrifuge tube. The centrifuge tube containing the original sample was filled with 3 ml ethyl acetate, and the same procedure as above was followed. This procedure was repeated until the centrifuge tube contained around 9 ml of extract.

The centrifuge tubes containing around 9 ml of extract were concentrated to almost dry. The tubes were filled up to 1 ml with MeOH : Milli-Q water (50:50), and the content of the tubes were mixed using a vortex shaker. The content in the centrifuge

tubes were transferred to 1 ml amber vials and stored in a freezer until analysis.

3.6.2 Analysis by UPLC-MS/MS

System information from the PFAS analysis using UPLC-MS/MS are found in Table 6. The instrument used was an Aquity UPC^2 with a Xevo^{TM} TQS detector. The column used was a Kinetex C18 column serially cennected to a Phenomenex guard column. The tune parameters used for the ESI ion source are found in Table 7. The UPLC-MS/MS method used for PFAS analysis is an optimized method from Kristine Vike-Jonas (PFCs 2020).

Table 6: System information for the analysis of PFASs by UPLC-MS/MS.

System information	**Value**
Instrument	Aquity UPC^2
	(Waters, Milford, CT, USA)
Detector	Xevo^{TM} TQS
	(Waters, Milford, CT, USA)
ESI ion Source	Zspray
	(Waters, Milford, CT, USA)
Column	Kinetex C18
	30x2.1mm, 1.3 μm, 100Å Phenomenex
	serially connected to a
	Phenomenex guard colum (C18 2.1mm)
Column temperature	30°
Mobile phases	Water phase(A): 2mM ammonium acetate
	Organic phase (B): Methanol
Flow rate	0.2 ml/min
Wash solvent	MeOH:ultrapure water (50:50)
	+ 0.1 % formic acid
Injection volume	4μL
Gradient	80%A : 20%B held for 0.2 min
	50%A : 50%B held for 0.6 min
	30%A : 70%B held for 0.7 min
	20%A : 80%B held for 1.3 min
	15%A : 85%B held for 1.7 min
	0%A : 100%B held for 1.0 min
	0%A : 100%B held for 0.1 min
	80%A : 20%B held for 0.4 min

Table 7: Tune parameters for the ESI ion source.

System parameter	**Value**
Capillary	2kV
Cone	25V
Source offset	40V
Desolvation temperature	450°C
Desolvation Gas flow	150 L/h
Cone	150 L/h
Nebuliser	6 bar
Source temperature	150°C

Sludge was used as a matrix for the extraction quality assurance/quality control (QA/QC). Pre-extraction matrix spiked samples were created by using 0.1g of the sludge and the sample were spiked with 2.5ppb, 25ppb and 50ppb of PFAS target analytes and they were extracted the same way as described in Section 3.6.1. Post-extraction matrix spiked samples (referred to as matrix-matched or MM samples) were made by the sludge by extracting the same way as in Section 3.6.1, and then the extract was spiked with 2.5ppb, 25ppb and 50ppb of the target analytes after the concentration was done. Three replicates were created of the spikes in each fortification level, and two replicates of the matrix-matched. The external and internal standards used in the PFAS analysis can be found in Table 21 and 22. Method blanks were made to check for contamination during the extraction, and solvent blanks(MeOH 50:50) were run frequently to check for carry-over or cross-contamination in the UPLC-MS/MS instrument.

4 Results

4.1 Elements in soil

In this project the main goal was to identify contaminants that may have been enriched in soil due to bird-influence. The elements P, Cd, As, Co, Cu, Li, Mn, Mo, Ni, Sb, Sr, K and Zn have been found in other studies to have an association with birds, and have been investigated in this project. Lead have also been investigated because of its known toxic properties. In Ny-Ålesund there has been mining activity in the past, and Ba is a known contaminant from mining activity. Ba have therefore also been investigated in this project. Mercury concentration on the other hand were under LOD in 16/32 samples, and have not been investigated.

In Table 8 the mean concentration of the selected elements from each location can be found. While the mean concentration of the selected elements in the guano from Innerholmen and Storholmen can be found in Table 9.

Table 8: Mean concentration of different elements, and standard deviation, from soil in the different locations Innerholmen (IH), Storholmen (SH), Leirholmen (LH), Ossian Sars (OS), Irgensfjellet (IrgF) and Botngjellet (BF). The concentrations are given in $\mu g/g$.

Element	**Innerholmen** n=4	**Storholmen** n=5	**Leirholmen** n=4	**Ossian Sars** n=4	**Irgensfjell** n=2	**Botnfjell** n=3
As	3.54±0.700	1.98±0.250	2.64±0.164	4.06±1.21	7.48±3.98	3.36±1.84
Cd	0.276±0.0946	0.308±0.0678	0.140±0.0122	1.21±1.16	0.228±0.144	1.37±0.609
Co	6.62±1.23	3.15±0.428	6.38±0.518	6.57±1.35	3.97±1.12	3.23±2.05
Cu	9.80±1.41	4.65 ±0.709	11.3±0.575	15.9±8.90	11.9±1.95	13.6±3.72
Li	16.1±3.63	7.23±1.02	17.4±1.45	15.2±3.52	7.65±2.26	56.4±69.4
Mn	304±49.3	216±51.2	316±20.5	351±44.6	201±47.8	112±67.6
Mo	0.352±0.109	0.325±0.0387	0.422±0.0638	0.269±0.0868	0.244±0.00125	0.552±0.107
Ni	15.6±3.30	6.40±0.688	14.9±1.01	14.1±2.88	9.32±0.387	24.8±16.1
Sb	0.0322±0.00943	0.0363±0.0145	0.0199±0.00333	0.0329±0.00643	0.0386±0.00252	0.130±0.0499
Sr	67,5±18,5	51.5±3.93	67.6±7.66	114±47.6	44.8±1.02	81.9±19.8
P	765±90.2	1090±110	984±185	5350±4260	839±228	3140±1540
K	6470±1240	3360±411	7320±661	7230±1660	3630±1110	3150±2040
Zn	55,2±17.7	24.0±5.29	49.6±0.756	79.0±38.4	26.7±9.68	66.1±35.8
Ba	137±17.5	58.6±6.39	165±27.3	151±19.3	56.9±18.3	107±35.5
Pb	8.79±1.36	10.1±2.01	8.23±0.715	6.35±1.40	8.86±3.26	15.4±11.8

Table 9: Mean concentration of different elements, and standard deviation, of the guano sampled from Innerholmen and Storholmen. The concentrations are given in $\mu g/g$.

Element	**Innerholmen** n=4	**Storholmen** n=4
As	1.13±0.189	0.757±0.530
Cd	0.357±0.171	0.459±0.134
Co	1.49±0.324	1.04±0.340
Cu	5.76±1.13	4.02±0.785
Li	3.82±1.26	2.45±0.746
Mn	102±5.99	135±6.36
Mo	0.997±0.358	0.325±0.0506
Ni	3.71±0.820	2.47±1.11
Sb	0.0107±0.00396	0.0137±0.0109
Sr	89.3±45.0	51.5±5.09
P	2250±568	3110±506
K	5190±1920	6250±891
Zn	74.6±32.7	67.6±16.8
Ba	58.9±9.51	36.9±5.66
Pb	1.93±0.348	1.42±0.510

4.2 Total organic carbon in soil

The total organic carbon content in the soil was measured in all the soil samples. The mean value of the TOC content in the soil from different sampling sites are found in Table 17. The variation of TOC between the sampling sites was tested with a Kruskal-Wallis test, and showed that they were significantly different with a p-value of 0.0005. A box-plot showing this variation can be found in Figure 12. The sample locations with the highest mean TOC content were Storholmen (20.8±3.18) and Botnfjell (20.7±8.04). The location with the lowest mean TOC content was Leirholmen (4.72±2.06).

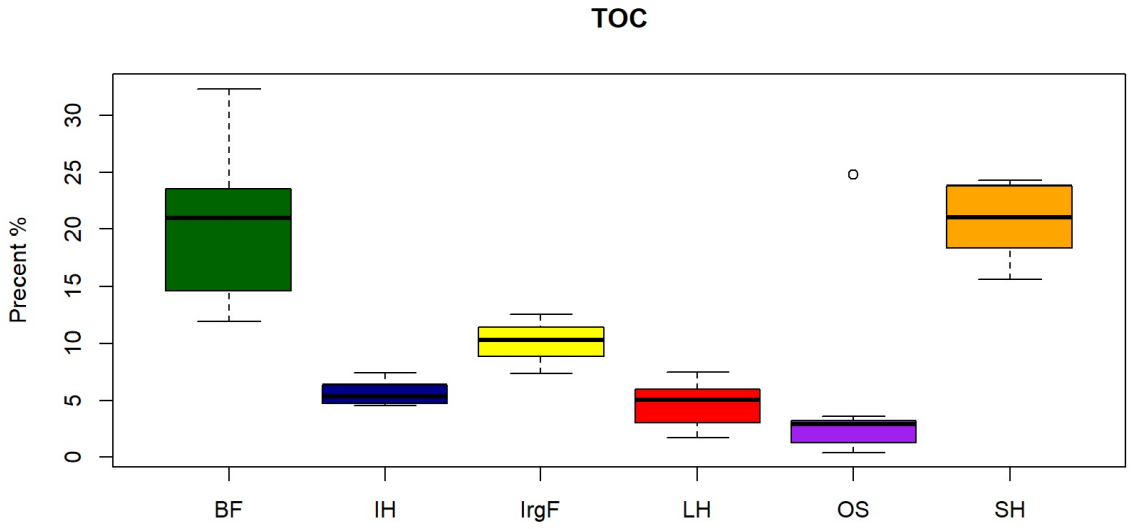

Figure 12: Box-plot of total organic carbon (TOC) in percentage at the different sampling sites. The sampling sites are Botnfjell (BF), Innerholmen (IH), Irgensfjell (IrgF), Leirholmen (LH), Ossian Sars (OS) and Storholmen (SH).

4.3 PCBs in organic soil

The soil and guano were analysed for PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153 and PCB-180. There were found peaks of the target analyte in some of the guano samples for PCB-52. None of the target analytes detected had concentrations over LOD. The LOD and LOQ for the different PCBs are found in Table 19 in the appendix.

In Table 10 the recoveries of the target analytes at different fortification levels are shown. Table 20 in the appendix shows the matrix effect in the target analytes at different fortification levels.

Table 10: Absolute and relative recoveries (Rabs, Rrel) given in percent, of PCB target analytes in organic soil analysed with GC-MS.

	50ng/ml		100ng/ml	
Analyte	**Rabs**[%]	**Rrel**[%]	**Rabs**[%]	**Rrel**[%]
PCB-28	88	98	67	78
PCB-52	86	96	64	74
PCB-101	89	101	69	76
PCB-118	88	101	68	75
PCB-138	88	100	70	77
PCB-153	87	99	70	78
PCB-180	89	101	73	81

4.4 PFASs in organic soil samples

The 35 soil samples from Ossian Sars (n=3), Botnbreen(n=2), Irgensfjellet(n=1), Storholmen(n=3), Leirholmen(n=2) and Innerholmen(n=2) were analysed for 31 PFAS, 4:2FTS, MeFOSAA and PFHpA were detected in the samples. Table 11 lists PFAS concentrations for the different samples. All detected PFAS was over LOD except in Storholmen one of the soil samples had a PFHpA concentration lower than LOD (0.00462 $\mu g/kg$). The LOD and LOQ for the three detected PFAS are found in Table 12. The recovery and matrix effect for each analysed PFAS can be found in table 23 and 24in the appendix.

Table 11: Concentration of the detected PFAS 4:2FTS, MeFOSAA and PFHpA in every soil and guano analysed for the PFAS. The concentration is given in $\mu g/kg$.

Sample	Matrix	4:2 FTS	MeFOSAA	PFHpA
Innerholmen 2	Soil			
Innerholmen 5	Soil		7.27	
Storholmen 1	Soil			0.00462
Storholmen 4	Soil			8.96
Storholmen 7	Soil			
Leirholmen 2	Soil			
Leirholmen 5	Soil			
Ossian Sars 2	Soil			
Ossian Sars 3	Soil		6.86	
Ossian Sars 4	Soil		8.52	
Irgensfjellet 2	Soil			
Botnfjell 3	Soil			
Botnfjell 5	Soil			
Innerholmen g1	Guano		8.02	
Innerholmen g2	Guano		8.46	
Innerholmen g3	Guano			
Innerholmen g4	Guano			
Innerholmen g5	Guano	4.37		
Storholmen g1	Guano		7.74	
Storholmen g2	Guano	7.79	7.69	
Storholmen g3	Guano	25.8	7.96	
Storholmen g4	Guano		8.90	

Table 12: Instrumental and sample LOD and LOQ for analysis PFAS using UPLC-MS/MS. The sample LOD and LOQ were obtained from 4 μL standard solution volume and 0.0001g sample weight that was analysed with UPLC-MS/MS.

	Instrument		Sample	
Analyte	**LOD(μg/ml)**	**LOQ(μg/ml)**	**LOD(μg/g)**	**LOQ (μg/g)**
4:2FTS	0.006	0.02	0.23	0.77
MeFOSAA	0.02	0.06	0.72	2.4
PFHpA	0.01	0.04	0.43	1.4

5 Discussion

5.1 Ranking of location based on bird-influence

The sample locations have been ranked for bird-influence, based on how many birds are present at the location and the diet of the bird species present at the location. The locations underneath the bird cliffs were anticipated to have highest bird-influence in the order: Ossian Sars > Irgensfjellet > Botnfjellet, from highest to lowest bird-influence. The islands were anticipated to have lower bird-influence than the bird cliffs in this order: Storholmen > Leirholmen > Innerholmen, from the highest to lowest bird-influence. The information for this ranking of bird-influence for the different locations are found in Table 16 in the appendix.

As described in Section 2.7 P can be used as an indicator of bird-influence and can be used as a proxy for bird-influence. In this study there was a Kruskal-Wallis test to see if the concentration of P differed significantly over the different locations. With a p-value of 0.009, the test showed that the concentration of P differed significantly between the different locations. However, the mean P concentration for the different locations did not follow the expected ranking of bird-influence. Ossian Sars was expected to be the location with the highest influence by birds and was the location with the highest mean value of P with a concentration of $5346 \mp 4264\ \mu g/g$. Irgensfjellet (P: $838.8 \mp 227.8\ \mu g/g$) was ranked to be the second most bird-influenced location but had the second lowest mean concentration of P. Due to limited available time at the last sampling location, samples had to be taken further away from Irgensfjellet than planned. It was also limited time to find the appropriate soil. This location had the lowest number of samples, with only two samples, which can affect the significance of the mean value. Botnfjell (P:$3140 \pm 1540 \mu g/g$) was ranked to have the third highest bird-influenced soil, and had the second highest concentration of P. However, the unexpected ranking of Botnfjell had more to do with the low concentration of P in the samples from Irgensfjellet than in the samples from Botnfjell. All three islands were ranked to have the lowest bird-influence with Storholmen as the most influenced and Innerholmen as the least influenced by birds. This is reflected in the P concentration as Storholmen (P:$1087 \pm 110.4 \mu g/g$) had the highest mean concentration, Leirholmen (P: $984.0 \pm 185.3 \mu g/g$) had the lowest and Innerholmen (P: $765.0 \mp 90.17 \mu g/g$) had a concentration inn between those two.

Compared to each other they had the expected concentration of P compared to the ranking shown in table 16.

5.1.1 New ranking of bird-influence

Based on the P concentration a new ranking of the locations in bird-influence can be done as this: Ossian Sars > Botnfjell > Storholmen > Innerholmen > Irgensfjellet > Leirholmen, with Ossian Sars as the most bird-influenced and Leirholmen the least influenced location.

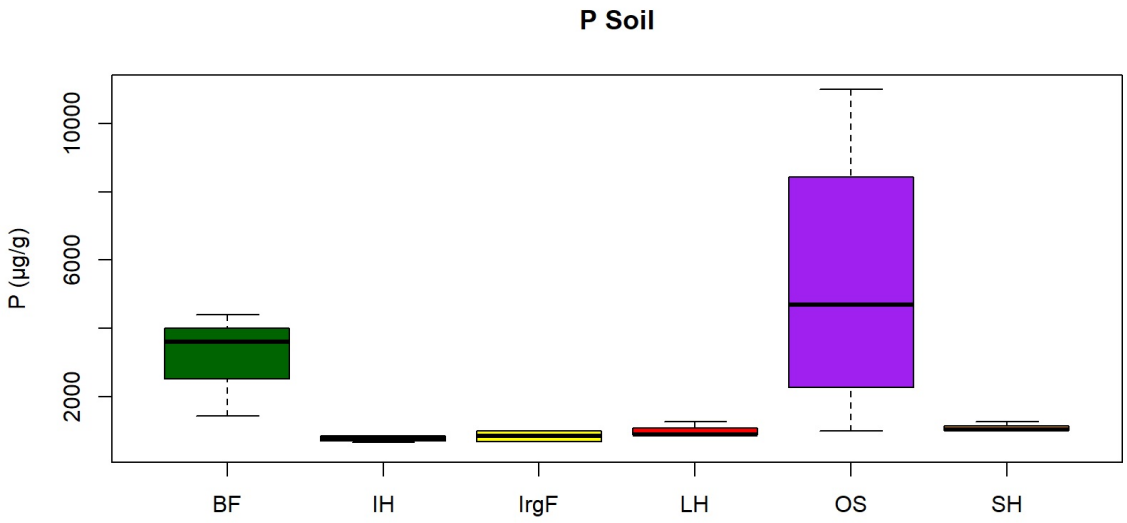

Figure 13: Boxplot of P content at the different locations. The sampling sites are Botnfjell (BF), Innerholmen (IH), Irgensfjell (IrgF), Leirholmen (LH), Ossian Sars (OS) and Storholmen (SH).

