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Study of mercury and selected trace elements in soil in the Norwegian Arctic, Svalbard

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Abbreviations

Ag	Silver
Al	Aluminum
As	Arsenic
B	Boron
Ba	Barium
BDL	Blank detection limit
Be	Beryllium
Bi	Bismuth
Br	Bromine
Ca	Calcium
Cd	Cadmium
Ce	Cerium
Cl	Chloride
Co	Cobalt
Cr	Chromium
Cs	Cesium
Cu	Copper
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
dw	Dry weight
FA	Fulvic acid
Fe	Iron
Ge	Germanium
HA	Humic acid
Hf	Hafnium
Hg	Mercury
IDL	Instrumental detection limit
La	Lanthanum
Li	Lithium
MeHg	Methylmercury
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
MWUT	Mann-Whitney *U* test
Na	Sodium
Nd	Neodymium
Ni	Nickel
NOM	Natural organic matter
OH	Hydroxyl
OM	Organic matter
Pb	Lead
POM	Particulate organic matter
Pr	Praseodymium
Rb	Rubidium
S	Sulfur
Sb	Antimony
Sm	Samarium
SOM	Soil organic matter
Sr	Strontium
STD	Standard deviation
SUVA	Specific ultraviolet absorption
THg	Total mercury
Ti	Titanium
Tl	Thallium
TOC	Total organic carbon
TT	Two-paired t-test
V	Vanadium
WT	Welch’s t-test
Y	Yttrium
Zn	Zinc
Zr	Zirconium

Abstract

In this study elemental composition and soil organic matter (SOM) content of surface and mineral soils in Svalbard are presented. The aim is to provide new data on soils in the Arctic and to gain more knowledge about the role of the soil in the biogeochemical cycling of mercury (Hg). Concentrations are reported for As, Al, Cd, Cu, Cr, Fe, Hg, Mn, Ni, Pb, S and Zn. Samples were taken in Adventdalen and the Bayelva area in 2015. The sampling areas were chosen to represent background values in Svalbard and to minimize local influences. We obtained a mean concentration of Hg of 0.110 ± 0.0346 µg/g in surface soils (range 0.0540 to 0.180 µg/g). Hg levels in the mineral soils were lower than in the surface soils (mean: 0.0279 ± 0.0073 µg/g; range: 0.0174 to 0.0401 µg/g). An average of soil organic matter content of 53.5 ± 10.8 % was determined. Hg strongly accumulates in the upper soil layer and significantly correlates with SOM and Cd. Hg concentrations in the surface soil were slightly lower compared to the humus layer in Norway and comparable to other levels in soils in the Arctic. An inverse association was found with elements attributed to the mineral soil and indicate that Hg is presumably derived from atmospheric deposition.

Keywords Mercury; Arctic; Soil; Svalbard; Surface soil; Trace elements; Soil organic matter

1 Introduction

The Arctic is a very vulnerable ecosystem and affected by anthropogenic activities occurring in the temperate and industrial areas. Svalbard (74-81°N) as a remote archipelago in the Arctic is subjected to long-range transport of contaminants and surface soils can be used to identify these.[1] Only few sources emit locally contaminants (e.g. coal mining, power plant, airport and local traffic). Atmospheric deposition, riverine input and exchange processes between different environmental compartments are the reasons for elevated contaminant concentrations. Trace elements emitted at lower latitudes and featuring volatility and persistence in the atmosphere can be long-range transported. Main sources for heavy metal emissions are fossil fuel combustion, non-ferrous metal production and waste incineration.[2] These can increase the amount of contaminants cycling in the environment compared to natural levels. Natural emissions of heavy metals to the atmosphere derive from biogenic sources, volcanic emissions, soil-derived dusts and sea salt aerosols. Emitted as particulates or in their gaseous form, they follow wind trajectories and can then be deposited in the Arctic. Cold dense air and darkness in winter time lead to an accumulation and possible deposition. The AMAP assessment from 2002[2] postulated that the anthropogenic emissions in and outside the Arctic account for more than 50 % of the observed heavy metal concentrations in the Arctic than natural sources. An accumulation in biota and enrichment of them with trophic levels give rise to hazards and risks for animals and people inhabiting the Arctic and consuming wildlife.[3]

Special interest is placed on the heavy metal mercury (Hg) in the Arctic. Hg is a naturally occurring element with low abundance in the Earth’s crust. Its known role as a global pollutant is originating from additional release from anthropogenic activities.[4] For more than 100 years emissions from anthropogenic sources have led to elevated concentrations of Hg in the environment.[5,6] They are derived from ongoing activities such as fossil fuel combustion, coal and gold mining, cement production or waste incineration.[6] Hg in its elemental state is highly volatile. Its atmospheric lifetime of 6 to 24 months enables long-range transport.[7–9] Therefore, Hg can be easily transported on a global range. Further transport is possible via ocean currents or rivers.[6] Hg, which originates from industrial release, can be measured in the atmosphere in the Arctic, e.g. in Ny-Ålesund[10] in Svalbard. Elevated concentrations of mobile Hg are followed by an increased risk for bioaccumulation and biomagnification, especially, when transformed to methylmercury (MeHg), which is highly toxic.[6] Elevated Hg concentrations in higher trophic levels are reported in e.g. humans, polar bears and Arctic marine wildlife. These levels can exceed threshold values and introduce neurotoxic, reproductive toxic and/or immunotoxic effects.[6] Weathering of rocks and atmospheric deposition are the main pathways for Hg introducing it into terrestrial environments in the Arctic.[11] During spring time the atmospheric Hg depletion events (AMDEs) occur in the Arctic and deposit Hg by oxidizing Hg(0) to Hg(II). They were first reported in 1998 by Schroeder et al.[12] Photochemical initiated reactions and the involvement of halogens delivered presumably by sea ice[13] lead to a rapidly decrease in the atmospheric Hg concentrations causing depositions on snow, ice or ocean surface. Once deposited on the snow, parts of the amount of Hg can be reemitted again or be further retained, transformed and transported into other environmental media. Further pathways in soil and in the terrestrial ecosystems are under debate.[14] Snow, ice and soils on land function as “key reservoirs”[11] when Hg is deposited from the atmosphere. The reservoirs then supply Hg via soil erosion or melting during spring/summer to freshwater and marine ecosystem.[11] Accumulation in soil could also lead to a possible terrestrial exposure route for biota. Knowledge about the role of soil in the biogeochemical cycling of Hg is limited and only few studies on Hg concentrations in Arctic soils have been reported.[2,6,15] Therefore, terrestrial fates of Hg cycling are important to investigate.

The atmospheric deposition of heavy metals from anthropogenic sources can alter the natural surface soil composition. Trace elements in surface soils are derived from local geology and airborne supply. The detection of contaminants in surface soils is important to understand the cycling of contaminants in terrestrial ecosystems and in interaction with other compartments. Surface soils in the Arctic reflect atmospheric deposition over longer periods (e.g. compared to mosses which reflect atmospheric deposition over 3 to 5 years).[2] Nevertheless, there is a lack of data on the soil composition in the Arctic and relatively few studies present heavy metal concentrations. With the effects of the ongoing climate change like precipitation changes and longer snow-free periods more focus in research is placed on soil characteristics in the Arctic.[16,17]

To investigate associative effects of different heavy metals and constituents of soil, following elemental concentrations are presented and discussed: aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), Hg, manganese (Mn), nickel (Ni), lead (Pb), sulfur (S) and zinc (Zn). The aims of this study are to provide new background data on the composition of soils in Svalbard, in particular of Hg, to compare them to existing data of soils in the Arctic and Norway and to link the concentrations to the Hg cycling and detect possible sources explaining the detected levels.

2 Theory

2.1 Soil and Soil organic matter (SOM) in Svalbard

2.1.1 Development and constituents

Soil is formed by processes of addition, losses, transformations and translocations of earth material and living organisms. Influences by, e.g. climatic, geological and biological factors determine local specific characteristics of the soil. The interaction of these processes leads to visibly, chemically and/or physically distinct layers in soils that are called horizons. Svalbard is covered with permafrost. Soil types are often referred as cryosols and are driven by cryogenic (low-temperature) processes. These are correlated with soil water wandering from warmer towards frozen parts of the soil. Their upper layer thaws and freezes annually whereas the deeper layers (minimum 5 cm thick) remain frozen for two or more consecutive years.[18] Oxidation processes lead to relatively low organic matter (OM) content in the soil.[19] Root systems are shallow and vegetation with lichens and mosses in the tundra is sparsely to continuous. Svalbard is dominated by the tundra biome. Soil profiles show typically mineral (A), (mineral subsurface horizon (B)) and parent material (C) horizons. Soil is normally poorly developed.[20] Leptic Cryosols (present in Adventdalen, see 3.1) are non-cryoturbated permafrost-affected soils over hard rock (continuous rock between 25 and 100 cm[20]). Soil materials of Regosolic Cryosols (Canadian System of Soil Classification and present in the Bayelva area, see 3.1) have developed in the recent past and can be found “on well-drained knolls and slopes”[21].

SOM plays an important role in understanding metal- (esp. Hg-) retaining abilities of soils after atmospheric deposition. SOM is enriched in the surface soils and consists of decomposed residues from plants and organisms. The amount of SOM depends on factors influencing the soil composition, e.g. geology, geography, climate and ecology, and on anthropogenic influences, e.g. farming, agriculture and forestry, and also varies within the soil profile. Organic horizons contain high amounts of SOM while mineral horizons have lower amounts.[22] Depending on its decomposition degree, chemical and physical character, SOM can be divided into different subgroups, e.g. living and non-living components. Furthermore, they are classified by the size of SOM. Water-extractable OM (dissolved OM: DOM) is distinguished from particulate OM (POM) by a filter pore size of 0.45 µm. DOM concentrations in soil are low, but it features a high mobility and lability, which increases the importance for the transport and availability of contaminants and their toxicity.[16] Humus displays the predominant accumulated material in soil[22] and is highly resistant to further degradation. It includes parts of SOM after removal of DOM and macroorganic matter.[23] Humic and non-humic substances are present in humus. Non-humified materials contain still identifiable amounts of their precursors, e.g. lipids, proteins. Humic substances are biogenic and heterogeneous organic substances and can be distinguished by color, high molecular weight and refractory.[24] Humic acids (HA), fulvic acids (FA) and humin are classified as humic substances. Aquatic OM mainly consists of HA and FA and smaller amounts of more hydrophilic compounds. Metals which strongly bound to HA and FA are reported to be transported with dissolved organic carbon (DOC).[25] In Svalbard, aquatic OM is mainly derived from outer input because it itself is poor in plants.

The environmental conditions, i.e. short summers and cold temperatures, are the reasons of a slow SOM decomposition and nutrient mineralization in the Arctic.[24] Soils store high amounts of carbon and even though there is a low plant production[26], the input by plants is higher than their decomposition.[16] This leads to less humified SOM.[24] Organic topsoil horizons have a high C:N ratio indicating a lower degree of decomposition or humification in Arctic tundra soils.[24] Soil moisture, soil temperature and SOM characteristics strongly affect the SOM decomposition rate.[17] Surface soils have a particularly interesting role because biological activity is most active and they exert interactions with vegetation patterns and with the atmosphere.[16] The surface soil composition is influenced by "(a) mixing with underlying mineral soil by bioturbation or physical processes, (b) transfer from the mineral soil by root uptake in plants and return to the humus layer by leaching or by decay of plant material, and (c) atmospheric transfer from marine environment."[27] Furthermore, anthropogenic activities can alter the composition by e.g. atmospheric deposition from pollutants originating from local and far sources.[27]

2.1.2 Metal binding by soil constituents

Metals can bind to various constituents in soil, e.g. humus, hydrous oxides and hydroxides, alumina-silicates, soluble ligands, and sparingly soluble calcium salts. This is depending on factors such as the form of the metal source material, affinity of metal ions for soil solids and soluble soil ligands, available adsorption surfaces in soil, soil-metal contact time and various local soil characteristics, e.g. pH, redox potential, water content, temperature, biological activity and salt concentration.[25] Metals can be held reversibly reacting fast to changes in the soil solution or as species which respond to changes in conditions over months and years: M_{labile}, $M_{non\text{-}labile}$, M_{inert} (see Figure 1).

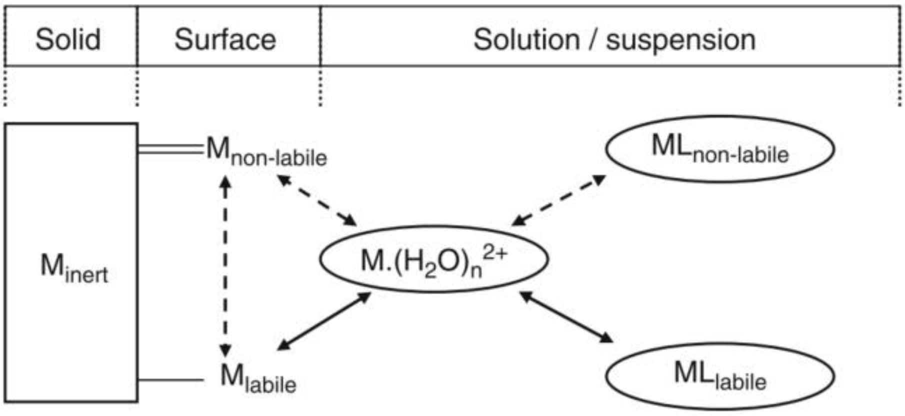

Figure 1. Possible fractionation and speciation of a divalent metal retained in soils. Dashed arrow: kinetically constrained reactions, solid arrows: instantaneous reactions.[25] (ML: metals bound to soluble ligands)

Surface soils are enriched in SOM. The ability and strength of metals to bind is relying on various parameters as mentioned above. SOM components such as HA and FA are particularly important because metals can bind to active sites on these humus subgroups. HA and FA have a high ratio of O, N and S (esp. important for Hg) donor atoms to the carbon backbone. The mobility of strongly bound metals depends on the solubility of humus itself. Furthermore, metals can bind to the minerals in soil. They can adsorb to Fe, Mn and Al hydroxides and hydrous oxides, alumino-silicate clays, and salts with low solubility (e.g. $CaCO_3$).[25]

2.2 Cycling of Hg in the Arctic

The Arctic is a fragile ecosystem with unique conditions and threatened by anthropogenic emissions in mid-latitudes. Hg enters the Arctic mainly via the atmosphere[28] and weathering of rocks[11], and the former is highly connected to anthropogenic input. The motivation to focus research on the environmental fate of Hg is presented by the facts that Hg is long-range transported via the atmosphere (or ocean), the possibility to be transformed to the highly toxic MeHg species and the observation of biomagnification. Dietary habits of indigenous people inhabiting the Arctic and the discovery of AMDEs[12] led to special interest on the cycling of Hg in the Arctic. Dietary habits include a high proportion of marine organisms which are enriched in Hg.

2.2.1 Emissions to the environment

Hg occurs naturally in low abundance in the Earth's crust and is found predominantly as the mineral cinnabar (HgS). Volcanic activities and weathering of rocks can emit Hg. Man-made activities, e.g. fossil fuel combustion, non-ferrous metal production, Hg and gold production, cement production, waste incineration, chlor-alkali plants, pig iron and steel production[6,29] increase the magnitude of Hg cycling in the environment. Asian emissions (65 %) dominate over European (7.9 %) and North American (8.3 %) anthropogenic Hg releases (status as of 2005).[6]

There are only few local Hg sources in Svalbard present such as power plants and mining. However, they have to be encountered. Analysis of sediments, ice cores, peat cores from ombrotrophic bogs and biological tissue[30] show that the magnitude of Hg emissions by human activity increased in post-industrial time the natural emissions by 2 to 3 times.[5] According to distribution in peat profiles in Norway this increase may have been considerably greater (possibly as much as 10 times).[31] Total anthropogenic Hg emissions are currently estimated from 1960 to 2800 Mg/year.[28] They are regarded to have shown the highest levels in the 1970s and are comparatively stable from 1990 to 2005.[32,33] No obvious trends of accumulated Hg in Arctic wildlife can be detected over the last decades.[6] Cycling Hg is observed to accumulate mainly in oceans and areas with vicinity to Hg emission sources.[28] This is accompanied with bioaccumulation and biomagnification in the marine environment.

2.2.2 Atmospheric transport and chemical speciation

Figure 2 shows the pathways of Hg in the Arctic with focus on atmospheric and oceanic species. The species dominating the environmental cycling are Hg(0), Hg(II) and MeHg. 98 %[28] of the atmospheric Hg is represented by gaseous elemental mercury (GEM) due to its high volatility and low solubility in water. The species mainly observed in wet deposition is Hg(II). It exhibits a higher solubility in water than GEM and is associated with inorganic and organic ligands (especially to S-containing compounds). In the atmosphere GEM, reactive gaseous mercury (RGM: Hg(II)) and particle-bound Hg (PHg: Hg(II) and Hg(I) oxidation states) are the predominant species. The lifetime of GEM of 6 to 24 months and its low reactivity evenly distribute its concentration in the hemisphere. The lifetime is determined by photochemically-driven oxidation associated with ozone and hydroxyl (OH) radicals. The removal has also been attributed to halogen species in the marine boundary layer, upper troposphere and during polar sunrise.[28] The RGM and PHg species have a relatively short lifetime and deposition of Hg occurs locally or after atmospheric reactions via dry or wet deposition.

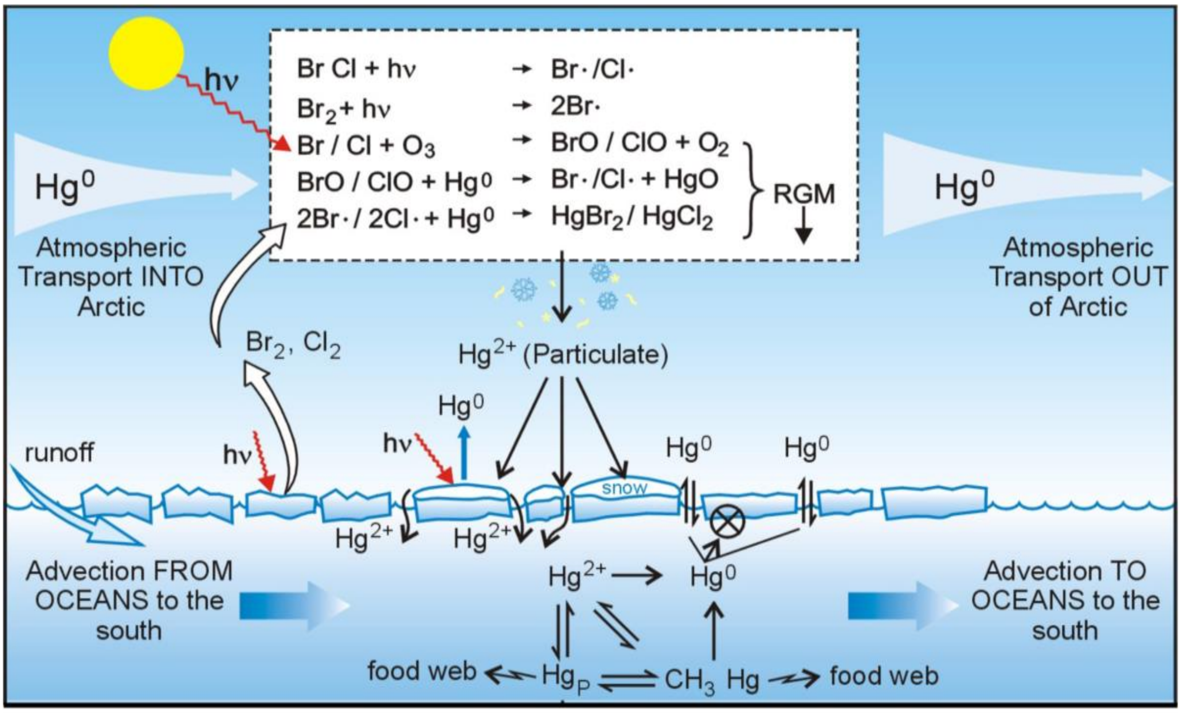

Figure 2. Cycling of mercury (Hg) in the Arctic (without terrestrial part).[13]

The atmospheric concentrations of RGM and PHg increase during AMDEs in the polar springtime. AMDEs are observed at various places in the Arctic.[10,13] They induce high amounts of Hg to be deposited onto snow, ocean and ice. During these events the lifetime of GEM in the atmosphere is strongly reduced (to 6 h to 2.5 days).[12] Fast depletion takes place via oxidation by halogens (esp. bromine (Br) oxides, presumably from marine origin) and destruction of ozone[13]. RGM species are formed, e.g. $HgCl_2$, $HgBr_2$, HgO, HgBr and HgOBr.[13] After oxidation Hg can bind to particles and/or be deposited.[10] Since the deposition during AMDEs is highly linked to halogens, sea ice and refreezing cycles on the ocean during polar sunrise display a great halogen source.[13] Furthermore, AMDEs are observed at low temperatures[10] and are limited vertically from the sea level to 1 km upwards[13]. The conditions for AMDEs to occur are the presence of Hg in the atmosphere, cold temperature, a stable inversion layer, sunlight and reactive halogens.[33] Reemission after deposition on snow occurs within the range of 50 to 80 %[11,28] and 100 to 300 tons of Hg per year can be deposited in the Arctic.[13] After the spring minimum of GEM, a maximum in the summer was observed by Steffen et al.[30] Modeling of the Arctic Hg cycle suggested additional Hg inputs into the ocean by rivers and coastal erosion.[34] These authors discussed the importance of involvement of riverine input besides atmospheric input from long-range transport. They proposed the boreal soils as “temporary reservoirs”[28] of deposited Hg.[28] Deposition of atmospheric Hg can increase the magnitude of possible biologically available Hg in aquatic and terrestrial ecosystems.[30]

2.2.3 Terrestrial environment

As outlined above, the terrestrial environment can play an important role in the Hg cycling (Figure 3), because of a possible transport of Hg from drainage basins to freshwater and marine ecosystems. “Snow, ice, and soils on land are key reservoirs for atmospheric deposition”[11] and can supply Hg during melting of terrestrial ice and snow and via soil erosion.[11] Terrestrial snow can act as a transitional environment[13] between the atmosphere and ecosystem uptake.[13] Half or more of the surface water runoff in the Arctic is represented by the spring melting period.[35] Rivers were shown to supply significant amounts of Hg to marine mammals in the Beaufort Sea during the melting period.[36] In the Canadian High Arctic most of the THg was delivered during June and early July in the snowmelt period and further transported with the outflow of the lake.[35] Hg(II) from snowpack transported during melting to the fjord was estimated to contribute from 8 to 21 % to the fjord’s THg content in Ny-Ålesund.[37] The possible fates of deposited Hg(II) on snow, ice and soil are summarized by Gamberg et al.[11] as followed: “1) reemission caused by photochemical reduction, 2) temporary storage in glacial ice or snow, 3) microbial methylation in soils and perhaps in snow, 4) possible transport with snowmelt, surface runoff and soil erosion to freshwater and marine ecosystem, 5) uptake by vegetation followed by reintroduction to snow or soils (caused by throughfall and litterfall) or accumulation in the terrestrial food chain through herbivores and returning to soils by decomposition."[11] These possible pathways can be dominated by one or occur as a mix in terrestrial ecosystems depending on diverse variables, e.g. climate, microbial community structure and activity, vegetation, geographical and geological factors.