The low number of samples can make it hard to use statistical tests. To make statistical tests more appropriate, the locations were grouped into two levels of bird-influence. Low bird-influence and high bird-influence. Storholmen (P: 1087±110.4$\mu g/g$, n=5), Innerholmen (P: 765.0±90.17$\mu g/g$, n=5), Irgensfjellet (P: 838.8±227.8$\mu g/g$, n=2) and Leirholmen (P: 984.0±185.3$\mu g/g$, n=4) were the locations in the low bird-influenced level. Ossian Sars(P: 5346±4264$\mu g/g$, n=4) and Botnfjell (P:3140±1540$\mu g/g$, n=3) were in the high influenced level. Looking at the visualisation of the distribution of P

between the different locations in Figure 36, it seems to be natural to have the locations divided into two levels. In Figure 22 in appendix, the locations Botnfjell and Ossian Sars are excluded, and this was done to get a better look at the distribution between the locations with lower P concentrations. After doing a Kruskal-Wallis test on the locations from the low level of bird-influence the locations were deemed significantly different (p=0.03) in distribution of P. However ,they were considered close enough in bird-influence to be grouped together.

5.2 Variation in selected elements by bird-influence

The selected elements P, Cd, As, Co, Cu, Li, Mn, Mo, Ni, Sb, Sr, K, Zn, Ba and Pb were chosen to be looked further into because of their association with birds or human activity. A non-parametric Kruskal-Wallis test was done of the distribution of these elements between the sampling sites, and the boxplot and the belonging p values can be found in Section E of the appendix. All the elements showed significant difference in distribution between the different sampling sites, except Pb (p=0.2). All the elements were further investigated, based on the new P-concentration ranking, found in Section 5.1.1. In this ranking there are two levels of bird-influence: the highly influenced locations Ossian Sars and Botnfjell (n=7) and the low influenced locations Storholmen, Innerholmen, Irgensfjellet and Leirholmen (n=15).

A Man-Witney U test was done to investigate the variation of the selected elements between high and low bird-influence. The elements P, Cd, Cu, Sb, Sr and Zn concentrations were significantly higher in the high bird-influenced level. However, the elements As, Co, Li, Mn, Mo, Ni, K, Ba and Pb were not significantly different between the two levels of bird-influence. All the boxplot and the belonging p values for this test can be found in Section F.

P: The distribution of P between high and low bird-influences was significantly different (p=0.0005). This is not a surprise since the level is based on the differences in P concentration. The mean concentration for the two sampling sites in the high level were $5346 \pm 4264 \mu g/g$ for Ossian Sars and $3140 \pm 1540 \mu g/g$ for Botnfjell. The difference in P concentration between these two sites is quite large. However, due to the low number of samples it was more appropriate to have Ossian Sars and Botnfjell grouped together in the high bird-influenced group, instead of in two different groups, to get a better statistical test. As described in Section 5.1.1, the distribution of P between the

sampling sites in the low level are significantly different from each other. Also, in this case it was more appropriate to have them in the same group to get a better statistical test.

Cd: The distribution of Cd between the high and low bird-influenced groups were significantly different (p=0.002) (Figure 14). A correlation between bird-influenced soil and Cd has been found in other studies [64, 70–72]. The sampling sites Ossian Sars and Botnfjell are sites which are dominated by Black-legged kittiwake, while the islands are dominated by the bird species Common eider and Barnacle goose (Table 16). The Black-legged kittiwake in the Barents sea have shown to have elevated levels of Cd compared to Common eider and Barnacle goose [97]. The elevated level of Cd is mainly connected to differences in diet. The Black-legged kittiwake is in a higher trophic level than the Common eider and Barnacle goose (described further in Section 2.6.1), and will therefore bioaccumulate more Cd in their bodies. The Cd soil content in the different areas may therefore be affected by different species composition present at the site.

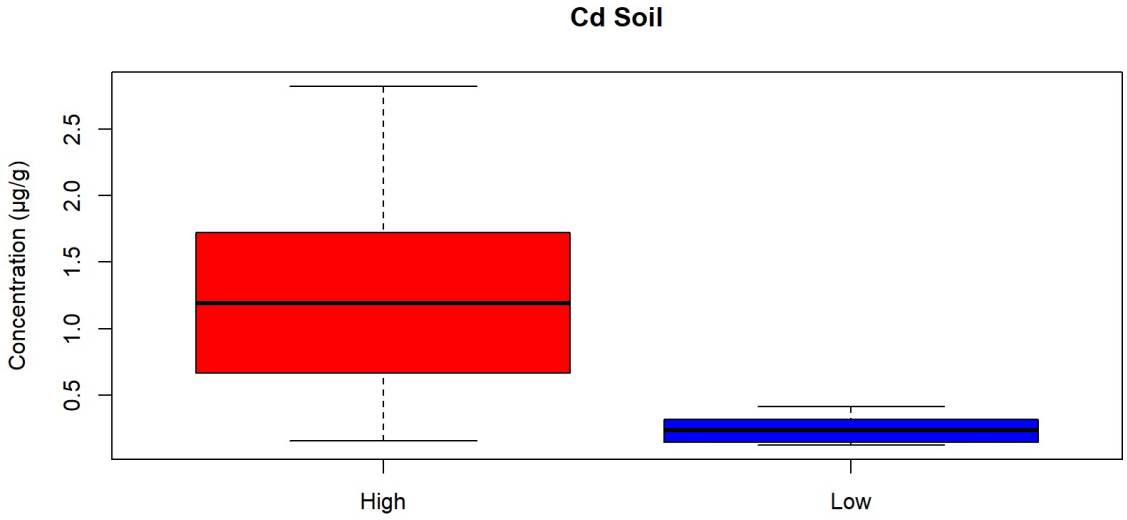

Figure 14: Boxplot of Cd content at high and low bird-influence. Cd concentrations are significantly different (p=0.002) in high and low bird-influenced areas.

Within the high bird-influenced level there is a large variation in the data which can be seen clearly in the standard deviation. This is especially clear at Ossian Sars (Cd:

$1.21 \pm 1.16 \mu g/g$) where the minimum value for Cd were $0.154 \mu g/g$ and the maximum value were $2.82 \mu g/g$. Also, for Botnfjell there is a large variation in concentration of Cd, although not as large as for Ossian Sars. The minimum value of Cd concentration at Botnfjell was $0.670 \mu g/g$ and the maximum $1.74 \mu g/g$. Samples with low Cd concentrations also have low P concentrations, meanings that the Cd content correlate with the P content. Also, the distribution of Cd is significantly higher for the high bird-influence level than for the low. This is an indication of elevated levels of Cd in soil due to bird-influence.

Cu and Zn: The concentrations of Cu and Zn are significantly higher in the high level of bird-influence than low (p=0.02, Figure 40 and 47). Ziolek et al found also a positive correlation between Cu and Zn concentration and P concentration in soil influenced by birds [72], and Brimble et al (2009) identified Zn as a seabird-derived element from a Northern fulmar colony, but not for Cu. They examined the tissue of the birds, and found low concentration of Cu. [71] The concentration of Cu in seabirds varies between different species, and are found to be highest in the Common eider [97]. Brimble et al (2009) found a correlation between Cu concentration and ornithogenic gradient, but not for Zn [70]. These two studies were done on the same Northern fulmar colony and the surroundings. This suggests that which elements are affected by the seabird might not only depend on the seabird species, but also on how the study is made.

In this study Cu and Zn were significantly higher in the locations with higher P concentration. This is an indication of Cu and Zn enrichment by birds, and other studies have found similar results [70–72]. However, the sampling number for each location in this study is quite small, and further studies with more samples are needed to give a statistically clear conclusion.

Sb and Sr: Sb were significantly higher in the high bird-influenced level (p=0.05, Figure 15). However, when looking at the distribution of Sb between the sampling sites (Figure 31) the sampling site at Botnfjell stands out with a higher concentration of Sb compared to all the other sampling sites. A Man-Witney U test was done between the low and high bird-influence level, excluding the Botnfjell site, and the two levels had no significant difference in the Sb concentration (p=0.6). Brimble at al (2009) found a positive correlation between Sb and Sr concentration and an ornithogenic gradient [70] Lakså found in her master thesis a significantly higher concentration of Sb at high bird-influenced sites than at low influenced sites [64]. In the project done now there was also found a significantly higher Sr concentration at the high bird-influenced sites than the

low (p=0.002, figure: 45). The cause for the association between Sr and bird-influence is unknown.

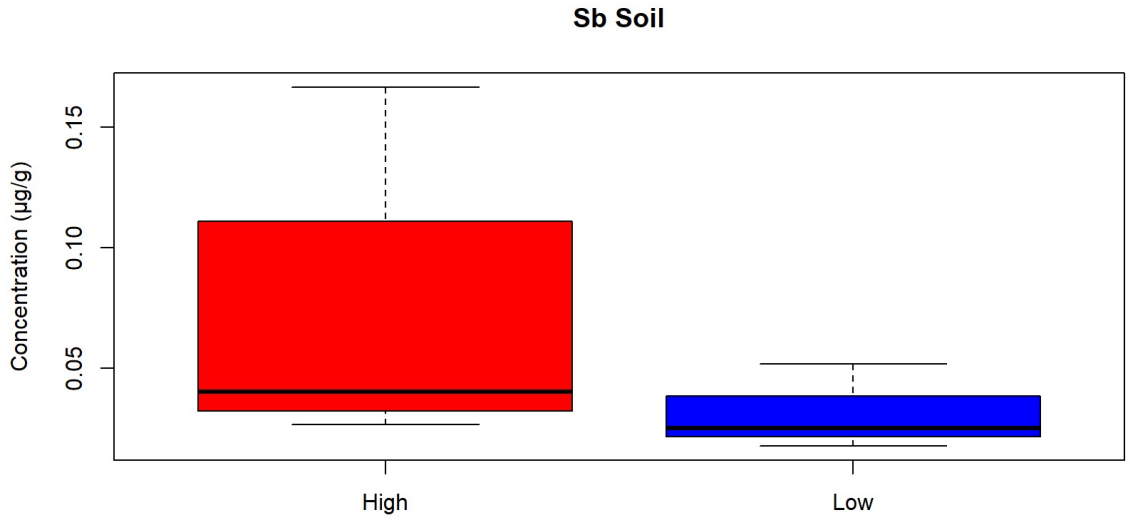

Figure 15: Boxplot of Sb content at high and low bird-influence. Sb concentration is significantly different (p=0.05) in high and low bird-influenced areas.

5.3 Comparison to a reference point

All the soil samples sampled in this project were from known breeding areas for different bird species. To provide data from soil which are not bird-influenced, data from Damhaug master thesis was used [98]. She had data on elements in humus soil from Knudsenheia. Knudsenheia has no bird nesting activity, and the area is considered to have low bird-influence (lower than at any of the sampling sites in this project). This site has no close anthropogenic pollution source either. Knudsenheia is therefore considered a good reference site for this project. A map of the position of this location is found in the Appendix in Figure 50. The data from the reference site has a low number of samples, and in this project there is only access to the mean value of the concentration. Therefore, no statistical tests have been done with this data. In Table 13 the mean concentration of some selected elements from the reference site and from the high and low bird-influenced sites are found.

Table 13: The mean value of some selected elements from the reference site (Knudsenheia), low bird-influenced sites (Storholmen, Innerholmen, Irgensfjellet and Leirholmen) and high bird-influenced sites (Ossian Sars and Botnfjell). The concentrations are given in $\mu g/g$.

	Reference site n=5	**Low** n=15	**High** n=7
As	1.81±0.64	3.31±2.13	3.76±1.41
Cd	0.54±0.12	0.24±0.098	1.28±0.90
Co	3.03±1.09	5.04±1.79	5.56±2.26
Cu	6.38±0.91	8.75 ±3.23	14.9±6.77
Mn	172±58	264±64.3	248±137
Mo	0.43±0.14	0.35±0.084	0.39±0.17
Ni	6.7±1.9	11.5±4.53	18.6±11.1
Sb	0.02±0.01	0.031±0.012	0.074±0.059
Sr	35.3±3.2	59.2±13.5	100±39.4
P	744±65	940±186	4400±3360
K	3730±761	5280±1960	5480±2740
Ba	77±17	108±51.7	132±34.1
Pb	10.13±1.27	9.10±1.75	10.2±8.40

The mean P value from the reference site (Knudsenheia) supports the theory that this site is less bird-influenced than the sites from both the low and high bird-influenced level. It is also possible to see that the mean concentration of K is lower in the reference point than in the bird-influenced soil, which is a further indication of enrichment of nutrients in bird-influenced soil.

Mean value of the Cd concentration from low bird-influence level is lower than Cd concentration from Knudsenheia, which indicates that there is no enrichment of Cd at low level of bird-influence. The reason for this might be because of the low trophic level of Common eider and Barnacle goose which are the dominant bird species on the islands. The islands are also the dominant part of the low bird-influenced group. The high level has a significantly higher mean Cd concentration, and this can be explained by the high number of high trophic-level birds at these sites (more explained in Section 2.6.1).

As, Co, Mn, Ni, Sb, Sr and Ba are all found in lower concentration in the reference soil

than in the bird-influenced soil. However, due to the lack of data from the reference site there will be no further discussion of the reason for this difference.

5.4 PCA plot with the soil samples

In the PCA-loading plot Al, Fe, Mg and K are strongly loaded in the positive direction of PC1. Si, Al, Fe, Mg, K, Na and Ca are found in high abundance in the earth crust [99]. Si is often found in silicates which are not digested with the HNO_3 in the UltraClave, and will not be detected in ICP-MS if the Si is not in another form. Na is not that strongly correlated with PC1 in the positive direction, but Na is also found in guano [100]. S is loaded in the negative direction of the PC1. PC1 is explaining 46% of the variance, and in the positive direction the variance seems to be explained by the influence of the parent material. All elements (P, Cd, Cu, Sb, Sr and Zn) which were found to be significantly higher in the high level of bird-influence compared to the low level of bird-influence (see section5.2) are found in the positive direction of PC2 (Figure 16). PC2 explains 21% of the variation. P and Cd are strongly loaded to PC2. In the negative direction Silicon (Si) is strongly loaded to PC2. Si is abundant in earth crust. The PC2 in the positive direction explains the variance by the bird-influence in the soil.

In the PCA-score plot (Figure 17) almost all samples from the highly bird-influenced areas are in the positive part of the PC2, and all the samples from the low bird-influenced areas in the negative part of the PC2. This can be an indication of a division between high and low bird impact which correlates well with the ranking from section 5.1.1. However, from Figure 13, a higher score of the samples from Ossian Sars on PC2 would be expected. In this case other elements, for example Sb (in which soil from Ossian Sars was low in) may be the reason for less association between Ossian Sars sampling site and PC2.