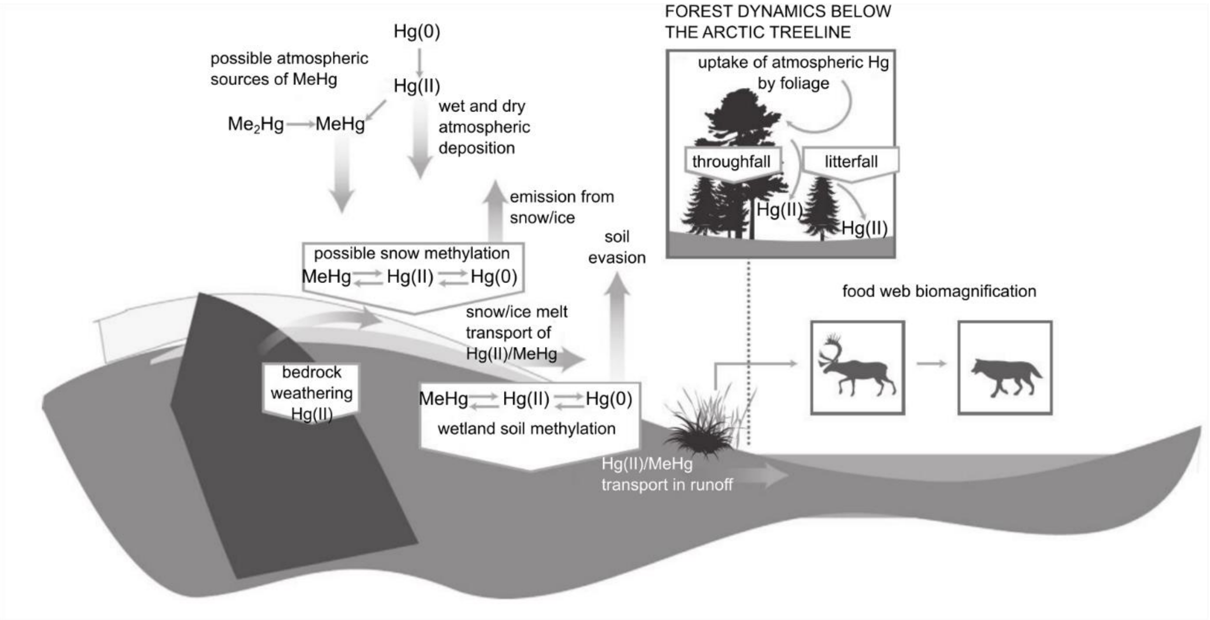

Figure 3. Mercury (Hg) cycling in terrestrial environments in the Arctic.[11]

Chemistry of Hg in soils

The chemistry of Hg in soil is predominated by adsorption/desorption and complexation reactions[38] and might also be influenced by microbial transformations[25]. Hg occurs mainly in two oxidation states in soil: Hg(0) and Hg(II).[25] In particular, Hg(II) can be found in soils and surface waters.[39] Hydroxide (OH), chloride (Cl) and organic anions are the dominant ligands for Hg. The strong association of Hg with OM and thiol-groups is associated with the soft metal character of Hg. Hg interacts in reactions like "chelating, ionic exchange, inner and outer sphere complex formation, adsorption, coprecipitation".[38] These interactions depend on features of humic substances and pH. Factors such as surface area, soil pH, organic content, quantity and quality of DOM and inorganic soil colloids, cation exchange capacity, grain size, chemical form of the Hg introduced, have to be encountered for describing the sorption strength and bonding stability. Hg can also be present as low-solubility precipitates, e.g. sulfide and selenide.[25] Hg binding in soils is correlated with SOM content and therefore associated and accumulated in organic rich surface soils. For naturally occurring concentrations of Hg the binding to reduced S groups in OM seems to be the dominating binding mechanism.[40] However, DOM with little sulfide was the dominant ligand for Hg in arctic wet sedge meadow.[41] In neutral and slightly alkaline soils Fe oxides and clay minerals may also state an important ligand to bind for metals besides the sorption to OM.[25] However, binding to ligands like OH, Cl and clay minerals was shown in laboratory with higher Hg concentrations normally not observed in the environment.[40]

In forest soils a close relationship of SOM and Hg was shown for surface soil samples in Sweden, Norway and north-central USA.[40] High OM content in soils was also reported to enhance MeHg formation.[39] Additionally, the association of Hg with OM is important for the mobilization and transport into water.[39] The content of thiols and other reduced S groups in HA and FA is attributed to a high affinity for Hg(II) for these SOM fractions.[39] Therefore, also DOM is an important factor to understand the cycling of Hg. Gu et al.[14] reported a dual role played by DOM in the reduction and complexation of Hg depending on the amount of reduced HA. This indicates an important influence of DOM on the Hg complexation capacity.

In Arctic soil, Hg can originate from atmospheric deposition or weathering of parent material. The accumulation of Hg is influenced by factors, e.g. snow-free periods, freeze-thaw cycles, wind action, erosion, runoff and biological activity.[35] Furthermore, characteristics of the soil, e.g. horizon development, pH, SOM content, SOM quality, are important. SOM content and qualitiy seem to be the most influencing factors.[35] In summer, when Arctic tundra soil is sun-exposed, photo-reduction and re-volatilisation[43] can lead to reemission of Hg. The photochemical Hg(II) reduction in soil depends on sunlight intensity, temperature, soil moisture and microbial activity. Moreover, abiotic or biotic oxidation abilities on GEM can retain Hg.[35] Another factor influencing OM content and humus quality is the type and amount of vegetation cover. In the northern hemisphere in temperate and boreal forest soils, the accumulation rate of soil THg is estimated to be about 5 $\mu g/m^2/year$. The barely vegetated tundra soil may have a lower rate.[44]

However, there are still knowledge gaps[11,35] on the role of the soil in the Hg cycling in the Arctic. Previous studies focused mainly on aquatic, biological and atmospheric cycles.[13] The present study provides new information on Hg concentrations in soil which can help in understanding the role of the soil in the Hg cycling after deposition on snow. Furthermore, it contributes to more available data on the soil composition in the Arctic. With the rising temperature in the Arctic more focus is placed on possible changes in reservoirs of contaminants.

2.3 Selected trace elements: As, Cd, Cr, Cu, Ni, Pb, Zn

In addition to Hg data the elemental concentrations of Al, Fe, S and of the trace metals As, Cd, Cr, Cu, Mn, Ni, Pb and Zn are presented in this study. Selection of these elements is based on environmental significance, reported observations of long-range transport and ICP-MS performance. Emissions from non-ferrous metal industry are major sources for the release of Cd, Cu, Pb, Ni (also oil combustion), As and Zn.[45]

Transport mechanisms of these trace elements include pathways in the atmosphere, freshwater, ocean, ice, sediment, and biota and exchange processes in between.[2] Spatial patterns are introduced by “location, quantity and timing of release from anthropogenic and natural sources, transport pathways and characteristics of the receptor compartments”[2]. The review by Steinnes and Friedland[1] highlighted As, Cd, Hg, Pb, Sb, Se and Zn as the heavy metals which are long-range transported in temperate, coniferous and boreal zones of North America and Europe. These observations were based on studies of air, precipitation, moss and peat from ombrotrophic bogs.[1] They also found also evidence that Ag, Bi, In, Mo, Tl and W experience similar fates. Studies in Norway reported an accumulation in mosses of V, Zn, As, Se, Mo, Cd, Sn, Sb, Tl, Hg, Pb, Bi. These elements also exhibit high enrichment factors in aerosols. Other elements such as Be, Ti, Cr, Mn, Fe, Co, Ni, Cu and Ba are less evident to be linked to atmospheric deposition after long-range transport.[1] In surface soils especially Pb, Hg and Zn are accumulated after atmospheric deposition, Cd is less evident. Additionally, the elements Ag, As, Bi, Mo, In, Sb, Se, Tl, W show indications of enrichment in surface soils.[1] Relatively low levels in soils compared to marine ecosystems are derived by long periods of snow cover and possible transport with the snowmelt to aquatic systems after deposition onto the snow.[3]

2.4 Analytical methods

2.4.1 Inductively-coupled plasma mass spectrometry (ICP-MS)

ICP-MS is a well-established method to detect and quantify elements in various matrices and has been commercialized since 1983.[46] The advantages of ICP-MS include very low detection limits, little preparation, the possibility to scan many elements at the same time and to obtain isotopic information. The quantification is possible in a ppt to ppm concentration range.[46] Ions are generated in an argon (here: with 0.04 % methane) plasma, transferred in a vacuum environment. A magnetic and electric sector analyze and focus the ions based on their mass-to-charge ratio. The ions are then detected by a mass spectrometer. ICP-MS is used in a wide range of application and environmental analysis represents the largest sector.[46] Trace element concentrations are obtained for, e.g. drinking water, airborne particles, wastewater and sediments. ICP-MS has been used for 20 years in determination of heavy metals in soils.[25,27,47–49]

Interferences that are possible to occur during analysis and lead to erroneous data can be divided in spectral and matrix effects. Spectral interferences result from similar/or close masses of the analyte and other ions in the ion beam, e.g. argon and water which can create a large number of single-atom and polyatomic ions in the plasma that can overlap with the analyte peak. They occur when isotopes of two different elements have an almost similar atomic mass (isobaric) or when a polyatomic ion in the beam has a nearly similar mass to that of the analyte (polyatomic). The latter one is more common and is associated with the plasma/nebulizer gas, matrix components and other elements in the solvent, sample and gases derived from air.[46] The interference of those components can cause increased signals. An examples is the overlapping of argon and oxygen ion with Fe or an argon and Cl (origin from sample dilution) ion with As. This can be avoided by preliminary separation and preconcentration techniques like chromatography, background correction, collision/reaction cells and interfaces and operation of mass analyzers with high resolving power (double sector).[46]

Matrix interferences cause a change in peak height compared to reference values which contain the same concentration without the matrix.[50] Matrix components can physically affect the droplet formation and size selection and suppress the analyte (sample transport effect).[46] Furthermore, changing amounts of matrix components can affect ionization conditions and cause lower peak heights, e.g. ionization suppression can originate from alkali metals in the matrix and electrons generated by the alkali metals shift the ionization equilibrium of the analyte. Space-charge effects are derived by reciprocal repulsion of ions in the ion beam. Some of the analyte ions are pushed away (out of focus) and cause also lower peak heights (esp. for low-mass elements). Matrix interferences can be avoided by sufficient sample dilution, matrix matching when using internal standards or standard addition method. Space-charge effects can be prevented by applying voltages to individual lens components of ion optics navigating the analyte ions along to the mass analyzer while repelling the maximum number of matrix ions.[46]