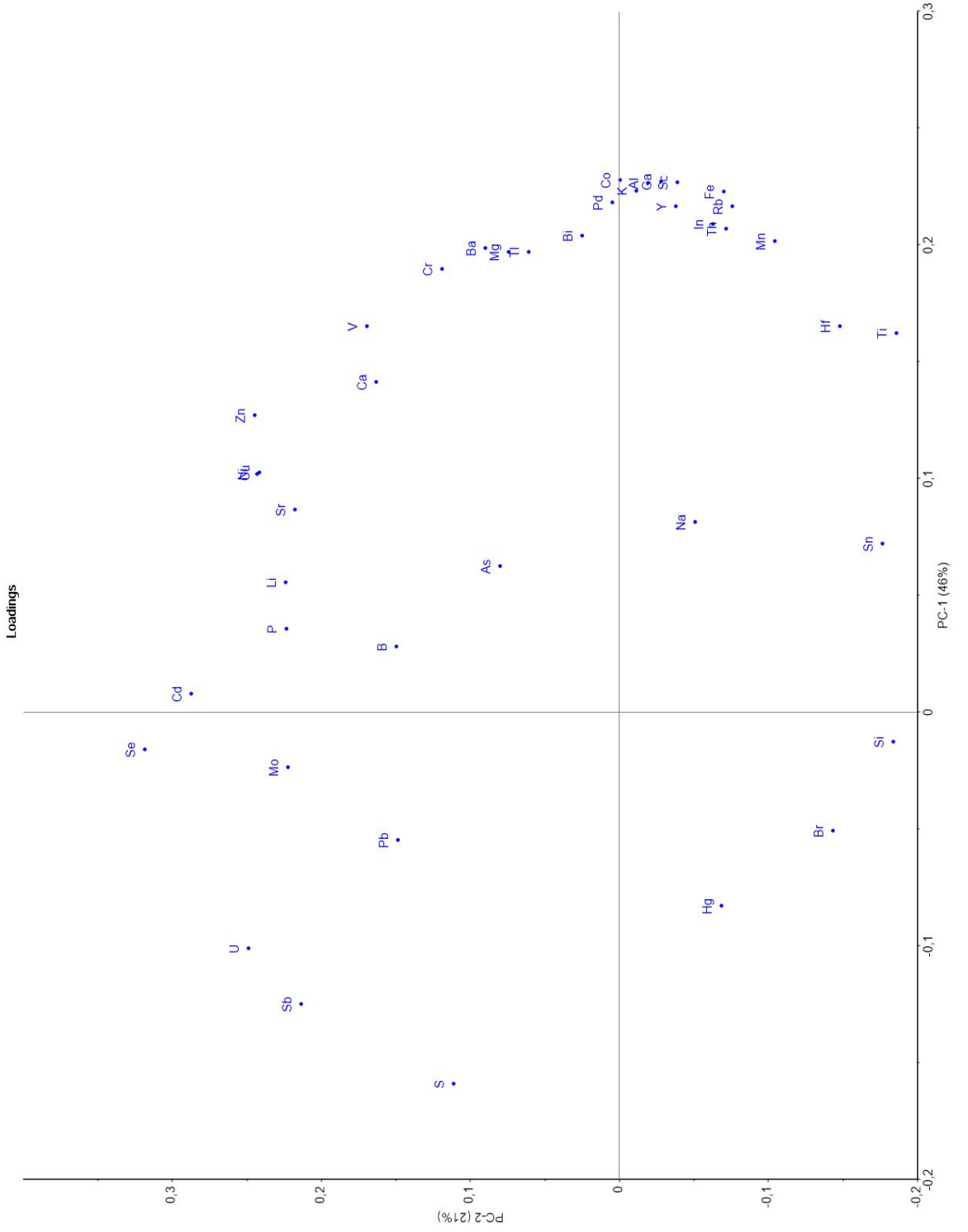

Figure 16: PCA loading-plot for selected elements in soil samples for PC1 and PC2.

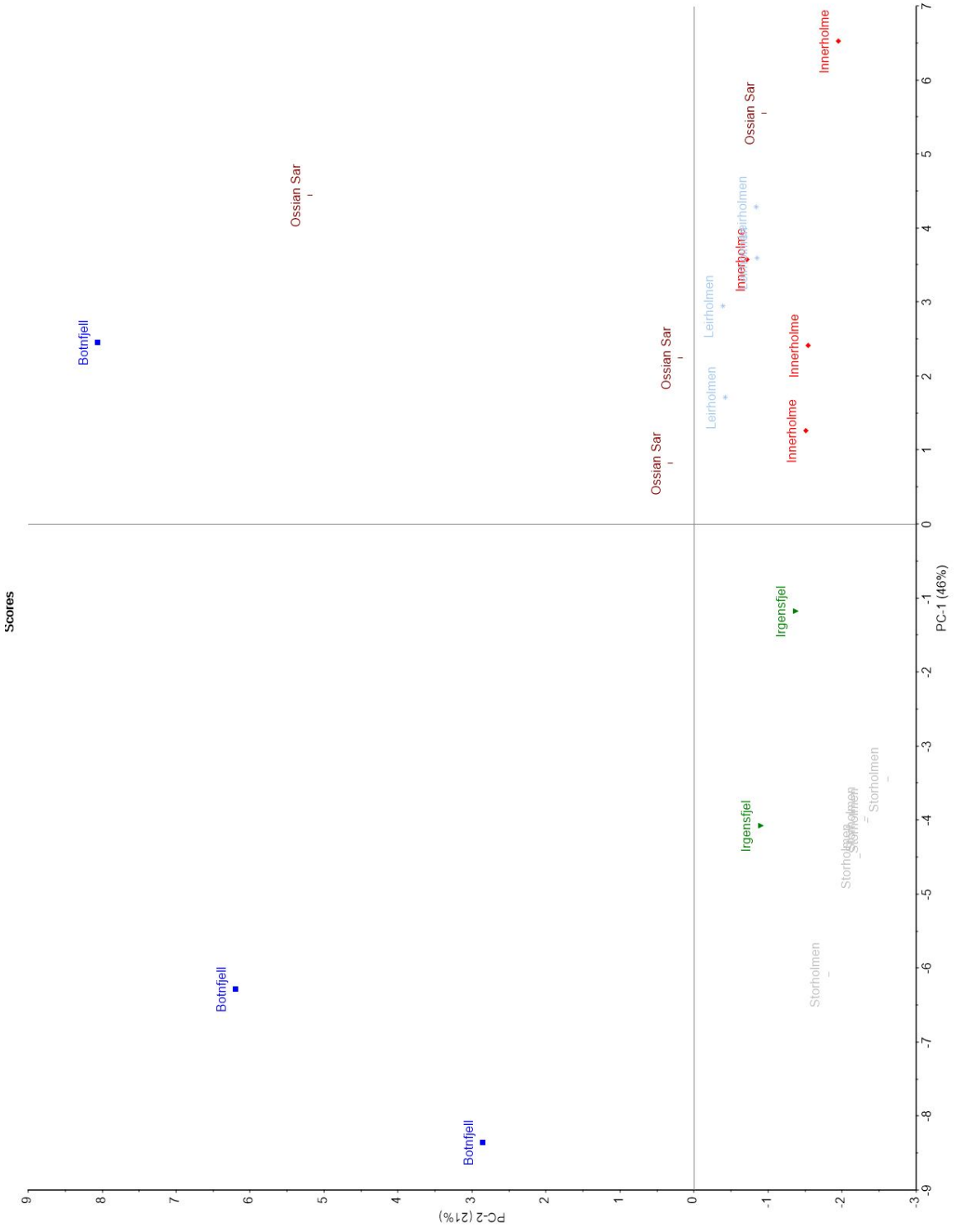

Figure 17: PCA score-plot for locations of soil samples for PC1 and PC2.

5.5 PCA plot with the soil and guano samples

A principle component analysis (PCA) plot containing some selected elements concentrations and TOC percentages. The Hg concentration in 16/32 of the samples were under LOD and a concentration between 0.0004-0.0005$\mu g/g$ were used for those samples for statistical treatment. The correlation with Hg in the PCA plot is therefore questionable. TOC contents were only determined for the soil samples. For the guano samples a TOC content between 27-32% were added in the dataset. This is considered a realistic TOC percentage for guano.

The PCA-plot in Figure 18 and 19 are based on the mean value of the elements and TOC percentage from each location. PC2 in the loading plot (Figure18) is dominated by U, Cd and Sb in the positive direction, and Si in the negative direction. Cd and Sb is an indicator of bird-influence, and Si is associated mostly with the parent material of the soil [99]. PC2 explains 21% of the variation in the dataset. PC1 explains 49% of the variation in the dataset, and is dominated by TOC, S, B and Na in the negative direction, which are usually found in higher content in guano than soil [100]. In the positive direction the elements Mg, Ba, Cr, Fe, Al and Co are dominating. The elements Fe and Al can be found in high abundance in the earth's crust and therefore also in soil. The PC1 seems to mostly explain the differences in the amount of guano.

In the PCA-score plot (Figure 19) Botnfjell and Ossian Sars are both in the positive part of PC2, while Storholmen, Irgensfjell, Innerholmen and Leirholmen is in the negative part. The guano is strongly associated with PC1 in the negative direction, while Ossian Sars is strongly associated with PC1 in the positive direction. Ossian Sars, Leirholmen and Innerholmen are associated with PC1 in the positive direction and are probably the most sites influenced by the parent material. While Storholmen is the site with soil most associated with PC1 in the negative direction and is probably the site most influenced by guano, and least associated with the parent material. This can be explained by the low trophic level of the birds breeding at Storholmen. Which means that the soil is highly affected by guano, but there is still no great effect in P-concentration or other elements known to be increased in bird-influenced soil. Si in soil is highly affected by the parent material, and Si is less soluble in soil with high carbonate content [101]. Botnfjell is the only sampling site with carbonate rocks as parent material, and this can explain why Botnfjell is negatively correlated with Si.

In Figure 51 and 52, the sampling sites are named with the bird species dominating

in the specific area. The guano samples are naturally clustered together. It is also possible to see that the sampling sites with Barnacle goose as dominating bird species are clustering together, and the sampling sites with Common eider as the dominating bird species are also clustering together. However, the sampling sites with Black-legged kittiwake as dominating bird species are not showing any specific trend in the PCA plot. Although almost all sites which are dominated by Black-legged kittiwake are in the positive part of PC2. Which is the principle component explained by bird-influence. This shows some indication that the bird species present at a location can influence the soil composition.

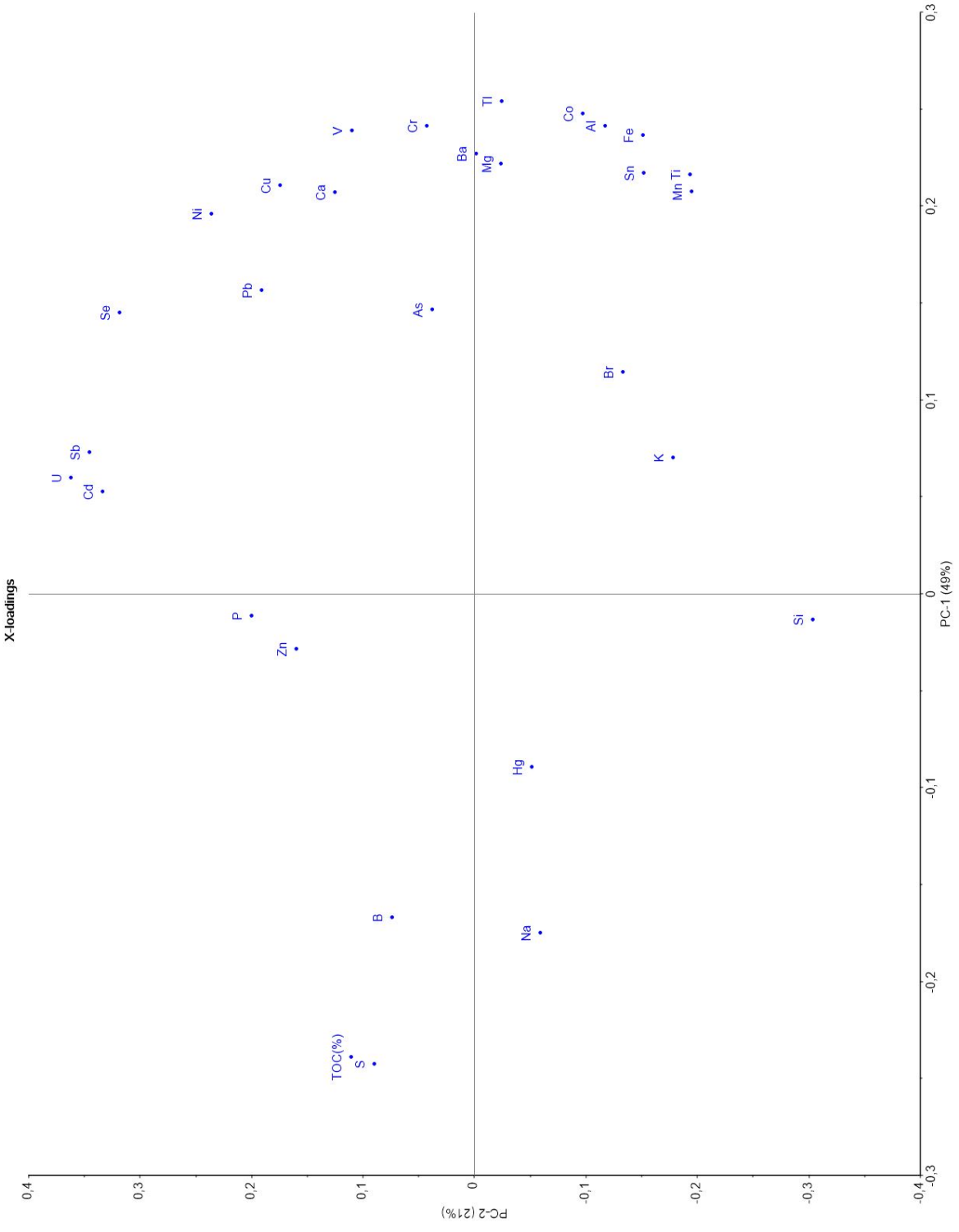

Figure 18: PCA loading-plot with selected elements and TOC(%). With mean from each location. PC1 and PC2.

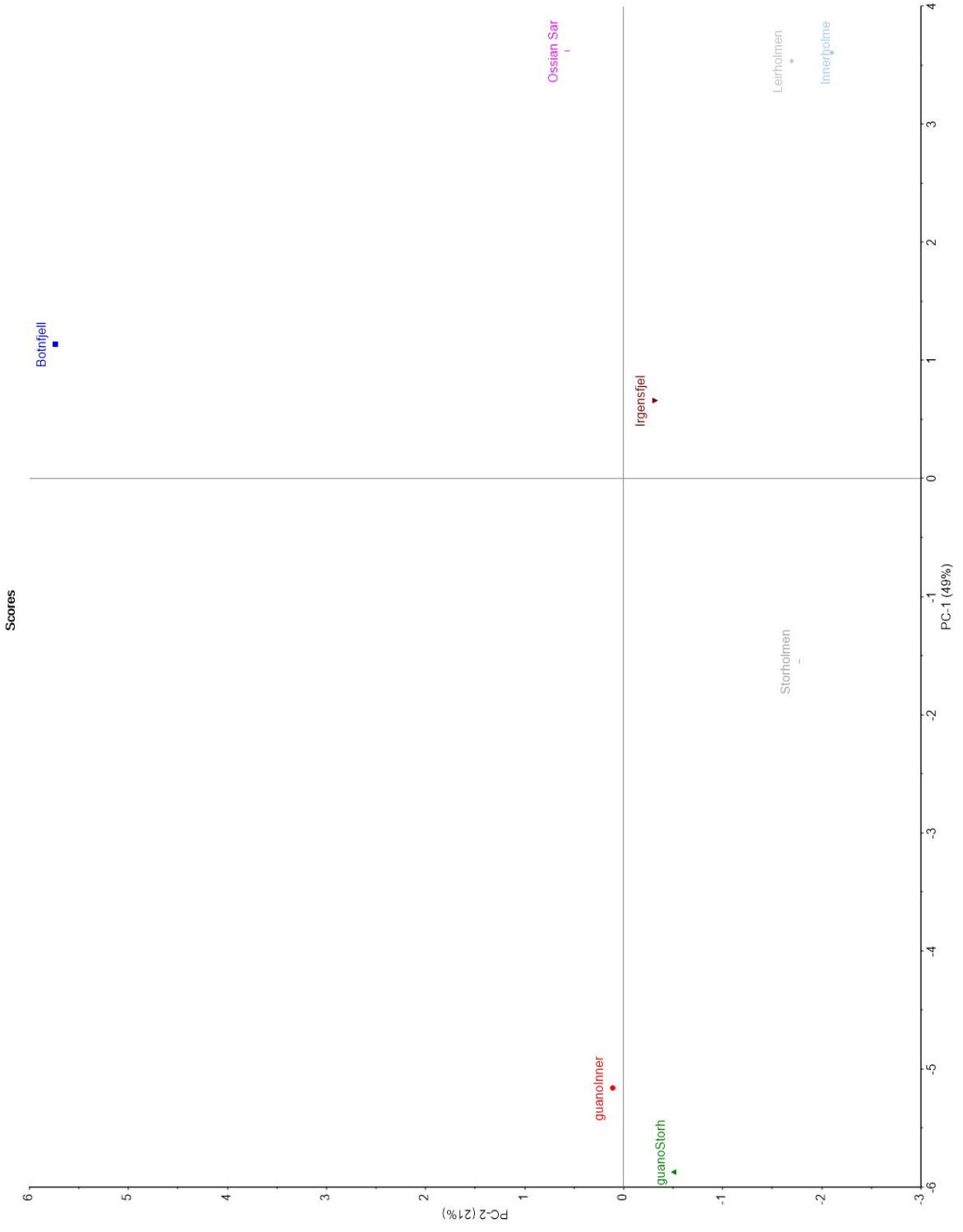

Figure 19: PCA score plot with the mean concentration from each location.

5.6 Persistent organic pollutants

None of the PCBss were detected over LOD in any of the samples. Kristiansen et al found $\sum$PCB soil concentration in Ny-Ålesund in the range of 0.211-0.353 ng/g, and at Krykkjefjellet (which is the same location as Botnfjell in this project)the $\sum$PCB were detected at $10.284 ng/g$. [8] The $\sum$PCB concentrations in this project were expected to be in the same range as Kristiansen et al. [8] As the LOD for the different PCB analytes was in the range 0.42-0.57ng/g this can explain why there were not detected any PCBs.

Three of the PFAS analysed for this project were detected. 3/22 samples were detected with 4:2FTS, 9/22 were detected with MeFOSAA and 2/22 with PFHpA. There was some trouble with the matrix and the recovery was down to 10% for some of the target analytes , while it was up to 200% for other target analytes. It is also important to note that sewage sludge was used as the matrix used in the quality control, which probably has a more complex matrix than both the soil and the guano. However, a cleanup step was skipped during the extraction. This cleanup step was done on the matrix used for calculating recovery and matrix effect. This can affect the results, but the difference is considered to be small.