2.4.2 Loss-on-ignition (LOI)

LOI is a semi-quantitative method to determine the OM content in soils. A certain amount of the sample is first dried and then ignited at a sufficient temperature. The weight loss represents the OM content. Difficulties in producing comparable results arise from various applied temperatures, durations and sample amounts.[51] Erroneous quantification can result from structural water-loss of minerals and decomposition of soil carbonates at high temperatures and incomplete destruction of SOM at low temperatures.[51]

3 Material and Methods

3.1 Study area

Sampling was conducted in August 2015 in Spitsbergen. Five sampling sites were chosen in Adventdalen and near Ny-Ålesund (Figure 4 and GPS data in Table 1). Spitsbergen is the largest island in the archipelago Svalbard. Svalbard is located between 74 and 81 °N and 10 to 28 °E in the High Arctic.[52] In 2015 2667 inhabitants lived in Svalbard.[53] Longyearbyen at Isfjorden represents the largest settlement. The climate is influenced by its latitude and the North Atlantic current. The latter leads to milder temperatures than in the Russian or Canadian Arctic at similar latitude. Average temperatures above zero can be observed from June till September.[54] The annual average temperature in 2015 was -2.2 °C.[55] Svalbard is underlain by continuous permafrost and shows only little vegetation and poorly developed soil and no forests or agriculture areas. Soils in Svalbard are covered with bryophytes, lichens, grasses and different sedges.[56–58] They are characterized as an active layer of the beneath permafrost and soil development is determined by freeze-thaw cycles[22]. An active layer thickness from 1.6-2.0 m was observed near Ny-Ålesund[59] (in 2008) and from 1-1.6 m in Adventdalen and Janssondalen[60,61] (in 2000). In the Soil Atlas of Circumpolar Regions[18] soils in Adventdalen are characterized as Leptic Cryosols (CRle). Bekku et al.[56] characterized the soil near the Bayelva river as Regosolic Cryosol.

Table 1. GPS Data of the sampling sites. (When coordinates are given for two samples, they were taken in a radius of 10-20 m from each other.)

Sample ID	°N	°E
1	78.1591	16.1986
2	78.1591	16.1982
3	78.1583	16.1928
4	78.1583	16.1925
5	78.1585	16.1879
6	78.1586	16.1890
7	78.1591	16.1854
8	78.1593	16.1860
9+10	78.1601	16.1952

Sample ID	°N	°E
11	78.1631	16.1815
12	78.1632	16.1815
13	78.1655	16.0987
14	78.1654	16.0984
15+16	78.1578	15.6412
17+18	78.9322	11.8323
19+20	78.9316	11.8266
21+22	78.9148	11.8470

Figure 4. Map of Spitsbergen (top) showing the sampling sites in Adventdalen (bottom left) and Ny-Ålesund (bottom right).

The sampling area Adventdalen (Figure 5), classified as a periglacial landform, is a 40 km long valley on the west coast of Spitsbergen opening into Adventfjorden and later into Isfjorden. Longyearbyen, the largest settlement in Svalbard, is situated in Adventdalen. This includes an all-year operated airport, a coal-firing power plant and the operation of the coal mine Gruve 7. The sampling areas in Adventdalen were chosen in order to prevent interferences with local pollution sources. Samples were taken in Endalen (n=2), Foxdalen A (n=12) and Foxdalen B (n=2). Geological characteristics of the Adventdalen Group (Middle Jurassic-Lower Cretaceous) can be seen in Figure 22 (Appendix A). The Adventdalen Group is built of two clastic sediment sequences: the lower Janusfjellet subgroup and the upper Carolinefjellet formation. Latter one is present in the sampling areas in Foxdalen A and B und Endalen and comprises of sandstone, siltstone and shale. It ends in fluvial and glacifluvial deposits.[58] Soil development was observed to be more pronounced in Adventdalen compared to Ny-Ålesund. This goes along with a relatively mild climate in Adventdalen resulting in a richer high Arctic tundra vegetation compared to other parts of Svalbard.[58]

Further samples were taken south-west (n=2) and west (n=4) (Bayelva area) of Ny-Ålesund (Figure 5). The settlement of Ny-Ålesund is located at Kongsfjorden further north than Isfjorden. “In the Ny-Ålesund area metamorphic rocks of Caledonian age are overlain by Late Palaeozoic to Tertiary sedimentary rocks.”[62] Sampled soils were mainly developed on limestone and glauconitic sandstone (Figure 23 in Appendix A).

Figure 5. Photos (taken in August 2015) of the sampling area in Foxdalen A (top left), Foxdalen B (top right), Endalen (bottom left), Bayelva region (bottom right) in Svalbard.

3.2 Sample collection

Suitable sample locations were chosen based on following main criteria: (i) remoteness from local anthropogenic pollution sources, (ii) not part of intertidal zone and at least 500 m away from the sea, (iii) full coverage with vegetation of soil and (iv) state of soil layer development (organic surface layer of at least 3 cm and total depths of the soil layers of at least 20 cm).

All soil samples were taken by cutting squares of approximately 18 x 18 cm using a normal stainless steel breadknife. Surface soil samples without removing the vegetation (mostly mosses) were cut in half and stored in paper bags. Mineral soil samples were taken with a small plastic shovel at a depth of ca. 20 cm where no influence of the vegetation was visible and stored in plastic bags. The sampling methodology can be seen in Figure 6. The soils in Adventdalen and Bayelva area exhibit only thin organic layers. Therefore, a mixing with the beneath mineral soil may have occurred during sampling (see for discussion 5.2). This can alter the composition and possible correlation between metals.

Figure 6. Pictures showing the soil sampling in Svalbard (August 2015): Soil profile (top left), surface soil sample (top right), mineral soil sample (bottom left), sample storage (bottom right).

3.3 Analysis

3.3.1 ICP-MS

The divided surface soil sample was separately analyzed and the mean of these two parts is shown in the results. Surface soil samples were air-dried for about one month until the change of weight was less than 0.5 % over one week. After that, samples were homogenized in a Retsch mill SM100 with a sieve size of 2 mm. Elemental composition was determined with ICP-MS.[25,27,47–49] This was carried out with a Thermo Scientific ELEMENT 2 HR-ICP-MS device. The analysis was performed by using 3 different resolutions: low (400), medium (5500) and high (10000) to avoid interferences. Samples were digested prior to analysis. For this purpose, 200 to 500 mg of air-dried organic material were weighed, 6 mL of 50% v/v HNO_3 added and digested. A dilution to 60 mL followed. For the mineral soils 200 to 300 mg were taken and mixed with 9 mL 50% v/v HNO_3. After digestion it was diluted to 108 mL. The digested and dilutes material was transferred to 15 mL PP-vials for ICP-MS analysis. Three blanks were run besides the samples following the digestion process of the surface soil and mineral soil sample, respectively. Levels obtained with ICP-MS analysis were corrected for these blank values. The reference materials Humus H3 and Soil GBW 07408 were used to validate the method. To determine the reproducibility three aliquots of the reference materials were decomposed and analyzed in parallel.

Following values were obtained:

> RSD <10 %: Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, S, Zn (Surface soils)
>
> RSD <10 %: Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, S, Zn (Mineral soils)

The accuracy was obtained by comparing measured elemental composition of the reference material with the certified values.

> Accuracy surface soils: Al, As, Cd, Cu, Fe, Hg, Ni, Pb, Zn (within 10 % or better of the certified value); Mn (10-20 %); Cr (20-25 %)
>
> Accuracy mineral soils: As, Cd, Cr, Hg, Mn, Ni, Zn (within 20-30 % of the certified value); Cu, Pb (30-40 %)

Detection limits of the ICP-MS analysis are given in Table 2. Instrumental detection limits (IDL) are calculated from the concentration yielding to 25 % of relative standard deviation (n=3 scans) and the correction for the baseline. Blank detection limits (BDL) are derived by three times the standard deviation (STD) of the blanks (n=3).

Table 2. Instrumental and blank detection limits (IDL and BDL) of the ICP-MS analysis (in µg/g).

	IDL Surface soil	IDL Mineral soil	BDL Surface soil	BDL Mineral soil
Al	0.030	0.086	1.3	0.95
As	0.0038	0.011	0.0055	0.016
Cd	0.0015	0.0043	0.0043	0.00080
Cr	0.00075	0.0022	0.084	0.022
Cu	0.0030	0.0086	0.025	0.0086
Fe	0.018	0.052	1.0	2.5
Hg	0.00015	0.00043	0.0034	0.0064
Mn	0.00090	0.0026	0.013	0.0087
Ni	0.0023	0.0065	0.056	0.044
Pb	0.00030	0.00086	0.018	0.0016
S	3.0	8.6	25	29
Zn	0.0060	0.017	0.044	0.18

3.3.2 LOI

The SOM percentage in soil can be determined by the semi-quantitative method LOI (see equation 1). The quantification follows the physical destruction of SOM by heat.[63]

$$\%LOI = \frac{Oven\ dried\ soil\ weight\ at\ 105\ °C - Soil\ weight\ after\ ignition}{Oven\ dried\ soil\ weight\ at\ 105\ °C} \times 100 \quad (1)$$

For tundra soil an ignition temperature of 550 °C with a duration of 3 h was chosen. 3 to 4 g of the surface soils in crucibles were dried at 105 °C overnight in a compartment drier and then placed at 550 °C in a muffle oven. Reproducibility was determined by igniting three aliquots of 3 soil samples (RSD<5 %), respectively. Furthermore, a fractionation by LOI was performed to estimate the fraction soil litter, fulvic and humic fraction, as proposed by Ratnayake et al.[64] Surface soil samples were ignited in 50 °C steps from 150 to 550 °C after overnight drying at 105 °C.

3.3.3 Water extraction of soil

Evidence of only a limited uptake of Hg by soil is present.[65] To gain information on the leaching to water, 50 mg of soil were soaked in Mili-Q water for 12 weeks. Glass beakers were covered with Parafilm and stirred continuously at 9 min^{-1}x100 at RT for 4 weeks. Afterwards, the beakers were placed in a refrigerator at 4 °C in the dark and stirred at irregular time intervals. In the end the soil-water was filtered through a 0.45 µm filter. The elemental composition (representing the labile form of the elements) was measured by ICP-MS. Total organic carbon

(TOC) measurement was conducted on a Teledyne Tekmar TOC Torch and UV analysis on a UV mini 1240 Shimadzu. Since the water was filtered through 0.45 µm, the TOC value represents the DOC content. To evaluate the aromaticity of the OM the specific ultraviolet absorption (SUVA)[66] was calculated by normalizing the absorbance to the DOC content.

3.3.4 Data treatment

A graphical presentation of the spatial distribution of the elements was performed using ArcMap 10.3. The topographic basemap datasets was provided by the Norwegian Polar Institute.[67]

Statistical analysis was carried out using R 2.14.2. The significance level for all tests was set as $p<0.05$ and classified as $p<0.05$, $p<0.01$, $p<0.001$. The obtained data were not always normal distributed. A log-transformation did not improve the data to fit a normal distribution. Therefore, parametric and non-parametric tests were used and the choice was evaluated for each case and element separately. Differences between areas and the soil sample type were evaluated with the two-paired t-test (TT) when a normal distribution (Shapiro test) and homogeneity of variances (Bartlett test) of the data were given. For heterogenic variances and normal distributed data, a Welch's t-test (WT) was performed. When a normal distribution of the data was not given, a Mann-Whitney *U* test (MWUT) was used. Two-tailed correlation between two variables was performed using Spearman's rank correlation coefficient because of the missing normality in some cases.