Kristiansen et al have also analysed for PFAS in soil influenced by birds. This study had some trouble with the matrix during the PFAS analysis, but their conclusion was that PFOS was more impacted by human activity than birds. [8] There is no indication either from Kristiansen et al study or from this project that bird-influence is affecting the PFAS concentration in soil in any way. However, it is needed a method development for analysis of PFAS in soil for this to be sure.

5.7 Quality of data

Several of the sampling locations were situated in the Kongsfjorden bird reserve, and one sample location was in the Blomstrandhamna bird reserve. Traffic in the bird reserves is prohibited during the nesting period, 15.may to 15. august. Therefore, the sampling was conducted during the period 16. august to 20.august [102]. Protection of Ossian Sars nature reserve says that traffic on, and in the area around Ossian Sars Mountain, must be conducted in a way which does not harm or deteriorate the environment. Activity in this area shall not disturb the wildlife [103].

During the fieldwork several of the samples were collected from adjacent locations and for that reason they have identical coordinates. This had to be done because of lack of suitable soil and time restrictions. In locations where it was hard to find suitable soil, soil quality was prioritised over, for example, soil depth. Finding deep enough soil was especially a problem at Leirholmen. Soil depth of the samples was not measured. Due to time limitations at the last sampling location (Irgensfjellet), soil quality was prioritised over sample size at this location.

The knife and garden trowel were picked as equipment because of their low weight and reliability in the field. The equipment was carried off and onto the boat several times and carried in challenging terrain. It was therefore important that the equipment was light and easy to handle. The sampling was also done in a remote location, and the equipment had to be reliable without any small parts that could easily be damaged. This equipment has been used several times by different projects at the department of Chemistry at NTNU and was considered reliable. The bread knife is made of stainless steel and can have contaminated the soil samples which were used for elemental analysis, but the contamination of metals of interest are considered small.

All samples were kept as intact as possible during sampling and transportation to prevent any loss of analyte of interest. Some of the analytes which were analysed in this project are semi-volatile and could be lost when the soil is disturbed. Some samples could not be taken from the ground in one piece and were therefore taken carefully with the garden trowel from the ground and into the aluminium box or paper bag. The loss of the analytes of interest because of this disturbance was considered minimal.

Aluminium boxes were used for storage of soil samples for organic analysis. They were used to prevent contamination of organic compounds to the soil, and to prevent evapo-

ration of semi-volatile compounds. Paper bags were used for storage of soil samples for elemental analysis. They were used to prevent contamination of metals, and because they are light and easy to handle. The paper bags have been used in several projects at NTNU and the metal contamination from the bags to the are considered negligible. For the guano samples, CC-cups were used for storage. They were used as they are light and easy to handle, and to prevent contamination of organic and metal analytes of interest.

During the transportation the samples were grouped together, in plastic bags, based on sampling location to prevent cross-contamination between the different sampling locations. On the transportation from Ny-Ålesund to NTNU Trondheim the samples for organic analysis were packed in aluminium foil, and the samples for elemental analysis were packed in additional paper bags to prevent contamination. Also, during this transport the samples from the same locations were grouped together in plastic bags to prevent cross-contamination.

The soil samples were air dried on the lab counter with the lid slightly open to let moist out. During this air drying there is a chance that some semi-volatile compounds of interest are lost. The loss of semi-volatile compounds was however considered as a smaller problem than potential mould growth. At air drying the temperature in the lab was assumed to be stable at 21 °C, and the loss of analyte of interest due to evaporation is therefore considered small. There is also a chance for contamination for the samples in the aluminium boxes when the lid was open. However, this contamination is also considered small.

Gloves were used during the whole sampling procedure to prevent contamination from the hands of the person doing the sampling, and cross-contamination. Due to time limitations the gloves were only changed between the different sampling locations, and not between each sample during the sampling procedure. During the homogenisation the gloves were changed between each sample to prevent cross-contamination. The gloves were also used to protect against soil parasites.

6 Conclusion

In this project soil samples were collected from the locations Ossian Sars, Botnfjell, Storholmen, Innerholmen, Irgensfjell and Leirholmen. All situated in Kongsfjorden, Svalbard. The sampling sites were divided into two groups, based on the P concentration in the soil, high and low bird-influence. The aim was to investigate a possible increase in pollution by seabirds. The sites were therefore divided into two groups: Ossian Sars and Botnfjell in the high bird-influenced group, and Storholmen, Innerholmen, Irgensfjell and Leirholmen in the low bird-influenced group.

Previous studies have shown an increase in Cd, As, Co, Cu, Li, Mn, Mo, Ni, Sb, Sr, K and Zn concentration in bird influenced soil. The distribution of these elements between the high and low bird-influenced group were tested with a Man-Witney U test. The elements Cd, Cu, Sb, Sr and Zn had significantly higher concentration in the soil in the high bird-influenced group than the low. In the PCA for the soil samples (section 5.4) the elements Cd, Cu, Sb, Sr and Zn all load strongly onto PC2 in the positive direction (Figure 16) which is identified as the direction where the variation is explained by bird-influence. These are all good indications that Cd, Cu, Sb, Sr and Zn are enriched in soil influenced by birds.

In both soil and guano, all the seven PCBs analysed for were under LOD. Three of the PFAS compounds were found in a few of the soil and guano samples. There is no indication that these pollutants are enriched in soil influenced by birds. However, a method development of PFAS in soil is needed for this conclusion to be more certain.

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7 Appendix

A Sampling site

Table 14: Information about the parent material at the different sampling sites. The information is found at GeoSvalbard [104].

Sampling site	**Parent material**
Innerholmen	Banded marble
Storholmen	Banded marble
Leirholmen	Banded marble
Ossian Sars	Mica schist
Irgensfjellet	Banded marble
Botnfjell	Carbonate rocks

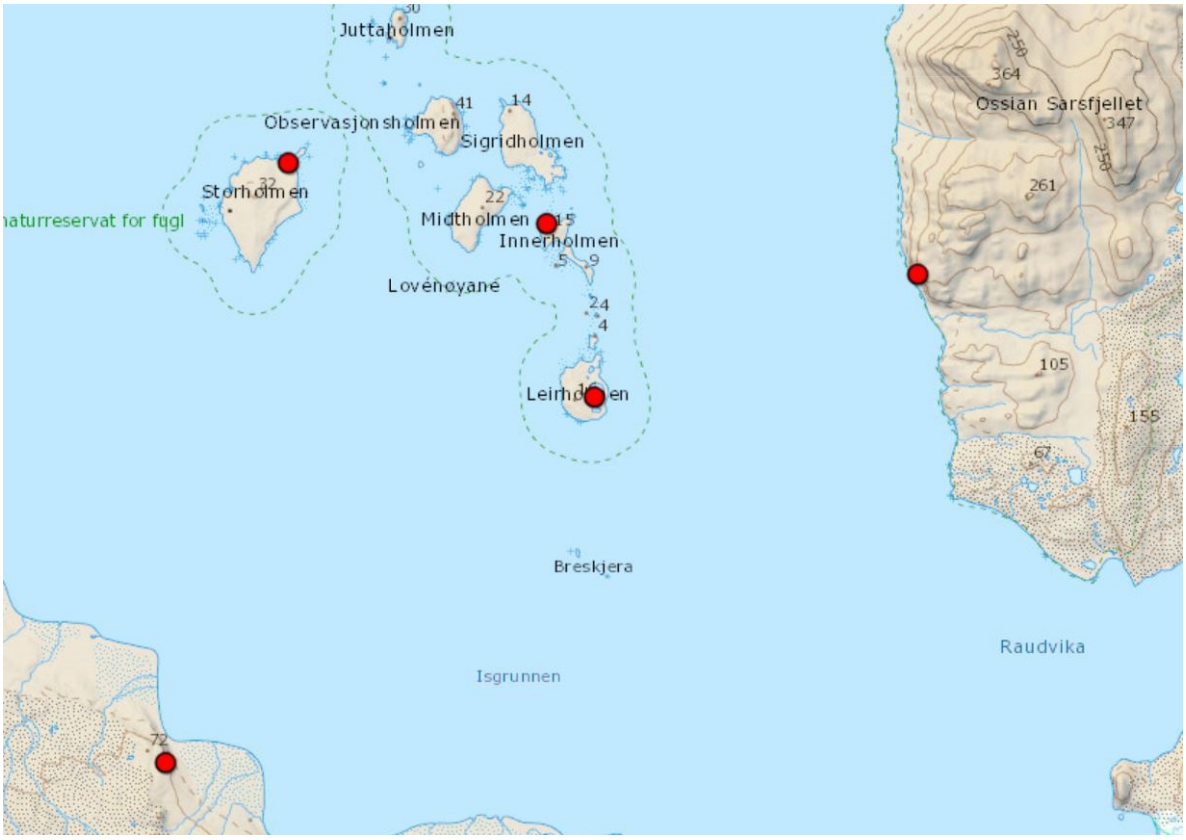

Figure 20: A detailed map of the locations of the sampling sites Botnfjell, Ossian Sars, Innerholmen, Leirholmen and Storholmen indicated with a red dot. Illustration made in TopoSvalbard [21], Norwegian Polar Institute.

Figure 21: A detailed map of Blomstrandhalvøya. The sampling location underneath Irgensfjellet is indicated with a red dot. Illustration made in TopoSvalbard [21], Norwegian Polar Institute.

Table 15: Sampling sites for soil samples with coordinates. E indicates the sample is taken for elemental analysis. O indicates the sample is taken for organic analysis.

Sample	**E/O**	**Latitude (N)**	**Longitude (E)**
Innerholmen 1	E	78°55.890	12°19.015
Innerholmen 2	O	78°55.890	22°19.017
Innerholmen 3	E	78°55.890	12°19.017
Innerholmen 4	E	78°55.890	12°19.017
Innerholmen 5	O	78°55.890	52°19.017
Innerholmen 6	E	78°55.890	12°19.001
Storholmen 1	O	78°56.088	12°13.662
Storholmen 2	E	78°56.088	12°13.662
Storholmen 3	E	78°56.086	12°13.649
Storholmen 4	O	78°56.086	12°13.641
Storholmen 5	E	78°56.086	12°13.641
Storholmen 6	E	78°56.085	12°13.648
Storholmen 7	O	78°56.088	12°13.660
Storholmen 8	E	78°56.088	12°13.660
Leirholmen 1	E	78°55.225	12°20.252
Leirholmen 2	O	78°55.225	12°20.254
Leirholmen 3	E	78°55.221	12°20.211
Leirholmen 4	E	78°55.228	12°20.217
Leirholmen 5	O	78°55.228	12°20.217
Leirholmen 6	E	78°55.228	12°20.217
Ossian Sars 1	E	78°55.757	12°26.602
Ossian Sars 2	O	78°55.751	12°26.649
Ossian Sars 3	O	78°55.750	12°26.707
Ossian Sars 4	O	78°55.750	12°26.707
Ossian Sars 5	E	78°55.750	12°26.707
Ossian Sars 6	E	78°55.750	12°26.707
Ossian Sars 7	E	78°55.750	12°26.707
Irgensfjellet 1	E	78°59.751	12°06.710
Irgensfjellet 2	O	78°59.751	12°06.710
Irgensfjellet 3	E	78°59.723	12°06.803
Botnfjell 1	E	78°53.770	12°11.802
Botnfjell 2	E	78°53.763	12°11.789
Botnfjell 3	O	78°53.763	12°11.789
Botnfjell 4	E	78°53.755	12°11.799
Botnfjell 5	O	78°53.755	12°11.799

Table 16: Ranking of sampling sites based on bird influence. The ranking were done on the basis of the observed number of birds and the bird species composition at the different locations. The sampling sites were ranked from highest to lowest bird influence, with 1 as higest and 6 as lowest bird influence. Ossian Sars was expected to have the highest bird influence and Innerholmen the lowest. The dominant bird species at the sampling sites was Common Eider (*Somateria mollissima*), Black-legged kittiwake (*Rissa tridactyla*), Barnacle goose (*Branta leucopsis*) and Brünnich guillemot (*Uria lomvia*). The birds were either counted as individuals (IN) or occupied nests (ON). The numbers in this table is from the SEAPOP program [105], personal comments from Geir Wing Gabrielsen* and personal comments from Pierre Blevin**.

Seabird influence	**Sampling site**	**Common Eider** (Ærfugl) *Somateria mollissima*	**Black-legged kittiwake** (Krykkje) *Rissa tridactyla*	**Barnacle goose** (Hvitkinngås) *Branta leucopsis*	**Brünnich guillemot** (Polarlomvi) *Uria lomvia*
1	Ossian Sars		2011: 1936 ON		2011: 1358 IN
2	Irgensfjellet		2011: 908 ON		2011: 239 IN
3	Botnfjell		2016: 350 ON**		2011: 50 IN
4	Storholmen	2020: 557 ON*		2019: 789 ON*	
5	Leirholmen	2021: 355 IN*		2021: 13 IN*	
6	Innerholmen	2021: 30 IN*		2021: 12 IN*	

B TIC, TOC and ROC results

Table 17: Mean TOC [%] value in soil from each sampling site. How many samples are taken from each sampling site is indicated by n.

Sampling site	**n**	**TOC [%]**
Innerholmen	6	5.63±1.09
Storholmen	8	20.8±3.18
Leirholmen	6	4.72±2.06
Ossian Sars	7	5.31±8.65
Irgensfjellet	3	10.1±2.60
Botnfjell	5	20.7±8.04

Table 18: Result of total organic carbon (TOC), residual oxidisable carbon (ROC) and total inorganic carbon (TIC) for all the soil samples.

Sample	**TOC (%)**	**ROC (%)**	**TIC(%)**
Innerholmen 1	4.72	1.56	1.87
Innerholmen 2	6.35	2.25	1.61
Innerholmen 3	5.53	2.17	2.20
Innerholmen 4	4.53	1.32	0.94
Innerholmen 5	5.25	1.72	1.15
Innerholmen 6	7.42	2.55	1.76
Storholmen 1	15.59	1.92	0.12
Storholmen 2	18.90	1.60	0.08
Storholmen 3	17.79	1.92	0.14
Storholmen 4	21.34	1.92	0.10
Storholmen 5	20.79	2.03	0.10
Storholmen 6	24.26	1.96	0.13
Storholmen 7	23.62	2.32	0.17
Storholmen 8	24.05	2.18	0.18
Leirholmen 1	3.03	1.12	2.36
Leirholmen 2	1.75	0.79	2.61
Leirholmen 3	7.46	1.94	1.72
Leirholmen 4	4.82	1.39	1.60
Leirholmen 5	5.27	1.53	1.47
Leirholmen 6	6.00	1.69	1.67
Ossian Sars 1	0.44	0.43	2.64
Ossian Sars 2	0.81	0.44	2.48
Ossian Sars 3	2.87	0.84	1.90
Ossian Sars 4	24.75	1.47	0.05
Ossian Sars 5	1.80	0.56	2.01
Ossian Sars 6	3.60	0.85	1.64
Ossian Sars 7	2.87	0.94	2.20
Irgensfjellet 1	7.33	2.38	1.05
Irgensfjellet 2	12.51	1.91	1.05
Irgensfjellet 3	10.33	2.44	0.71
Botnfjell 1	23.58	2.52	0.35
Botnfjell 2	32.33	1.57	0.27
Botnfjell 3	20.97	2.34	0.62
Botnfjell 4	11.87	2.36	1.79
Botnfjell 5	14.61[83]	1.70	0.65

C PCB analysis

Table 19: Instrumental and sample LOD and LOQ for analysis PCB with GC-MS. The sample LOD and LOQ were obtained from 1 ml standard solution volume and 0.5g sample weight that was analysed with GC-MS.

	Instrument		Sample	
Analyte	**LOD(ng/ml)**	**LOQ(ng/ml)**	**LOD(ng/g)**	**LOQ (ng/g)**
PCB-28	0.28	0.94	0.57	1.9
PCB-52	0.28	0.93	0.56	1.9
PCB-101	0.21	0.70	0.42	1.4
PCB-118	0.26	0.87	0.52	1.7
PCB-138	0.22	0.73	0.44	1.5
PCB-153	0.23	0.78	0.46	1.5
PCB-180	0.26	0.87	0.52	1.7

Table 20: Matrix effect(ME) given in percent, of PCB target analytes in organic soil analysed with GC-MS.

Analyte	**ME**[%] 50ng/ml	**ME**[%] 100ng/ml
PCB-28	-18	15
PCB-52	-15	18
PCB-101	-17	13
PCB-118	-8	28
PCB-138	-13	16
PCB-153	-9	23
PCB-180	-6	23

D PFAS analysis

Table 21: External standards purchased for PFAS analysis.