Factor analysis was performed with SPSS Statistics 23. The extraction of factors was done with principal component analysis and rotation with the Varimax method.

4 Results

4.1 Elemental composition of surface and mineral soils in Svalbard

Elemental concentrations are presented for Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, S and Zn. The mean concentrations of these elements in surface and mineral soils of all samples, respectively, are shown in Table 3 and Table 4. All concentration for the 12 selected elements and others for each sample, respectively, are listed in Table 15-20 in the Appendix B. The concentrations of the trace elements are displayed in Figure 7 and Figure 8.

Table 3. Elemental concentrations (µg/g) in surface soils (n=22) in Svalbard. (mean and standard deviation (std), median and range)

Element	Mean and std	Median	Range
Al	$18.4\cdot10^{3} \pm 7.1\cdot10^{3}$	$18.0\cdot10^{3}$	$6.66\cdot10^{3} – 36.5\cdot10^{3}$
As	5.20 ± 2.55	5.28	1.22 – 9.99
Cd	0.414 ± 0.205	0.349	0.128 – 1.00
Cr	25.3 ± 8.6	24.9	10.2 – 47.8
Cu	11.3 ± 3.0	11.5	5.51 – 16.7
Fe	$14.1\cdot10^{3} \pm 4.8\cdot10^{3}$	$14.4\cdot10^{3}$	$5.37\cdot10^{3} – 22.9\cdot10^{3}$
Hg	0.110 ± 0.035	0.0106	0.0540 – 0.180
Mn	201 ± 68	191	97.9 – 341
Ni	15.7 ± 5.3	16.4	5.58 – 24.9
Pb	9.45 ± 1.90	9.52	5.63 – 13.2
S	$1.36\cdot10^{3} \pm 0.24\cdot10^{3}$	$1.29\cdot10^{3}$	$800 – 1.79\cdot10^{3}$
Zn	64.5 ± 10.9	63.4	44.1 – 83.4

Table 4. Elemental concentrations (µg/g) in mineral soils (n=22) in Svalbard. (mean and standard deviation (std), median and range)

Element	Mean and std	Median	Range
Al	$32.1\cdot10^{3} \pm 10.8\cdot10^{3}$	$33.6\cdot10^{3}$	$6.64\cdot10^{3} – 52.0\cdot10^{3}$
As	8.40 ± 3.91	$9.76\cdot10^{3}$	0.689 – 14.1
Cd	0.0692 ± 0.0289	0.0596	0.0359 – 0.150
Cr	45.9 ± 14.1	45.8	8.78 – 72.3
Cu	14.1 ± 5.5	13.4	3.26 – 24.5
Fe	$25.1\cdot10^{3} \pm 8.9\cdot10^{3}$	$24.2\cdot10^{3}$	$4.87\cdot10^{3} – 43.0\cdot10^{3}$
Hg	0.0279 ± 0.0073	0.0280	0.0165 – 0.0401
Mn	264 ± 104	272	113 – 481
Ni	20.6 ± 8.0	20.1	4.01 – 35.3
Pb	10.3 ± 2.9	10.2	2.92 – 0.150
S	652 ± 292	673	$182 – 1.18\cdot10^{3}$
Zn	51.0 ± 14.7	49.0	25.4 – 80.2

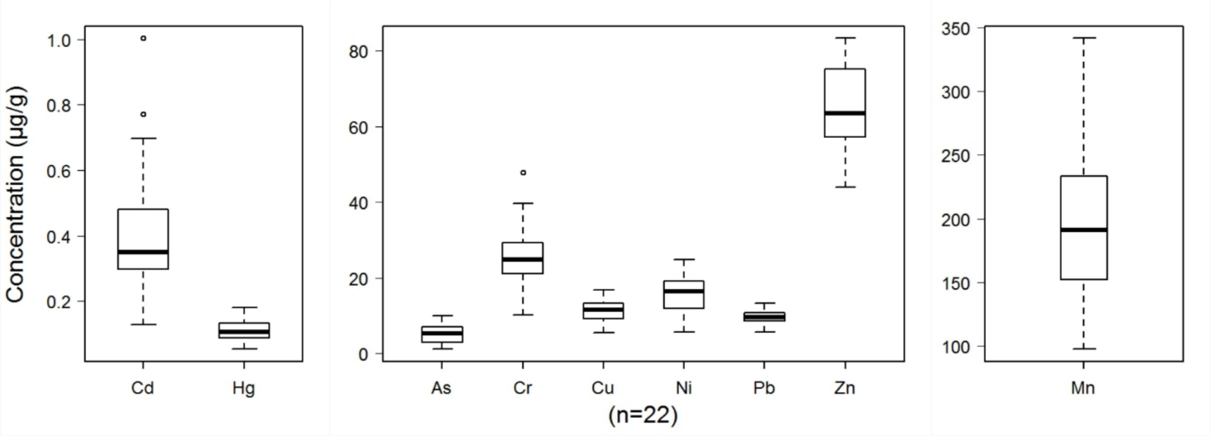

Figure 7. Boxplots of the trace elements in the surface soils (n=22) in Svalbard.

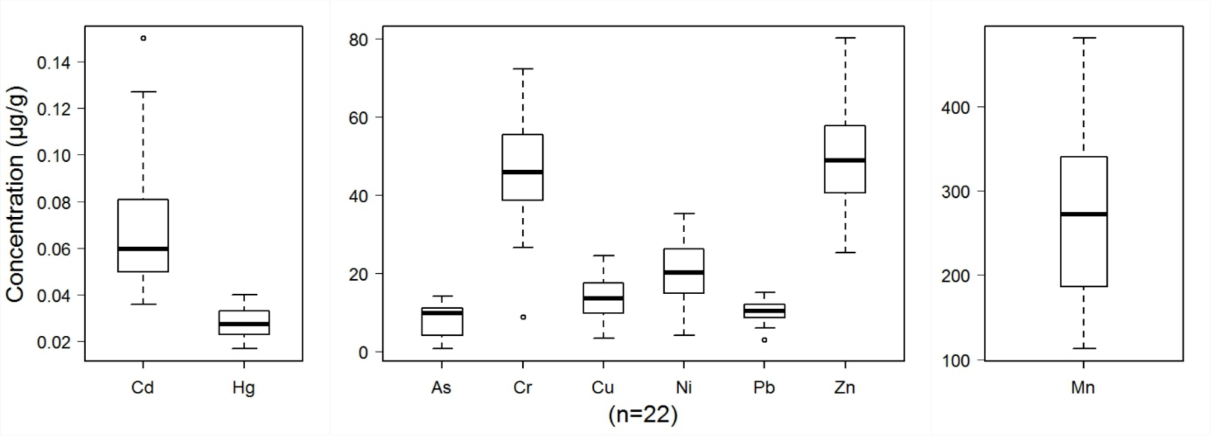

Figure 8. Boxplots of the trace elements in the mineral soils (n=22) in Svalbard.

The abundance of the elements between the surface and the mineral soil is featured in Figure 9. The elements Cd (WT: $p=9.1 \cdot 10^{-8}$), Hg (WT, $p=1.6 \cdot 10^{-10}$), Zn (TT: $p=1.3 \cdot 10^{-3}$) and S (TT: $p=4.4 \cdot 10^{-11}$) have significant higher levels in surface soils. As (TT: $p=2.5 \cdot 10^{-3}$), Cu (WT: $p=0.040$), Cr (WT: $p=1.2 \cdot 10^{-6}$), Ni (TT: $p=0.023$), Fe (WT: $p=1.4 \cdot 10^{-5}$), Al (TT: $p=1.1 \cdot 10^{-5}$) and Mn (WT: $p=0.022$) are significant more abundant in mineral soils. Table 5 summarizes the ratio of the concentrations in the surface soil to the mineral soil.

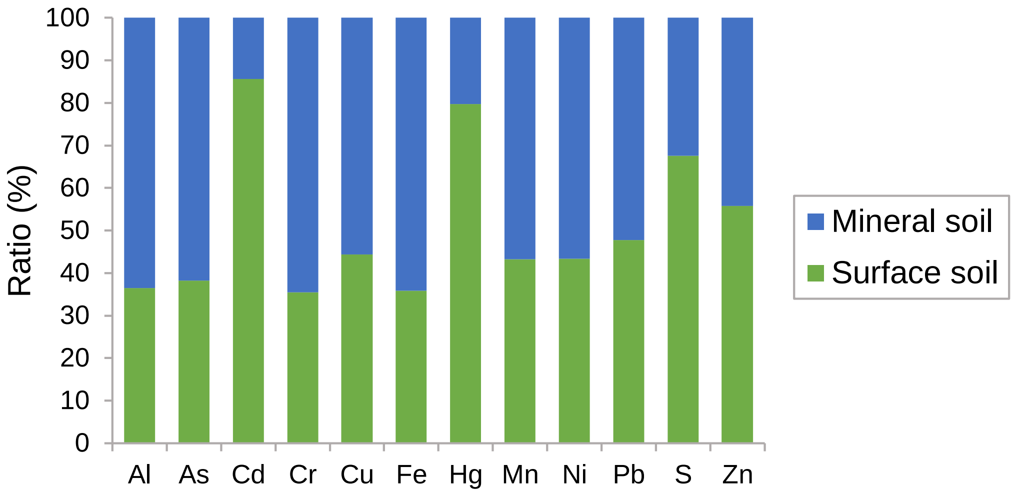

Figure 9. Distribution of 12 elements between surface soils (green) and mineral (blue) soils in Svalbard (n=22). Al ($p<0.001$), As ($p<0.01$), Cd ($p<0.001$), Cr ($p<0.001$), Cu ($p<0.05$), Hg ($p<0.001$), Fe ($p<0.001$), Mn ($p<0.05$), Ni($p<0.05$), S ($p<0.001$), Zn ($p<0.01$)

Table 5. Ratio of elemental concentrations in the surface soil to the mineral soil (n=22).

	Ratio
Al	0.61
As	0.67
Cd	6.5
Cu	0.88
Cr	0.59
Fe	0.61
Hg	4.4
Mn	0.88
Ni	0.83
Pb	1.1
S	2.6
Zn	1.4

4.2 Concentration variances between sampling sites

4.2.1 Foxdalen A and B, Endalen, Bayelva A and B

For discussion of differences resulting from the sampling site, mean concentration for Foxdalen A, Foxdalen B, Endalen, Bayelva A and Bayelva B are shown in Table 13 and Table 14 in Appendix B. These variations for selected elements are displayed in boxplots in Figure 24 in Appendix B. A geographical presentation for the five different sampling sites for all 12 elements and SOM content can be found in Figure 27 to Figure 38 in Appendix E. Attention should be drawn to their scaling. Since it is always the same symbol size scaling, differences might be visually lead to an overestimation or underestimation.

4.2.2 Adventdalen and Bayelva area

In order to evaluate the differences between Adventdalen and the Bayelva area in geology and the ones resulting from anthropogenic influences the elemental composition of surface and mineral soils, respectively, are separated according to the two areas, as seen in Table 6 and Table 7. The statistical comparison was performed including the 15 samples from the Bayelva area from 2014. In the surface soils As, Cr, Ni and Fe are significantly higher and Cd, Pb and Zn are significantly lower in Adventdalen (see Figure 10). As, Cr and S are significantly higher in the mineral soils in Adventdalen and Cd and Mn are significantly lower (see Figure 11).