Chemicals and materials	**Concentrations, specifications**	**Supplier**
DecaS	50 $\mu g/ml$ in methanol	Wellington Laboratories (Canada)
PFAC-MXA	mixture of PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFUnA, PFTriDA, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, and PFDoDS, 2 $\mu g/ml$ of each component in methanol	Wellington Laboratories (Canada)
P37DMOA	50 $\mu g/ml$ in methanol	Wellington Laboratories (Canada)
NaDONA	50 $\mu g/ml$ in methanol	Wellington Laboratories (Canada)
PFECHS	50 $\mu g/ml$ in methanol	Wellington Laboratories (Canada)
4:2FTS	50 $\mu g/ml$ in methanol	Wellington Laboratories (Canada)
6:2 FTS	50 $\mu g/ml$ in methanol	Wellington Laboratories (Canada)
8:2FTS	50 $\mu g/ml$ in methanol	Wellington Laboratories (Canada)
10:2FTS	50 $\mu g/ml$ in methanol	Wellington Laboratories (Canada)

Table 22: Internal and external standards purchased for PFAS analysis.

Chemicals and materials	**Concentrations, specifications**	**Supplier**
FOSAA	50 $\mu g/ml$ in methanol	Wellington Laboratories (Canada)
MeFOSAA	50 $\mu g/ml$ in methanol	Chiron AS (Trondheim, NO)
PFOSA	50 $\mu g/ml$	Wellington Laboratories (Canada)
MeFOSA	50 $\mu g/ml$ in acetonitrile	Chiron AS (Trondheim, NO)
EtFOSA	50 $\mu g/ml$ in methanol	Wellington Laboratories (Canada)
Gen-X	50 $\mu g/ml$ in methanol	Wellington Laboratories (Canada)
9Cl-PF3ONS	50 $\mu g/ml$ in methanol	Wellington Laboratories (Canada)
PFOA ($^{13}C_8$, 99%) (internal standard)	50$\mu g/ml$ in methanol	Cambridge Isotope Laboratories (Massachusetts, USA)
PFOS ($^{13}C_8$) (internal standard)	50 $\mu g/ml$ in methanol	Cambridge Isotope Laboratories (Massachusetts, USA)
6:2FTS ($^{13}C_2$) (internal standard)	50 $\mu g/ml$ in methanol	Cambridge Isotope Laboratories (Massachusetts, USA)

Table 23: Absolute and relative recoveries (Rabs, Rrel) given in percent, of PFAS target analytes in organic soil analysed with UPLC-MS/MS. Were the fortification level is under the limit of detection, the recovery is not calculated, this is indicated with "-".

	2.5 ppb		25 ppb		50ppb	
Analyte	**Rabs**[%]	**Rrel**[%]	**Rabs**[%]	**Rrel**[%]	**Rabs**[%]	**Rrel**[%]
DecaS	117	151	220	264	63	74
Gen-X	-	-	72	86	91	110
PFPeA	55	71	75	90	81	95
PFHxA	60	77	71	85	85	100
4:2FTS	71	91	90	110	92	110
7H-PFHpA	50	65	93	110	91	110
NaDONA	54	70	90	110	91	110
PFOA	55	72	82	98	82	96
6:2FTS	57	74	84	100	93	110
PFHpS	110	147	96	120	110	130
PFNA	54	69	73	87	94	110
P37DMOA	53	68	77	92	87	100
PFOSA	181	230	170	200	42	49
PFOS	53	69	70	83	82	96
MeFOSA	26	33	17	20	14	17
PFDA	49	64	77	92	89	100
EtFOSA	61	78	36	43	11	13
8:2FTS	59	76	79	94	91	110
9Cl-PF3ONS	58	75	77	92	94	110
FOSAA	28	36	19	23	18	22
PFUnA	32	41	74	89	80	94
MeFOSAA	9.1	12	15	18	15	18
10:2FTS	53	69	54	65	60	71
PFTriDA	29	37	37	45	28	32
PFPeS	50	65	68	82	85	100
PFHpA	41	53	74	88	82	96
PFHxS	49	63	72	86	85	100
PFECHS	57	74	82	99	96	110
PFNS	46	59	67	80	81	95
PFDS	44	57	62	74	70	82
PFDoDs	34	44	43	52	23	27

Table 24: Matrix factor (MF) and matrix effect (ME)(in %) of PFAS target analytes in organic soil analysed with UPLC-MS/MS. Were the fortification level is under the limit of detection, the MF and ME is not calculated, this is indicated with "-".

	2.5 ppb		25 ppb		50ppb	
Analyte	**MF**	**ME**[%]	**MF**	**ME**[%]	**MF**	**ME**[%]
DecaS	48	4700	0.64	-36	0.68	-32
Gen-X	-	-	1.2	24	1.1	5.7
PFPeA	1.63	63	0.69	-31	0.58	-42
PFHxA	1.4	44	0.76	-24	0.61	-39
4:2FTS	3.0	200	1.8	85	2.0	99
7H-PFHpA	0.79	-21	0.55	-45	0.65	-35
NaDONA	0.59	-41	0.48	-52	0.59	-41
PFOA	0.67	-33	0.50	-50	0.50	-50
6:2FTS	2.3	130	1.6	61	1.8	76
PFHpS	4.2	320	0.89	-11	0.85	-15
PFNA	0.44	-56	0.35	-65	0.27	-73
P37DMOA	0.85	-15	0.66	-34	0.82	-18
PFOSA	0.25	-75	0.25	-75	0.30	-70
PFOS	1.2	19	0.77	-23	0.67	-33
MeFOSA	0.41	-59	0.51	-49	0.30	-70
PFDA	0.64	-36	0.39	-61	0.39	-61
EtFOSA	0.17	-83	0.25	-75	0.15	-85
8:2FTS	1.8	78	1.3	30	1.5	51
9Cl-PF3ONS	0.75	-25	0.61	-39	0.77	-23
FOSAA	0.29	-71	0.22	-78	0.34	-66
PFUnA	0.40	-60	0.26	-74	0.32	-68
MeFOSAA	0.075	-93	0.077	-92	0.12	-88
10:2FTS	0.70	-30	0.57	-43	0.75	-25
PFTriDA	0.047	-95	0.032	-97	0.068	-93
PFPeS	1.3	26	0.88	-12	0.81	-19
PFHpA	0.90	-9.7	0.56	-44	0.47	-53
PFHxS	1.3	33	0.87	-13	0.80	-20
PFECHS	0.79	-21	0.63	-37	0.75	-25
PFNS	0.93	-6.7	0.67	-33	0.64	-36
PFDS	0.80	-20	0.53	-47	0.54	-46
PFDoDs	0.048	-95	0.045	-95	0.10	-90

E Boxplot of selected elements by sampling site

Non-parametric Kruskal-Wallis test were done on the selected elements P, Cd, As, Co, Cu, Li, Mn, Mo, Ni, Sb, Sr, K, Zn, Ba and Pb by sampling sites Botnfjell (BF), Innerholmen (IH), Irgensfjellet (IrgF), Leirholmen (LH), Ossian Sars (OS) and Storholmen (SH). All elements were significantly different distributed over the different sampling sites except for Pb which were not.

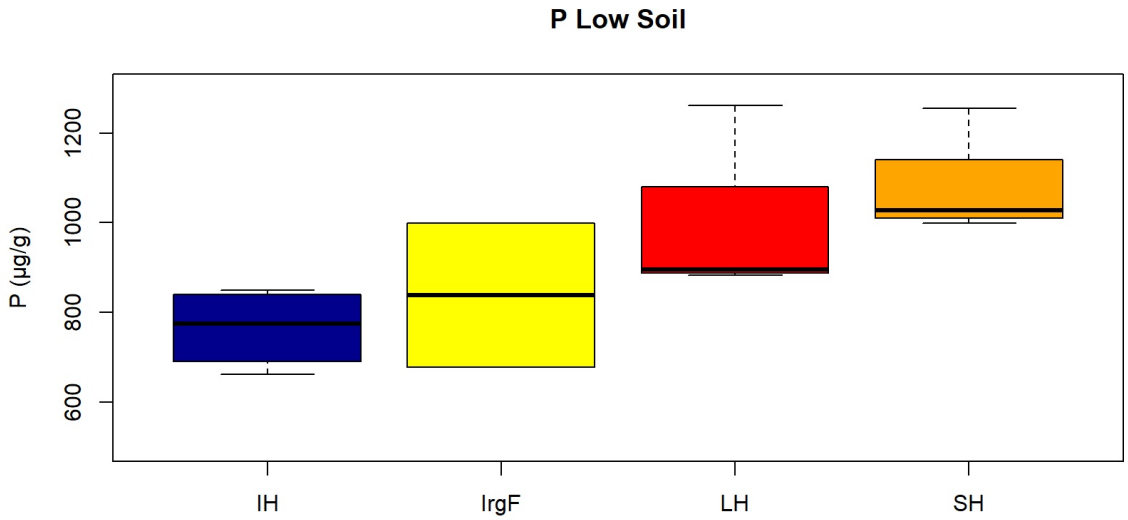

Figure 22: Boxplot of P content at Irgensfjell(IrgF), Storholmen (SH), Innerholmen (IH) and Leiholmen (LH). The P concentration is significantly different (p=0.03) across sampling sites. This boxplot have excluded the sampling sites Botnfjell (BF) and Ossian Sars (OS) which had the highest P concentration.

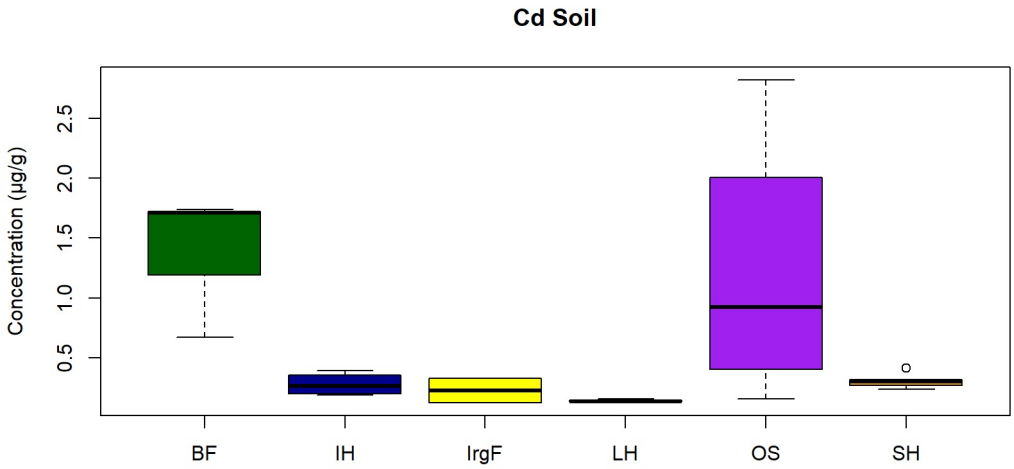

Figure 23: Boxplot of Cd content at the different locations. The Cd concentration is significantly different (p=0.02) across sampling sites. The sampling sites are Botnfjell (BF), Innerholmen (IH), Irgensfjell (IrgF), Leirholmen (LH), Ossian Sars (OS) and Storholmen (SH).

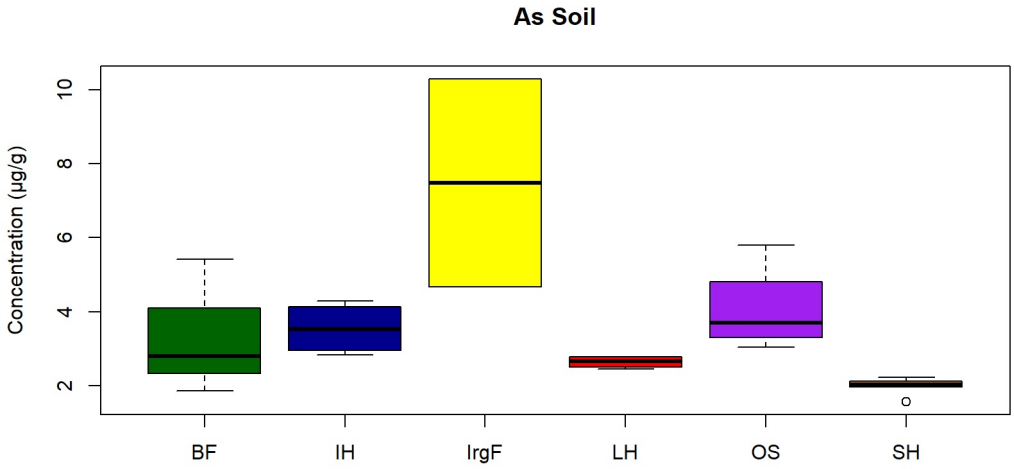

Figure 24: Boxplot of As content at the different locations. The As concentration is significantly different (p=0.009) across sampling sites. The sampling sites are Botnfjell (BF), Innerholmen (IH), Irgensfjell (IrgF), Leirholmen (LH), Ossian Sars (OS) and Storholmen (SH).

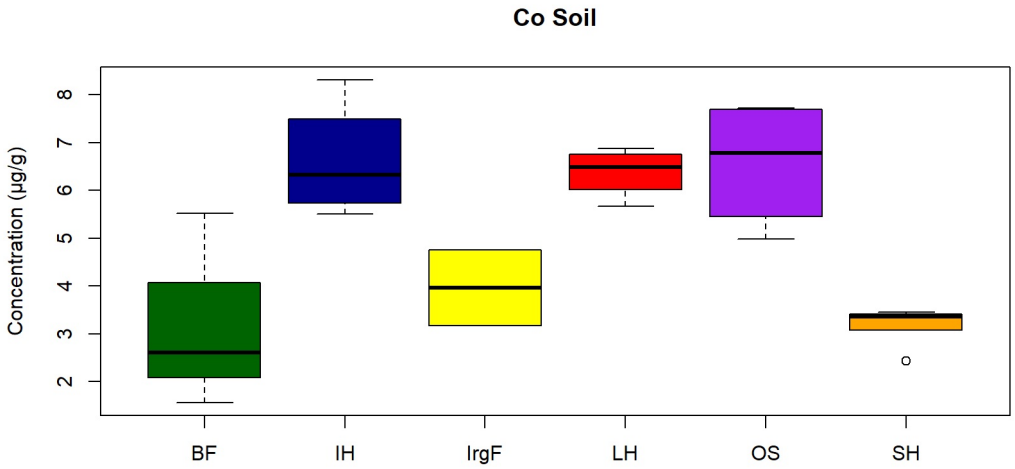

Figure 25: Boxplot of Co content at the different locations. The Co concentration is significantly different (p=0.01) across sampling sites. The sampling sites are Botnfjell (BF), Innerholmen (IH), Irgensfjell (IrgF), Leirholmen (LH), Ossian Sars (OS) and Storholmen (SH).

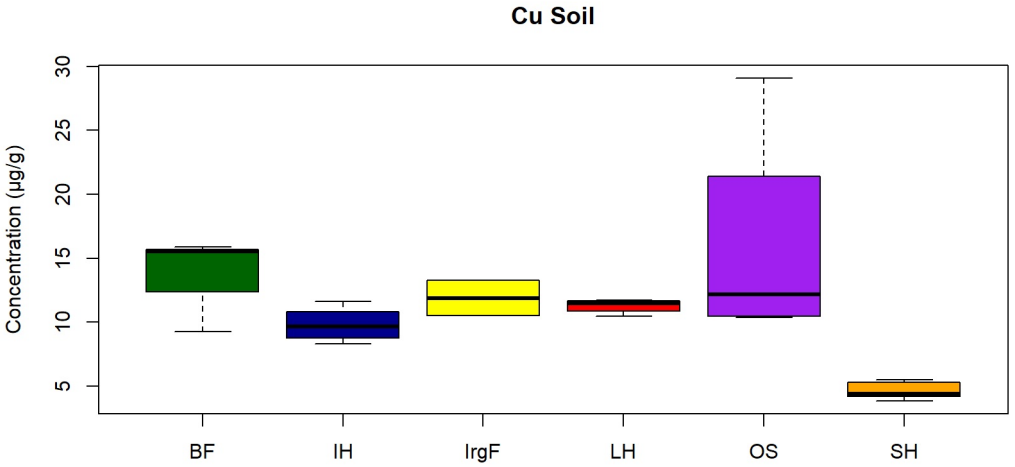

Figure 26: Boxplot of Cu content at the different locations. The Cu concentration is significantly different (p=0.02) across sampling sites. The sampling sites are Botnfjell (BF), Innerholmen (IH), Irgensfjell (IrgF), Leirholmen (LH), Ossian Sars (OS) and Storholmen (SH).

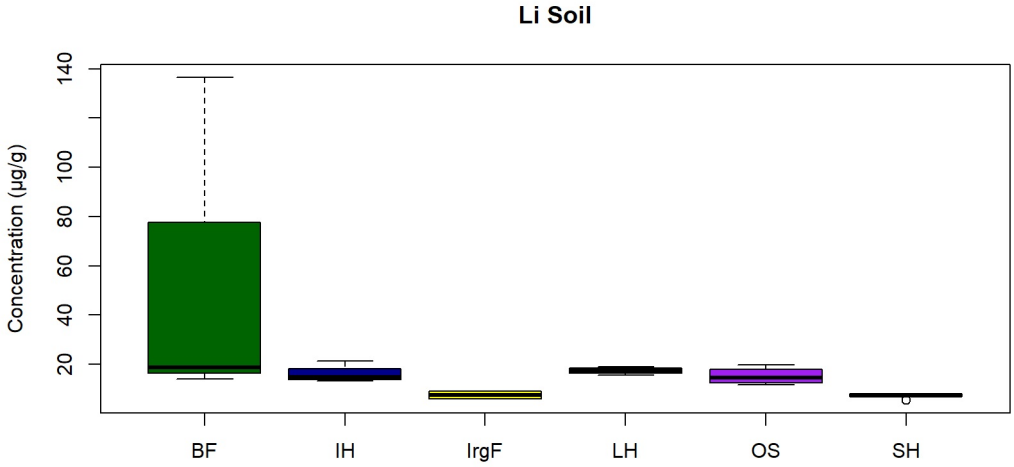

Figure 27: Boxplot of Li content at the different locations. The Li concentration is significantly different (p=0.01) across sampling sites. The sampling sites are Botnfjell (BF), Innerholmen (IH), Irgensfjell (IrgF), Leirholmen (LH), Ossian Sars (OS) and Storholmen (SH).

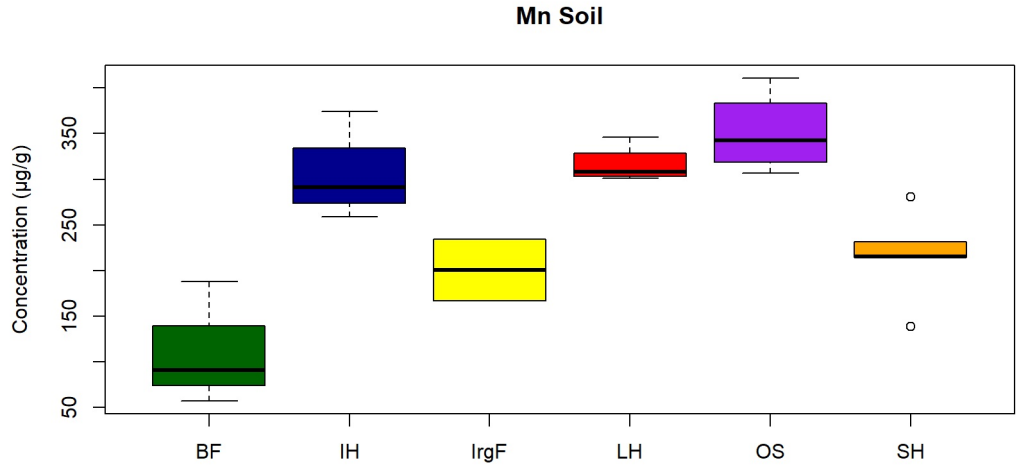

Figure 28: Boxplot of Mn content at the different locations. The Mn concentration is significantly different (p=0.004) across sampling sites. The sampling sites are Botnfjell (BF), Innerholmen (IH), Irgensfjell (IrgF), Leirholmen (LH), Ossian Sars (OS) and Storholmen (SH).

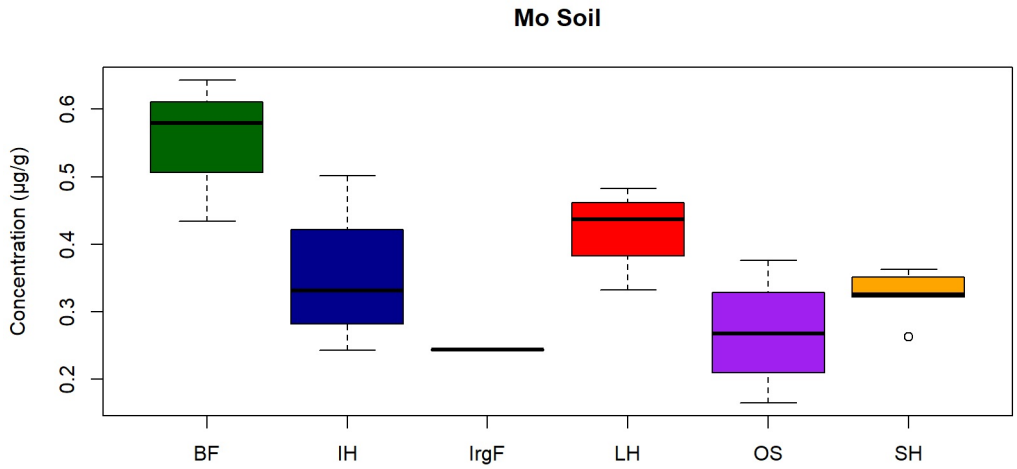

Figure 29: Boxplot of Mo content at the different locations. The Mo concentration is significantly different (p=0.03) across sampling sites. The sampling sites are Botnfjell (BF), Innerholmen (IH), Irgensfjell (IrgF), Leirholmen (LH), Ossian Sars (OS) and Storholmen (SH).

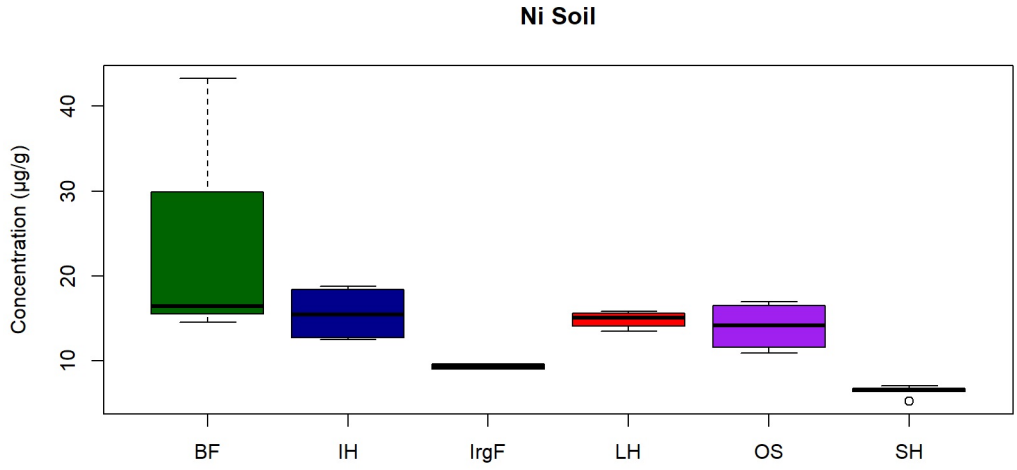

Figure 30: Boxplot of Ni content at the different locations. The Ni concentration is significantly different (p=0.01) across sampling sites. The sampling sites are Botnfjell (BF), Innerholmen (IH), Irgensfjell (IrgF), Leirholmen (LH), Ossian Sars (OS) and Storholmen (SH).

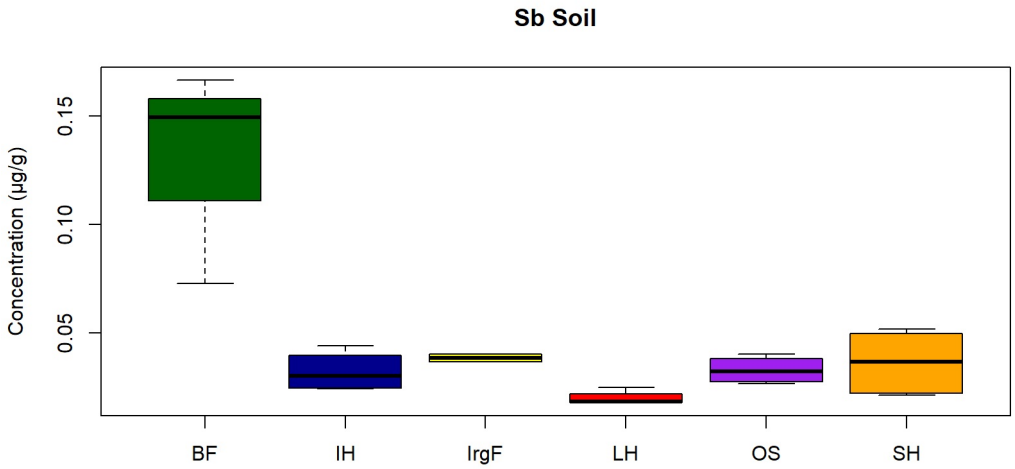

Figure 31: Boxplot of Sb content at the different locations. The Sb concentration is significantly different (p=0.02) across sampling sites. The sampling sites are Botnfjell (BF), Innerholmen (IH), Irgensfjell (IrgF), Leirholmen (LH), Ossian Sars (OS) and Storholmen (SH).

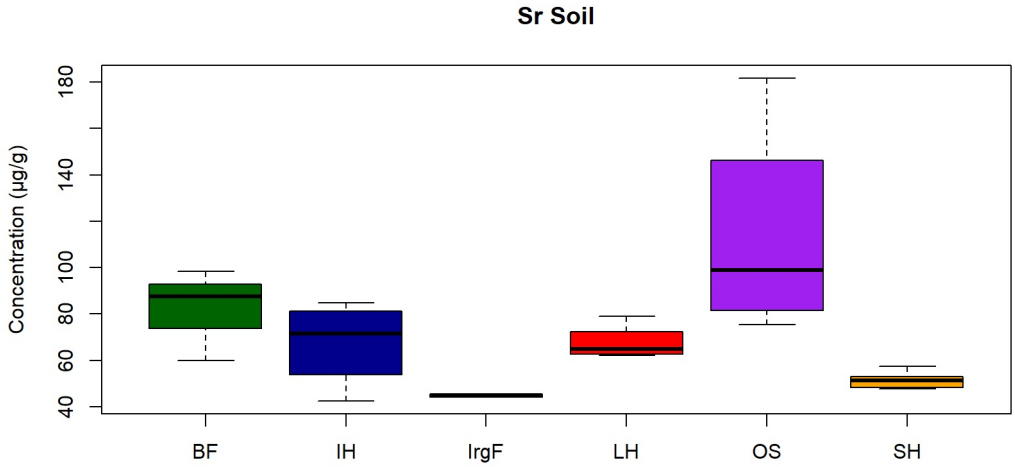

Figure 32: Boxplot of Sr content at the different locations. The Sr concentration is significantly different (p=0.02) across sampling sites. The sampling sites are Botnfjell (BF), Innerholmen (IH), Irgensfjell (IrgF), Leirholmen (LH), Ossian Sars (OS) and Storholmen (SH).

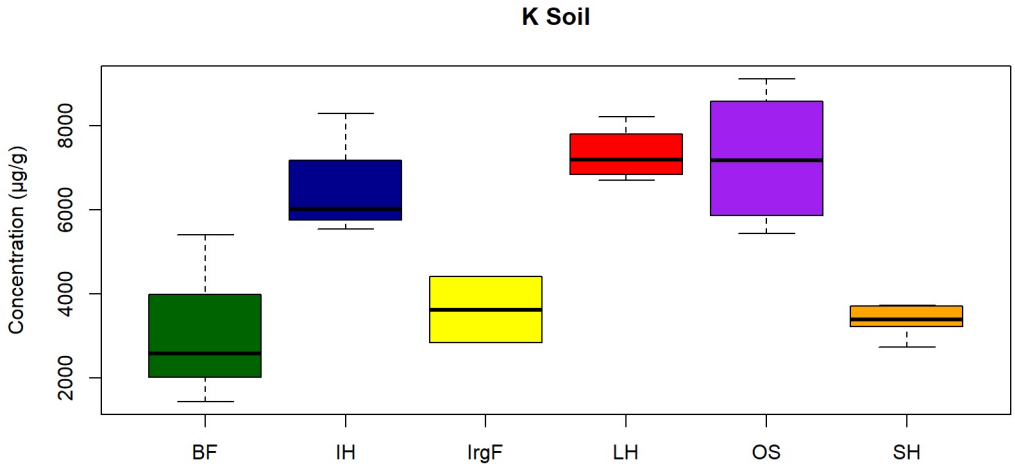

Figure 33: Boxplot of K content at the different locations. The K concentration is significantly different (p=0.006) across sampling sites. The sampling sites are Botnfjell (BF), Innerholmen (IH), Irgensfjell (IrgF), Leirholmen (LH), Ossian Sars (OS) and Storholmen (SH).

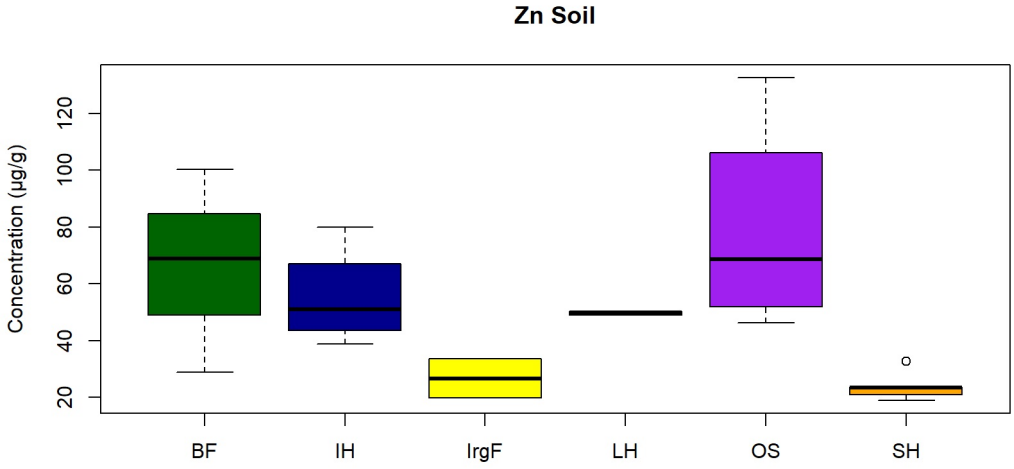

Figure 34: Boxplot of Zn content at the different locations. The Zn concentration is significantly different (p=0.02) across sampling sites. The sampling sites are Botnfjell (BF), Innerholmen (IH), Irgensfjell (IrgF), Leirholmen (LH), Ossian Sars (OS) and Storholmen (SH).

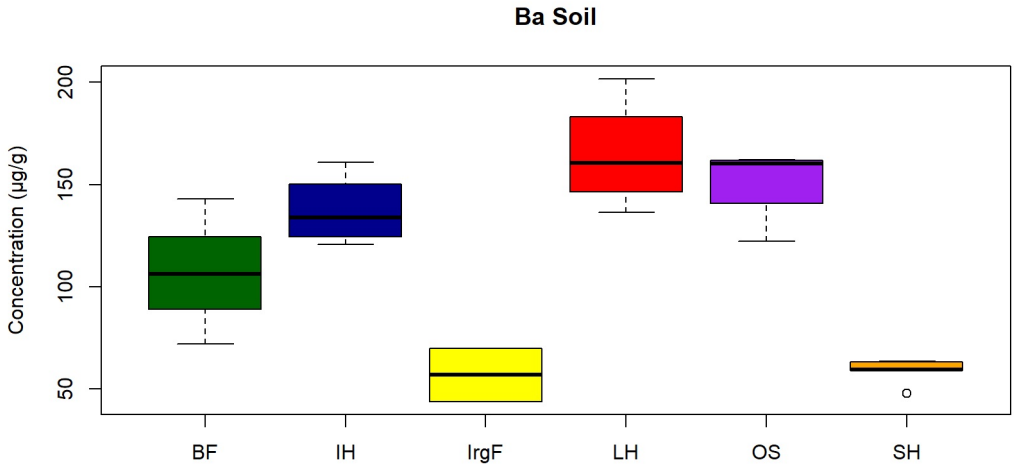

Figure 35: Boxplot of Ba content at the different locations. The Ba concentration is significantly different (p=0.006) across sampling sites. The sampling sites are Botnfjell (BF), Innerholmen (IH), Irgensfjell (IrgF), Leirholmen (LH), Ossian Sars (OS) and Storholmen (SH).

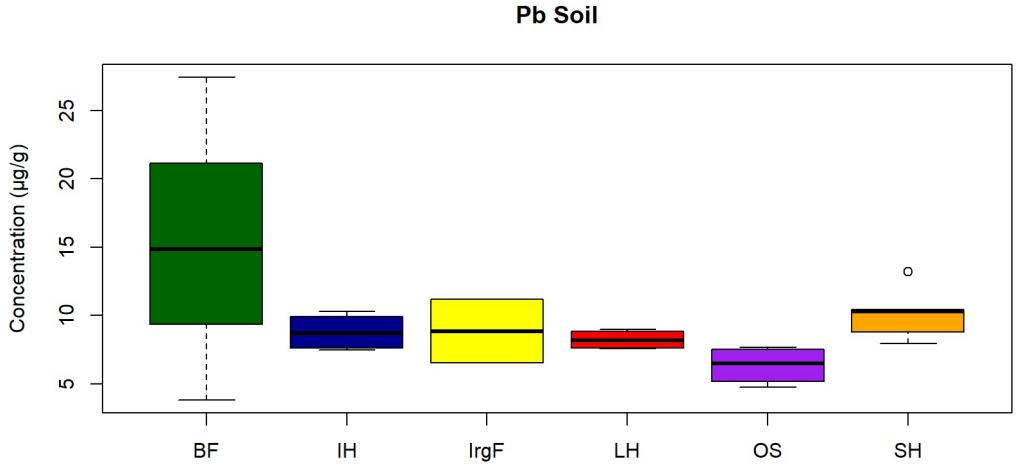

Figure 36: Boxplot of Pb content at the different locations. Pb concentration is **not** significantly different (p=0.2) across sampling sites. The sampling sites are Botnfjell (BF), Innerholmen (IH), Irgensfjell (IrgF), Leirholmen (LH), Ossian Sars (OS) and Storholmen (SH).