Following significance was observed:

Surface soils: As (TT: $p=5.3\cdot10^{-10}$), Cr (TT: $p=0.011$), Ni (TT: $p=0.011$), Fe (TT: $p=8.4\cdot10^{-3}$), Cd (MWUT: $p=7.1\cdot10^{-4}$), Pb (WT: $p=1.7\cdot10^{-5}$), Zn (TT: $p=0.024$)

Mineral soils: As (TT: $p=1.7\cdot10^{-9}$), Cr (TT: $p=0.042$), S (TT: $p=7.9\cdot10^{-4}$), Cd (WT: $p=3.9\cdot10^{-7}$), Mn (TT: $p=2.1\cdot10^{-5}$)

Table 6. Concentrations (µg/g) of 12 elements in surface soils in Svalbard. (mean and standard deviation)

Element	Adventdalen (n=16)	Bayelva area (n=21)
Al	$19.8\cdot10^3 \pm 6.5\cdot10^3$	$16.7\cdot10^3 \pm 8.6\cdot10^3$
As	6.48 ± 1.60	2.54 ± 1.22
Cd	0.363 ± 0.192	0.571 ± 0.180
Cr	27.7 ± 7.8	19.9 ± 9.4
Cu	12.5 ± 2.3	10.5 ± 3.6
Fe	$15.7\cdot10^3 \pm 4.0\cdot10^3$	$11.3\cdot10^3 \pm 5.4\cdot10^3$
Hg	0.110 ± 0.034	0.122 ± 0.043
Mn	202 ± 64	250 ± 1238
Ni	17.8 ± 4.2	12.9 ± 5.9
Pb	8.77 ± 1.55	14.3 ± 4.5
S	$1.43\cdot10^3 \pm 0.20\cdot10^3$	$1.43\cdot10^3 \pm 0.46\cdot10^3$
Zn	63.4 ± 9.0	73.2 ± 14.9

Table 7. Concentrations (µg/g) of 12 elements in mineral soils in Svalbard. (mean and standard deviation)

Element	Adventdalen (n=16)	Bayelva area (n=21)
Al	$34.2\cdot10^3 \pm 9.9\cdot10^3$	$33.5\cdot10^3 \pm 11.9\cdot10^3$
As	10.3 ± 2.6	4.57 ± 1.78
Cd	0.0558 ± 0.0124	0.134 ± 0.049
Cr	50.0 ± 7.9	41.6 ± 11.7
Cu	15.5 ± 5.1	15.1 ± 6.4
Fe	$2.75\cdot10^3 \pm 8.42\cdot10^3$	$24.8\cdot10^3 \pm 6.8\cdot10^3$
Hg	0.0299 ± 0.0068	0.0294 ± 0.0156
Mn	240 ± 88	433 ± 137
Ni	22.1 ± 7.9	22.4 ± 7.9
Pb	10.7 ± 2.6	12.8 ± 4.3
S	762 ± 243	466 ± 308
Zn	53.0 ± 16.3	56.6 ± 14.4

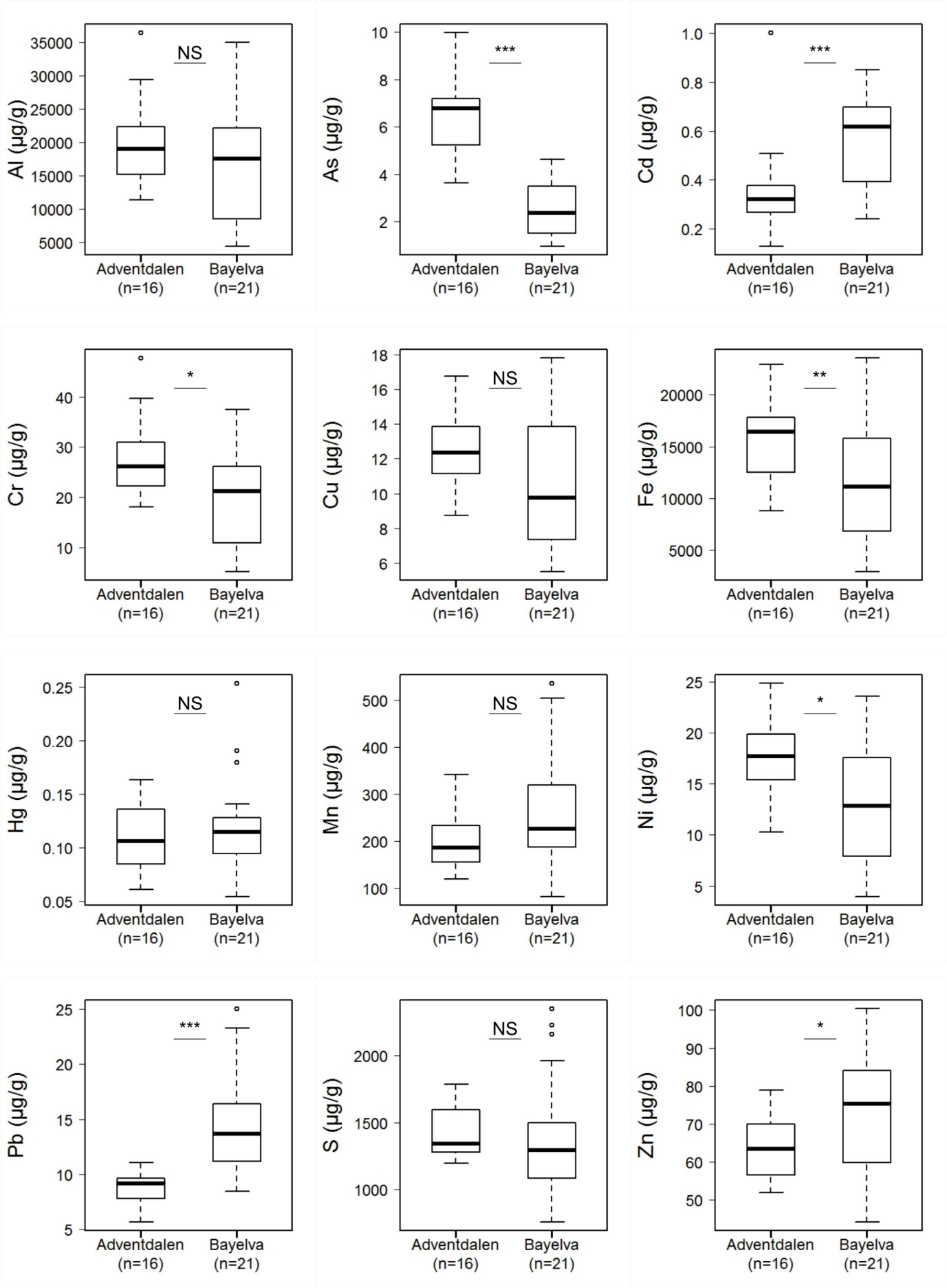

Figure 10. Boxplots of the elemental distribution in surface soils in the Bayelva area (left) and Adventdalen (right) in Svalbard. Significance indicated by: NS: not significant; *: p<0.05; **: p<0.01; ***: p<0.001

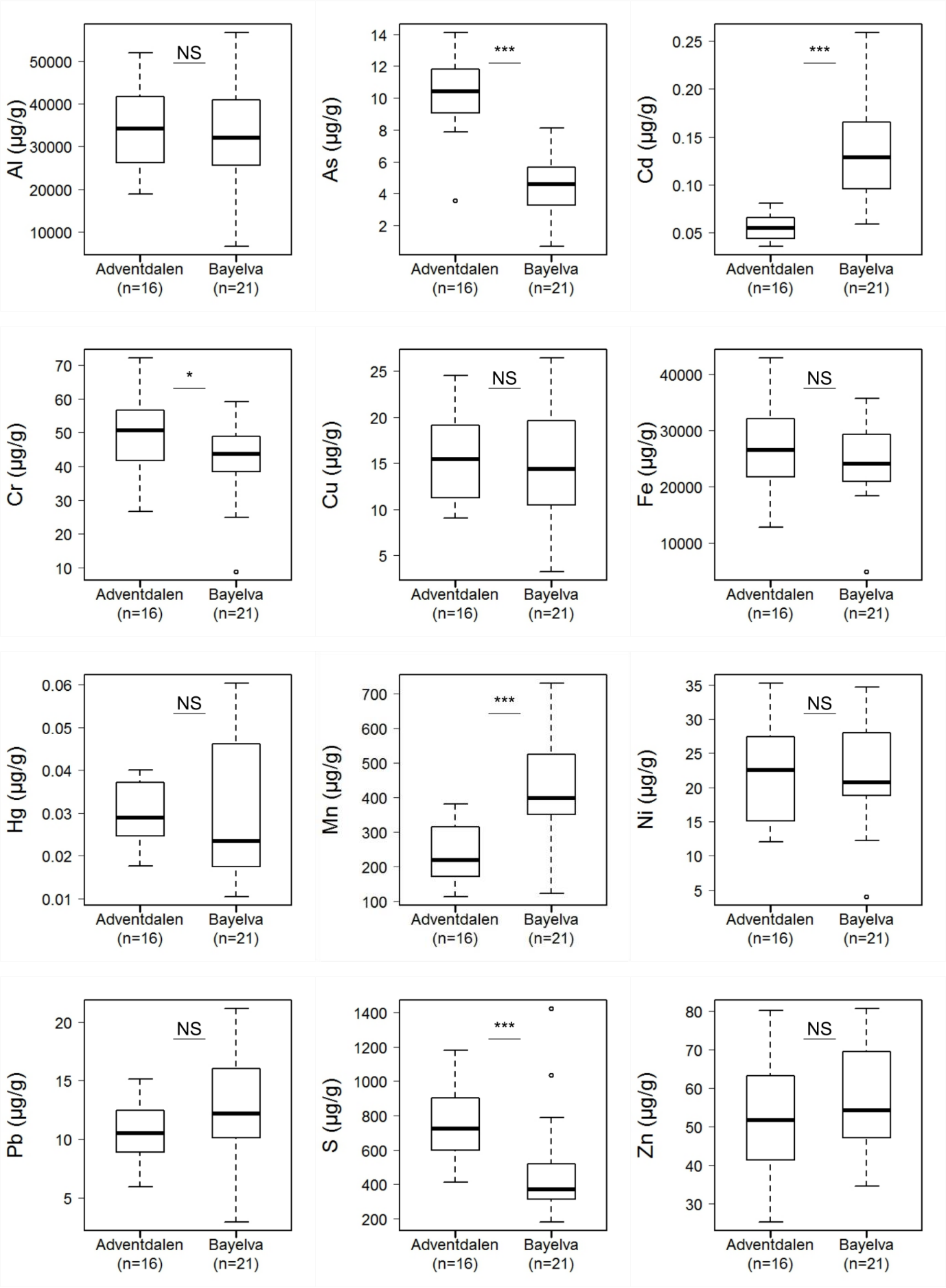

Figure 11. Boxplots of the elemental distribution in mineral soils in the Bayelva area (left) and Adventdalen (right) in Svalbard. Significance indicated by: NS: not significant; *: p<0.05; **: p<0.01; ***: p<0.001

A significant higher abundance of Cd (WT: $p=2.3\cdot10^{-6}$, MWUT: $p=2.2\cdot10^{-3}$), Hg (WT: $p=2.3\cdot10^{-6}$, MWUT: $p=5.0\cdot10^{-3}$) and S (MWUT: $p=6.7\cdot10^{-9}$, TT: $p=8.0\cdot10^{-5}$) in surface soils in Adventdalen and Bayelva and of Cr (WT: $p=1.2\cdot10^{-6}$, TT: $p=0.030$) and Fe (WT: $p=9.5\cdot10^{-5}$, TT: $p=0.021$) in mineral soils is observed (Figure 12). Al (TT: $p=3.3\cdot10^{-5}$), As (WT: $p=0.042$), Cu (WT: $p=0.039$), Ni (WT: $p=0.042$) and Pb (WT: $p=0.018$) are significantly higher in the mineral soil compared to the surface soil in Adventdalen. Zn (TT: $p=0.011$) is significantly higher in the surface fraction in the Bayelva area.