F Boxplot of selected elements by bird influence

Non-parametric Mann Whitney U test were done on the selected elements P, Cd, As, Co, Cu, Li, Mn, Mo, Ni, Sb, Sr, K, Zn, Ba and Pb by sites with high or low bird influence. The elements P, Cd, Cu, Sb, Sr and Zn showed significant higher concentration at high bird influenced sites than at low bird influenced sites. The elements As, Co, Li, Mn, Mo, Ni, K, Ba and Pb showed no significant difference in concentration from high and low bird influenced sites.

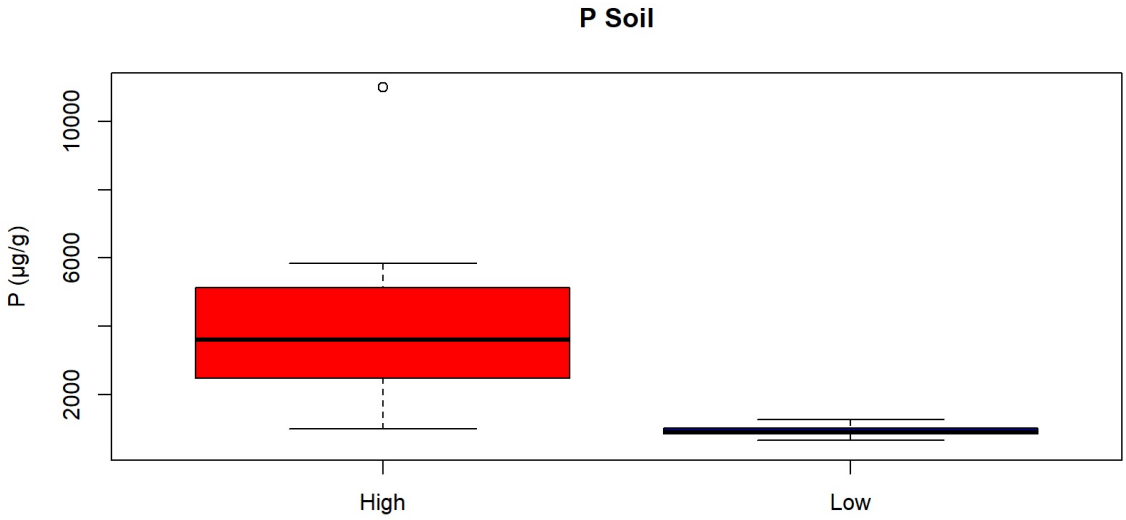

Figure 37: Boxplot of P content at high and low bird influence. P concentration is significantly different (p=0.0005) in high and low bird influenced areas.

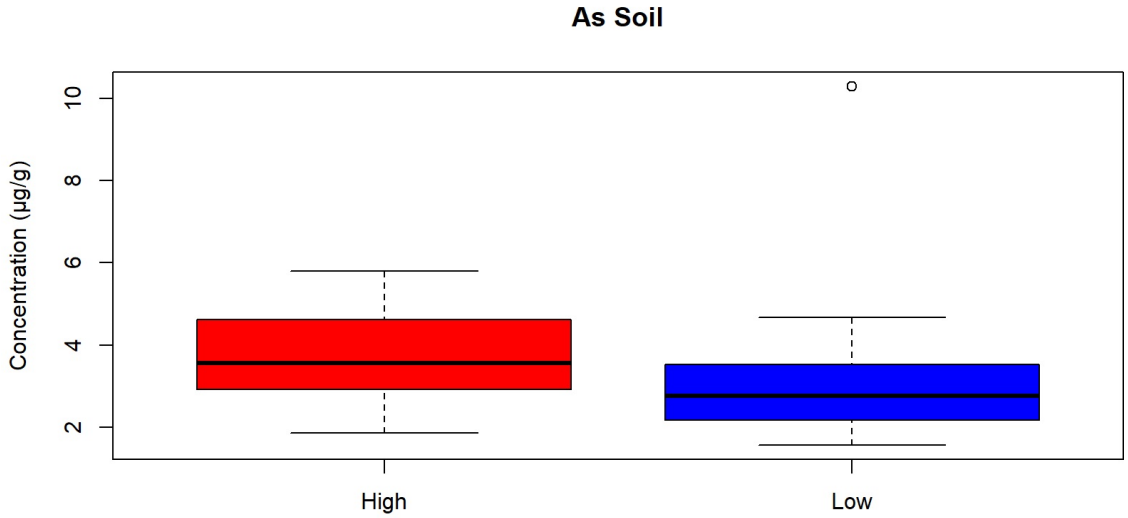

Figure 38: Boxplot of As content at high and low bird influence. As concentration is **not** significantly different (p=0.2) in high and low bird influenced areas.

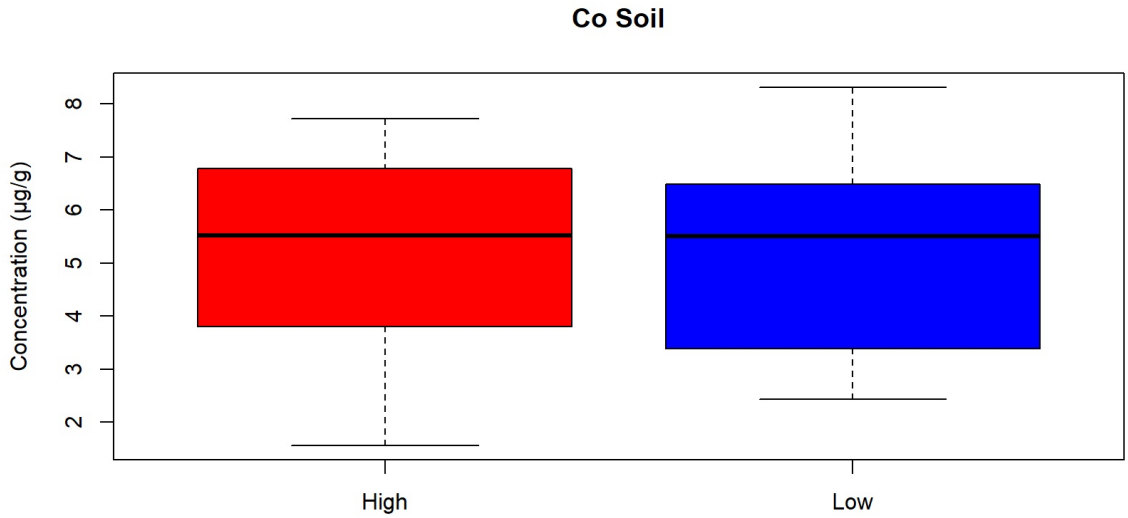

Figure 39: Boxplot of Co content at high and low bird influence. Co concentration is **not** significantly different (p=1) in high and low bird influenced areas.

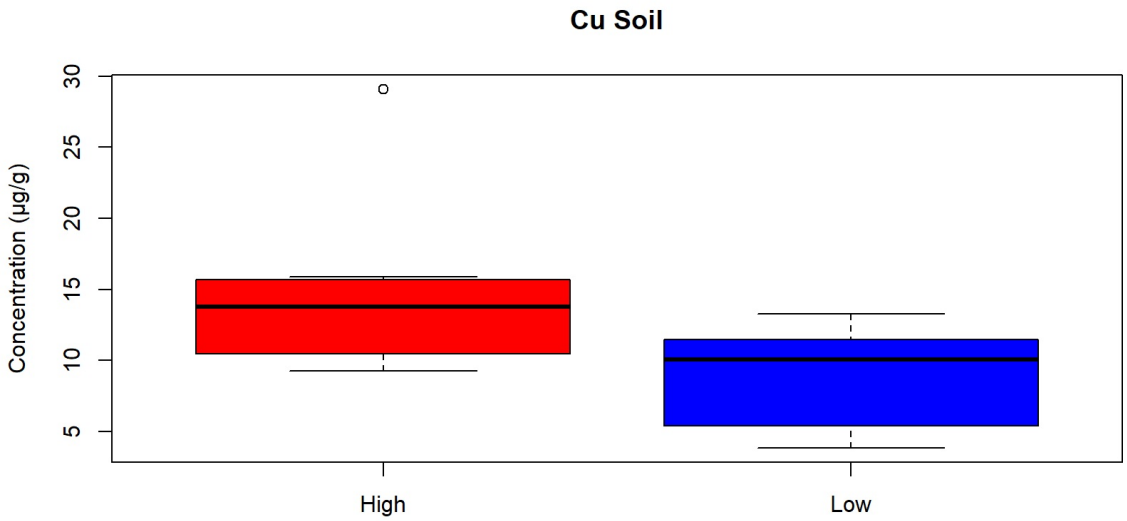

Figure 40: Boxplot of Cu content at high and low bird influence. Cu concentration is significantly different (p=0.02) in high and low bird influenced areas.

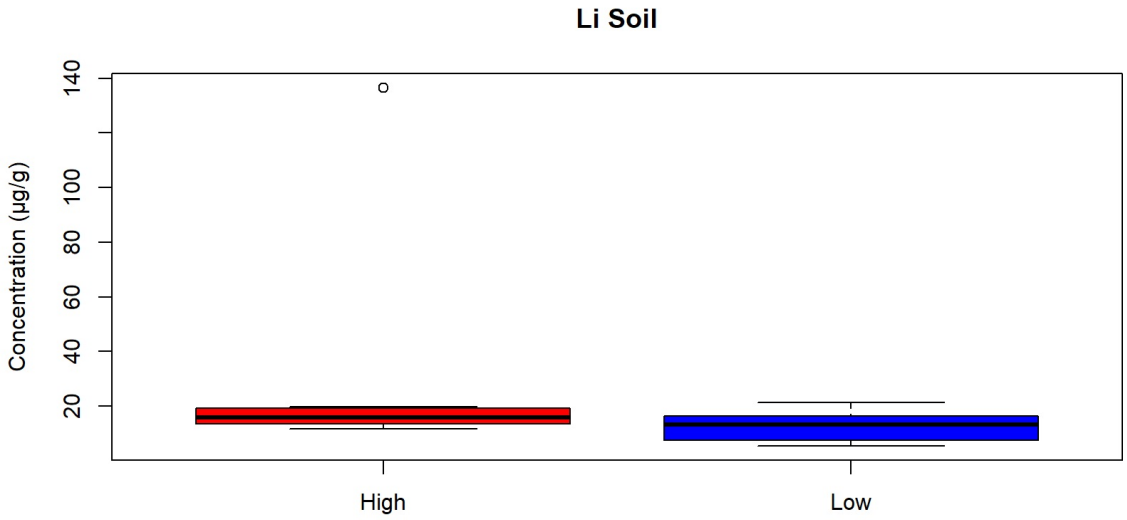

Figure 41: Boxplot of Li content at high and low bird influence. Li concentration is **not** significantly different (p=0.1) in high and low bird influenced areas.

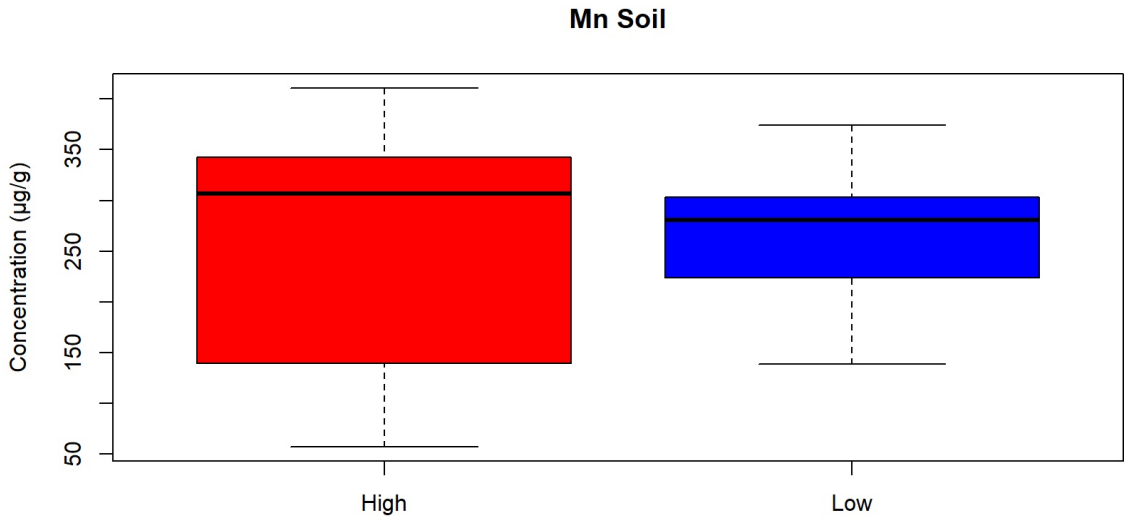

Figure 42: Boxplot of Mn content at high and low bird influence. Mn concentration is **not** significantly different (p=0.8) in high and low bird influenced areas.

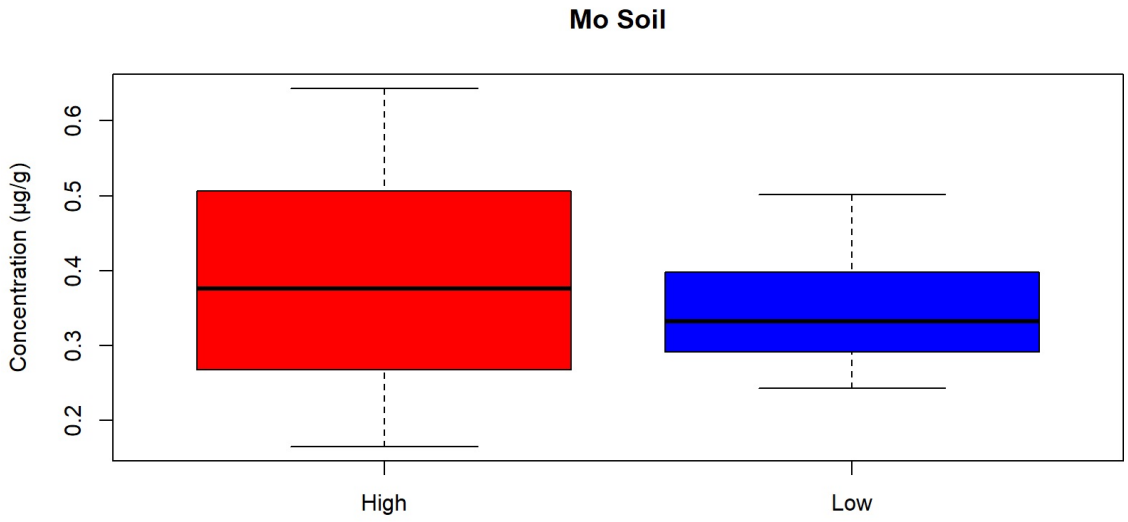

Figure 43: Boxplot of Mo content at high and low bird influence. Mo concentration is **not** significantly different (p=0.6) in high and low bird influenced areas.

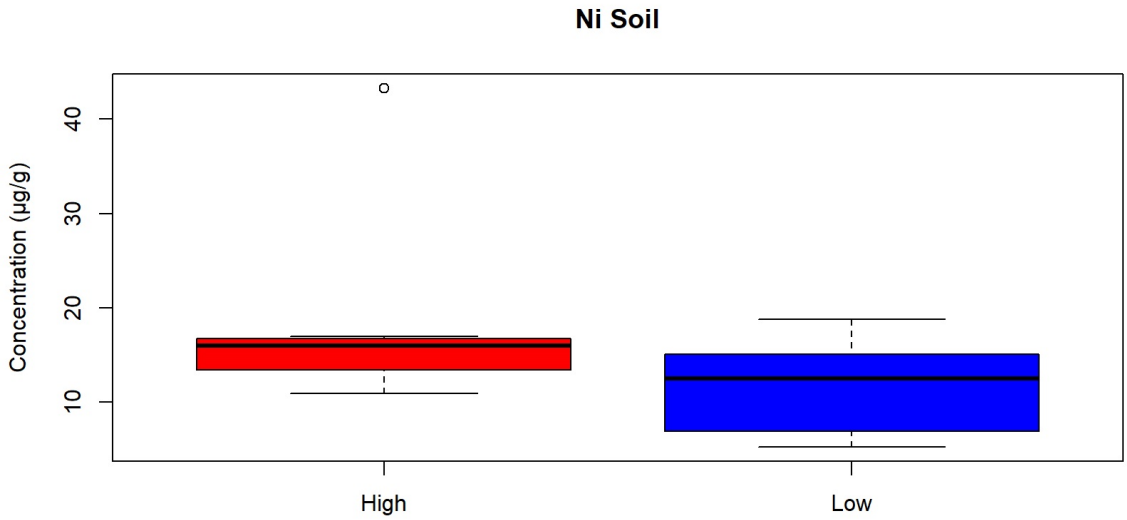

Figure 44: Boxplot of Ni content at high and low bird influence. Ni concentration is **not** significantly different (p=0.08) in high and low bird influenced areas.