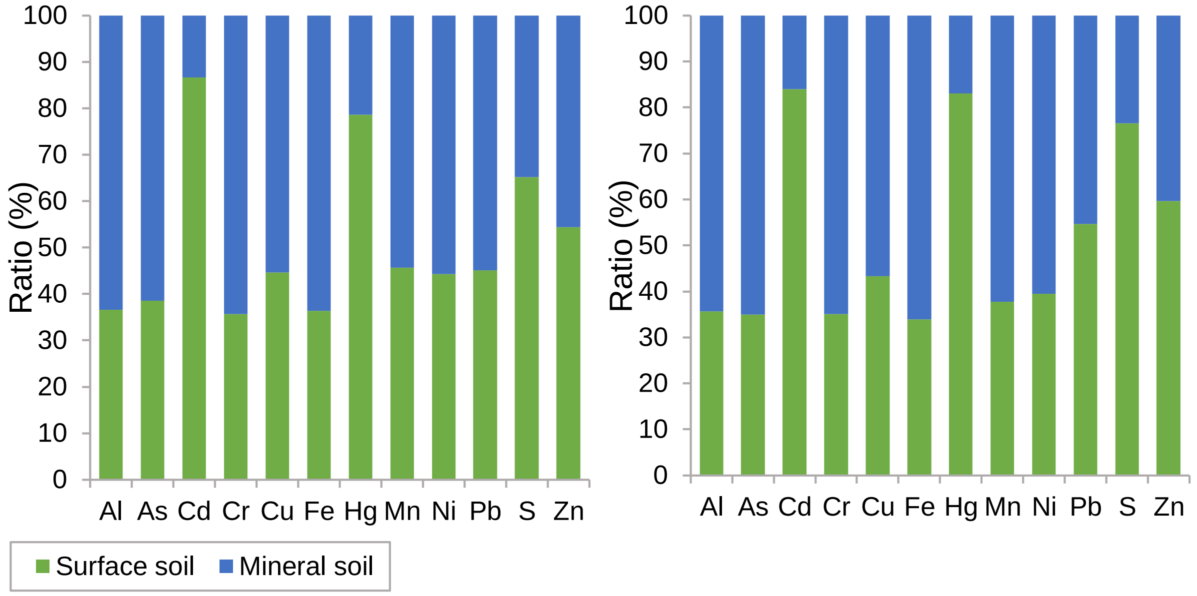

Figure 12. Distribution of 12 elements between surface soils (green) and mineral (blue) soils in Adventdalen (left) and Bayelva area (right) in Svalbard. Adventdalen: Al ($p<0.001$), As ($p<0.05$), Cd ($p<0.001$), Cr ($p<0.001$), Cu ($p<0.05$), Fe ($p<0.001$), Hg ($p<0.001$), Ni ($p<0.05$), Pb ($p<0.05$), S ($p<0.001$); Bayelva area: Cd ($p<0.01$), Cr ($p<0.05$), Hg ($p<0.01$), Fe ($p<0.05$), S ($p<0.001$), Zn ($p<0.05$)

The survey by Gulinska et al.[68] in soils in Billefjorden assessed geological differences by the plotting of the ratio of strontium (Sr) to zirconium (Zr) against of magnesium (Mg) to Al. Carbonate rock (e.g. limestone in the Bayelva area) is usually higher in Sr and Mg and clastic rock (e.g. sandstones present in Adventdalen and Bayelva area) in Zr and Al. Figure 13 shows similar behaviors of the sampling sites Foxdalen A and B and Endalen. The site Bayelva A and Bayelva B show different ratios of these elements, respectively.

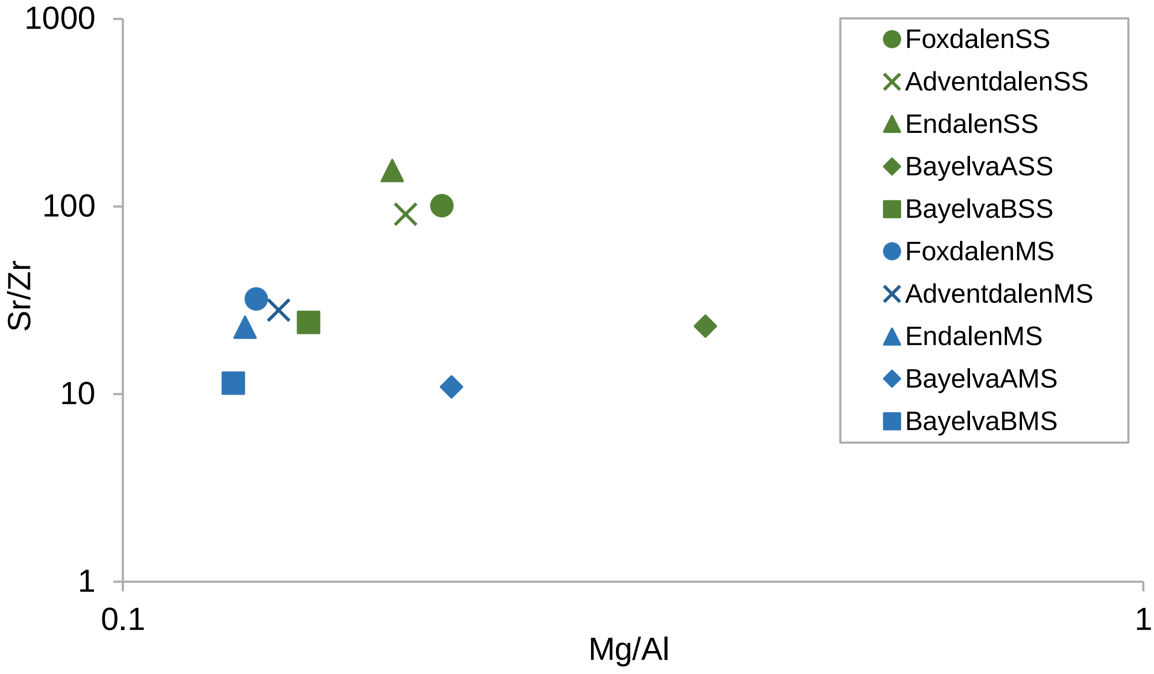

Figure 13. Ratios of Mg/Al and Sr/Zr to assess geological differences between Adventdalen and Bayelva. Elevated levels of Sr and Mg are usually attributed with carbonate rocks and higher Zr and Al levels for clastic rocks. (Green: surface soil (SS), blue: mineral soil (MS))

4.3 SOM content

Figure 14 illustrates the SOM content in the surface soil samples (mean values and water loss at 105 °C can be found in Table 8). SOM content determined by LOI ranged between 33.8 and 72.7 % for the surface soils (mean 53.5 ± 10.8%). The LOI data for the stepwise ignition (see also Figure 14) reveals a higher OM loss at 250 °C for Endalen and Bayelva A. Bayelva A loses at 400 °C 15 % OM again, Foxdalen A and Endalen only less than 10 %.

Table 8. Soil organic matter (SOM) and water loss (WL) at 105 °C of surface soils in Svalbard.

	n	SOM (%)	WL (%)
Foxdalen A	12	51.6 ± 11.0	8.71 ± 1.47
Foxdalen B	2	52.3 ± 1.7	9.06 ± 0.04
Endalen	2	60.9 ± 7.6	9.52 ± 1.90
Bayelva A	4	56.8 ± 16.9	9.48 ± 2.26
Bayelva B	2	52.4 ± 4.1	8.12 ± 0.56
Average	22	53.5 ± 10.8	8.90 ± 1.59

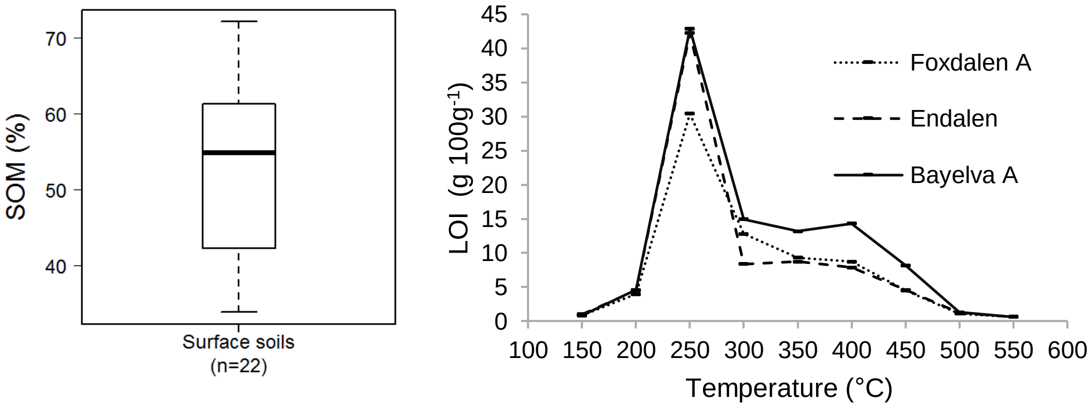

Figure 14. Soil organic matter (SOM) content (left) and Loss-on-ignition (LOI) in 50 °C steps (right) for surface soils in Svalbard.

In addition, SOM content analysis for surface soil samples from 2014 was performed (see Table 9).[65]

Table 9. Soil organic matter (SOM) and water loss (WL) at 105 °C of surface soils (sampled in 2014) in Svalbard.

	n	SOM (%)	WL (%)
Bayelva A	10	50.6 ± 10.5	7.51 ± 1.48
Bayelva B	5	66.4 ± 16.7	9.56 ± 2.49
London	10	75.9 ± 6.6	11.4 ± 1.1
Bøtnbreen	5	50.2 ± 17.6	8.31 ± 2.79
Knudsenheia	5	62.9 ± 12.0	10.0 ± 1.5
Average	35	61.7 ± 15.6	9.40 ± 2.31

4.4 Correlations between Hg, SOM and other elements

Significant correlation of Hg-Al (ρ=-0.53, p=0.012), Hg-Cd (ρ=0.65, p=$1.0\cdot10^{-3}$), Hg-Cr (ρ=-0.54, p=$9.2\cdot10^{-3}$), Hg-Fe (ρ=-0.49, p=0.020) and Hg-SOM (ρ=0.67, p=$7.1\cdot10^{-4}$) in the surface soils was obtained (Figure 15).