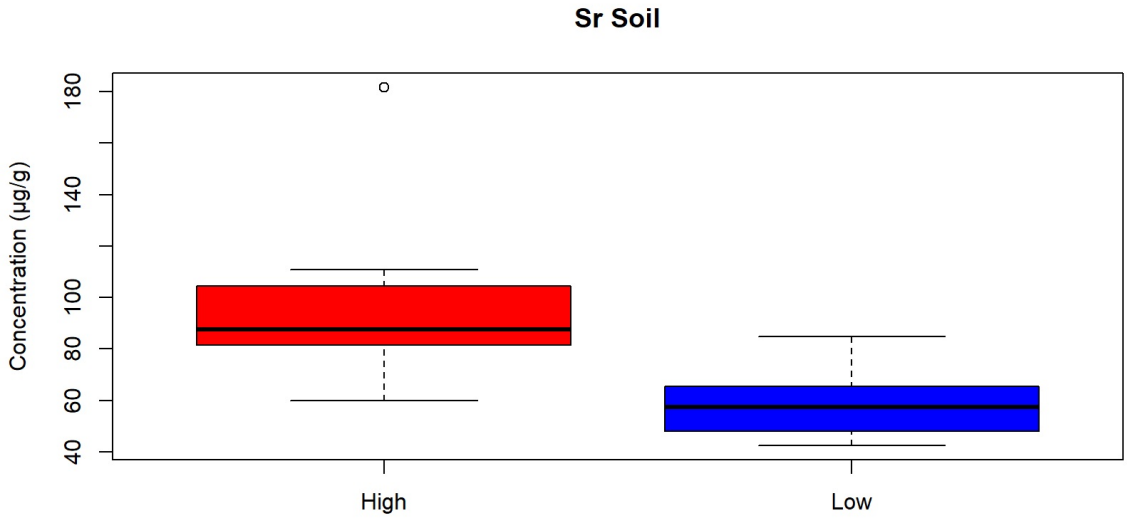

Figure 45: Boxplot of Sr content at high and low bird influence. Sr concentration is significantly different (p=0.002) in high and low bird influenced areas.

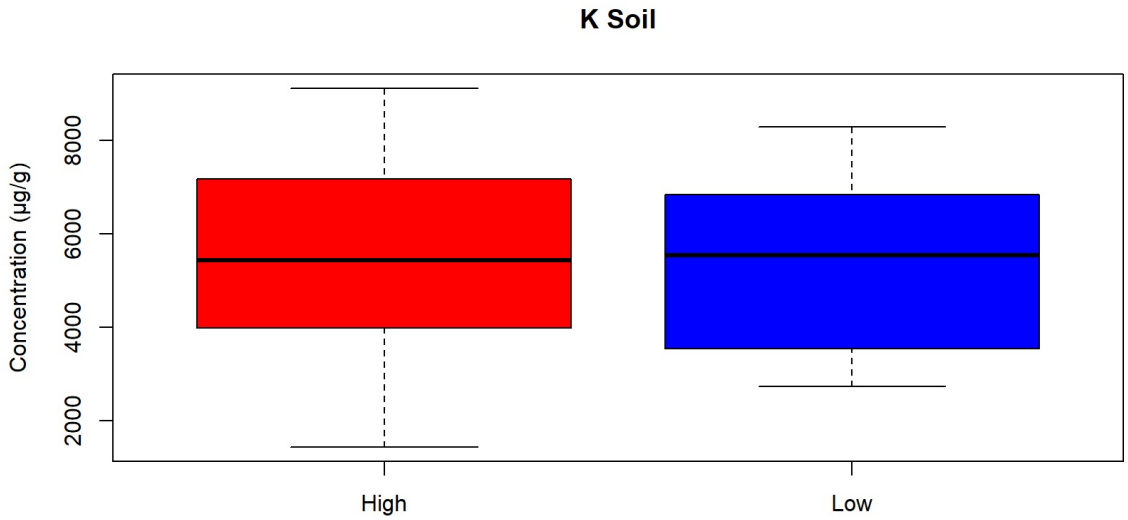

Figure 46: Boxplot of K content at high and low bird influence. K concentration is **not** significantly different (p=1) in high and low bird influenced areas.

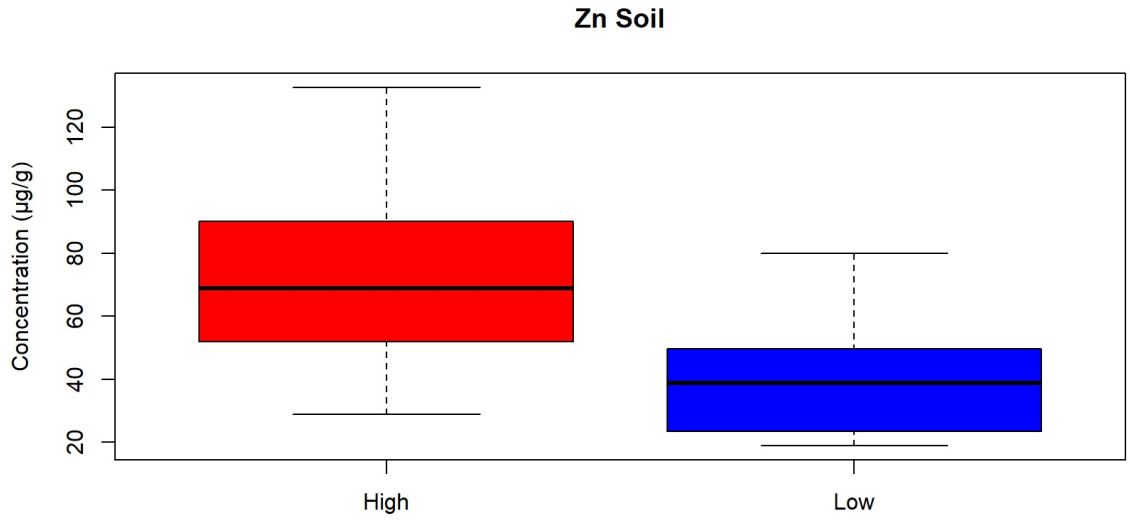

Figure 47: Boxplot of Zn content at high and low bird influence. Zn concentration is significantly different (p=0.02) in high and low bird influenced areas.

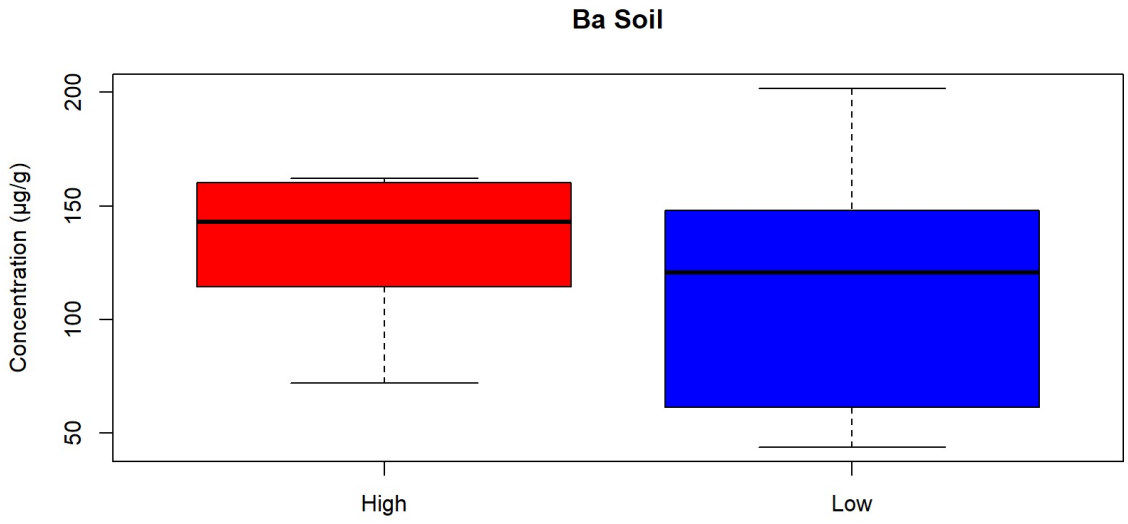

Figure 48: Boxplot of Ba content at high and low bird influence. Ba concentration is **not** significantly different (p=0.2) in high and low bird influenced areas.

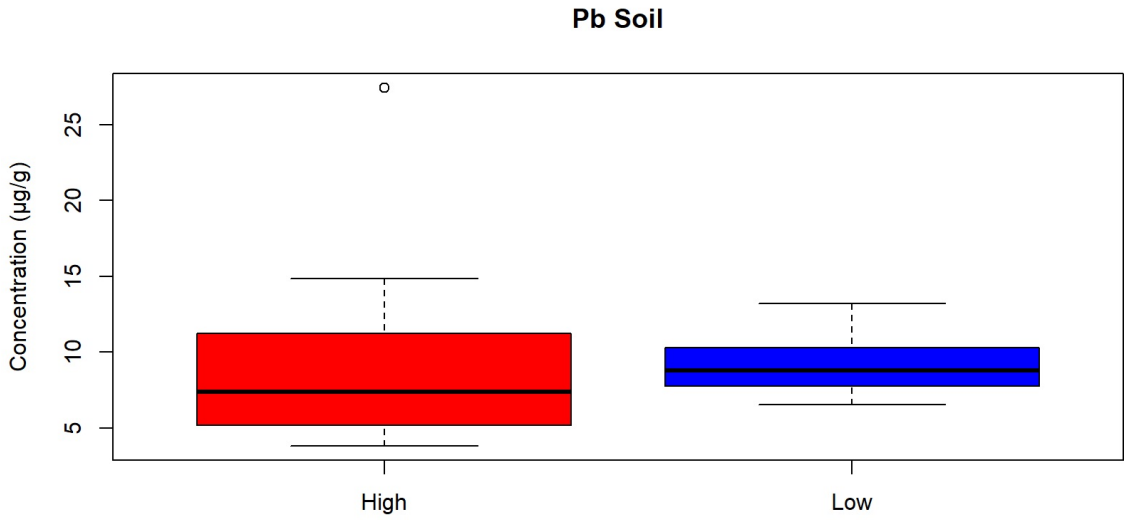

Figure 49: Boxplot of Pb content at high and low bird influence. Pb concentration is **not** significantly different (p=0.2) in high and low bird influenced areas.

G Reference site

Figure 50: A map of Kongsfjorden. Knudsenheia is indicated by a red dot. Illustration made in TopoSvalbard [21], Norwegian Polar Institute.

H PCA plot

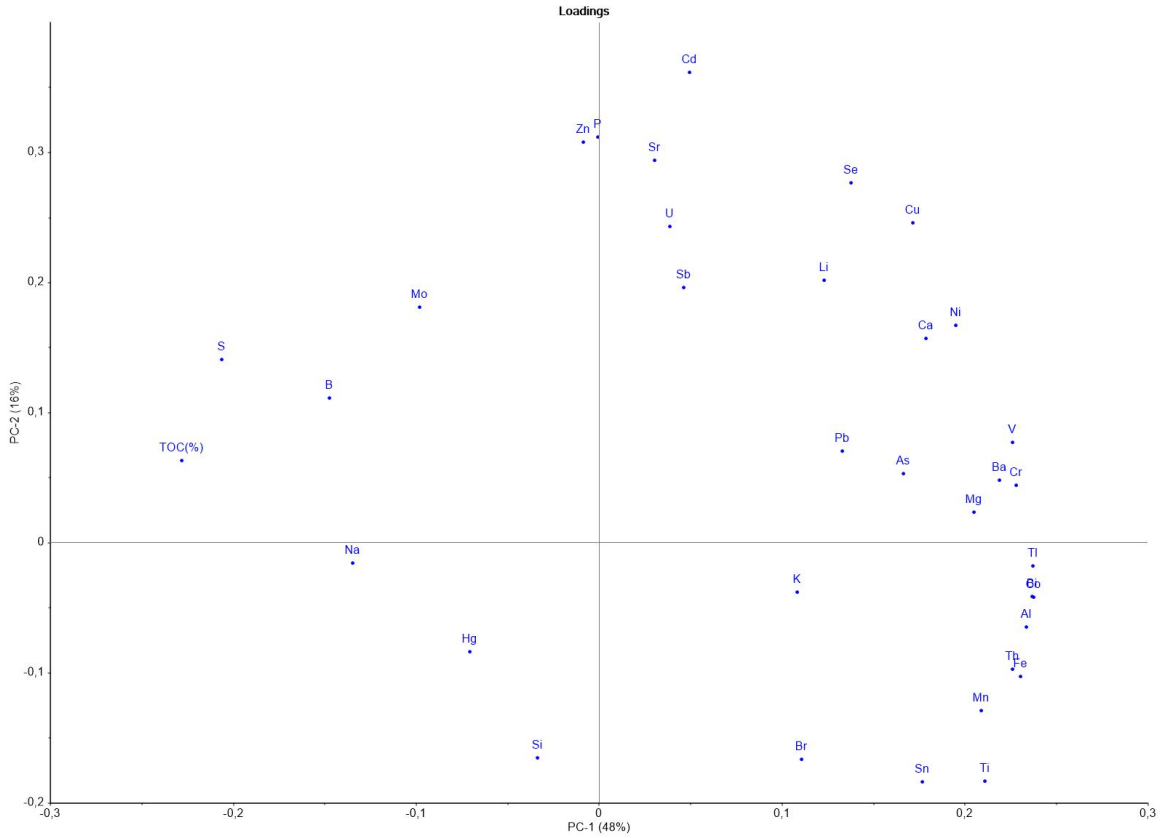

Figure 51: PCA-loading plot for selected elements in soil and guano samples for PC1 and PC2 based on the bird specie dominating at the sampling site.

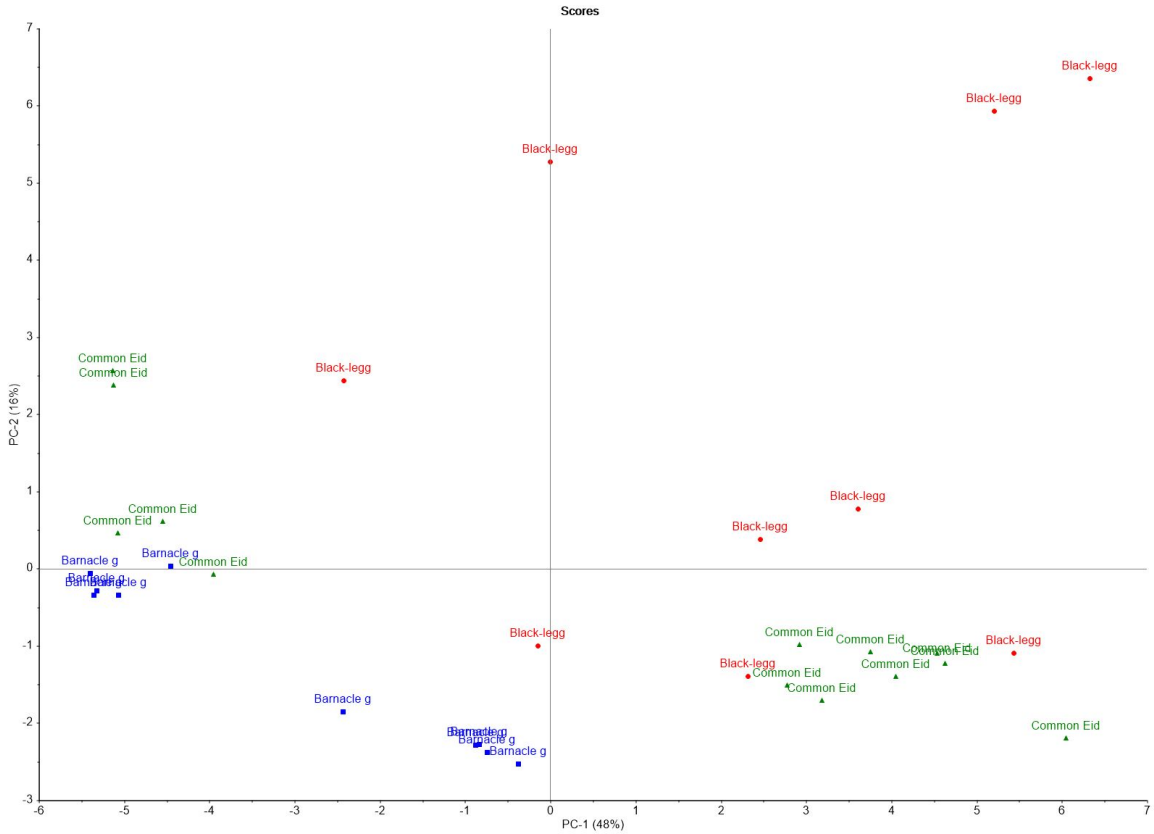

Figure 52: PCA score-plot for selected elements in soil and guano samples for PC1 and PC2 based on the bird specie dominating at the sampling site. Common eider is marked in the color green, Barnacle goose in blue and Black-legged kittiwake in red. Please note that the samples strongly associated with PC2 in the neagtive direction in the plot, far left, is the guano samples.

Mathilde K. Syvertsen

Long-range transport of pollutants to arctic areas by seabirds

NTNU
Norwegian University of
Science and Technology