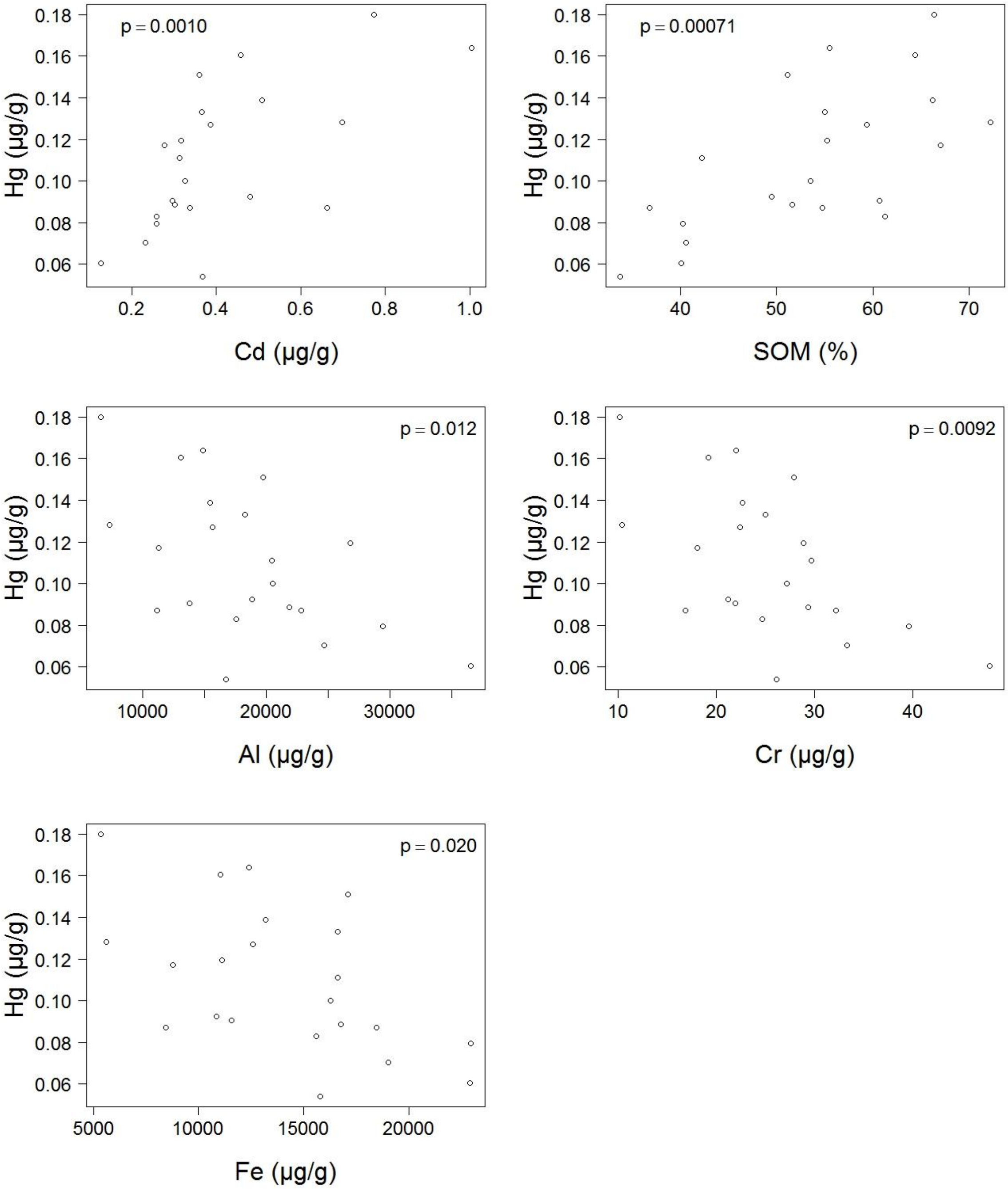

Figure 15. Significant positive between mercury (Hg) and soil organic matter (SOM) and cadmium (Cd) or significant negative correlation between Hg and aluminum (Al), chromium (Cr) and iron (Fe) in surface soils (n=22) in Svalbard. (Al: ρ=-0.53, $p<0.05$; Cd: ρ=0.65, $p<0.01$; Cr: ρ=-0.54, $p<0.01$; Fe: ρ=-0.49, $p<0.05$; SOM: ρ=0.67, $p<0.001$)

The sample set of all samples (n=57) from 2014 and 2015 showed a significant positiv correlation between Hg and Cd (ρ=0.27, $p<0.046$) and SOM (ρ=0.37, $p<0.064$).

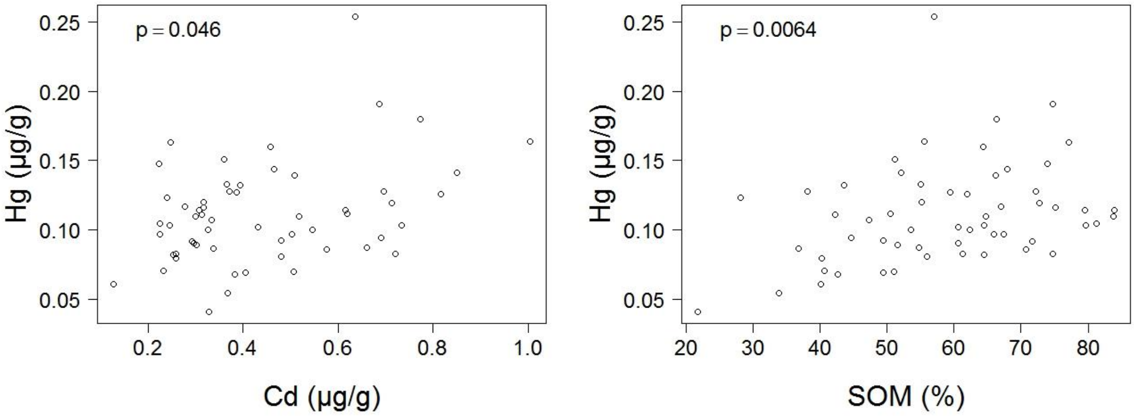

Figure 16. Significant positive between mercury (Hg) and soil organic matter (SOM) and cadmium (Cd) in surface soils (n=57) in Svalbard. (Cd: ρ=0.27, $p<0.05$; SOM: ρ=0.37, $p<0.01$)

In the mineral soil Hg significantly correlates with As (ρ=0.51, $p<0.015$) and Cr (ρ=0.44, $p<0.043$). A significant correlation of Hg-As (ρ=0.54, $p=1.5\cdot10^{-5}$), Hg-Al (ρ=0.55, $p=7.9\cdot10^{-6}$), Hg-Cr (ρ=0.60, $p=7.9\cdot10^{-7}$), Hg-Cu (ρ=0.55, $p=1.0\cdot10^{-5}$), Hg-Ni (ρ=0.54, $p=1.5\cdot10^{-5}$), Hg-Pb (ρ=0.50, $p=8.7\cdot10^{-5}$), Hg-S (ρ=0.63, $p=1.6\cdot10^{-7}$), Hg-Zn (ρ=0.45, $p=4.4\cdot10^{-4}$) and Hg-Fe (ρ=0.39, $p=2.6\cdot10^{-3}$) among the 57 mineral soil samples was obtained.

4.5 Comparison with the soil samples taken in 2014

In the master thesis by M. Fors[65], concentrations of the same selected elements for surface and mineral soils are presented. These samples were taken in the Bayelva area, London (Blomsterhalvøya), Bøtnbreen and Knudsenheia in August 2014.

The concentrations of Al (MWUT: $p=2.5\cdot10^{-3}$), As (MWUT: $p=6.1\cdot10^{-5}$), Cr (MWUT: $p=1.1\cdot10^{-4}$), Fe (MWUT: $p=1.7\cdot10^{-3}$) and Ni (MWUT: $p=8.0\cdot10^{-4}$) in surface soils were significantly higher and of Pb (WT: $p=1.2\cdot10^{-4}$) and S (WT: $p=0.014$) significantly lower than for samples taken in 2014[65]. Significant differences in the mineral soils were obtained for Cd (MWUT: $p=8.1\cdot10^{-5}$) and Mn (MWUT: $p=5.7\cdot10^{-5}$) (significant lower than samples from 2014) and As (WT: $p=2.2\cdot10^{-3}$), Hg (MWUT: $p=0.016$) and S (MWUT: $p=0.012$) (significant higher than samples from 2014). A comparison between the samples taken in the Bayelva area revealed significant lower concentrations of Cu (MWUT: $p=0.045$) and Pb (MWUT: $p=6.1\cdot10^{-3}$) in surface soils in 2015. These were both reported higher in 2014. Our concentrations were significant lower in As (TT: $p=0.042$), Pb (TT: $p=0.019$), Mn (TT: $p=4.8\cdot10^{-3}$), Cu (TT: $p=0.030$), Zn (TT: $p=0.021$), Ni (TT: $p=0.028$) and Fe (MWUT: $p=6.2\cdot10^{-3}$) in the mineral soil than samples from 2014 in the Bayelva area.[65]

4.6 Factor analysis

To see underlying factors influencing the elemental concentrations, multivariate statistics in form of the factor analysis were performed. The rotated factor loadings are shown for the surface and for the mineral soils, respectively, in Table 10. With the loadings assigned to the factors, similar sources and associative effects among the variables can be identified. Loadings which are ≤-0.4 and ≥0.4 are shown.[69] Scree plots and communalities are shown in Appendix D. The loadings for the factors are plotted in Figure 17 and Figure 18.

Table 10. Rotated component matrix for surface soil samples (left) and mineral soil samples (right) in Svalbard. Surface soils: f1 explains 49.6 %, f2 14.9 %, f3 11.1 % and f4 10.0 % of the total variance. Mineral soils: f1 explains 55.0 %, f2 18.6 % and f3 15.6 % of the total variance.

	f1	f2	f3	f4
SOM	-0.771	0.424		
Al	0.913			
As	0.736	0.468		
Cd	-0.729		0.430	0.462
Cr	0.964			
Cu	0.907			
Fe	0.967			
Hg	-0.614	0.510		
Mn			0.906	
Ni	0.921			
Pb		-0.582	0.506	
S		0.863		
Zn				0.974

	f1	f2	f3
SOM	-0.624	-0.482	0.528
Al	0.938		
As		0.744	
Cd		-0.932	
Cr	0.870	0.426	
Cu	0.911		
Fe	0.886		
Hg			0.663
Mn	0.821		
Ni	0.948		
Pb	0.923		
S			0.887
Zn	0.926		

Four factors for the analysis of the surface soils were extracted based on the criterion Eigenvalue ≥1. Factor 1 (f1) explains 49.6 % of the total variance and influences positively the elements Al, As, Cr, Cu, Fe and Ni and negatively SOM, Cd and Hg. The group of elements explained by Factor 2 (f2) (14.9 % of the total variance) includes SOM, As, Hg, Pb and S. F2 influences Pb negatively. Loadings for factor 3 (f3) are high for Cd, Mn and Pb. F3 explains 11.1 % of the total variance. Cd and in particular Zn predominate Factor 4 (f4) (10.0 % of the total variance). For the mineral soil three factors were extracted. F1 includes SOM (negative association), Al, Cr, Cu, Fe, Mn, Ni, Pb and Zn. It explains 55.0 % of the total variance. SOM and Cd are negatively influences by f2 (18.6 % of the total variance) and As, Cr and Cd positively. SOM, Hg and S predominate the loadings of f3 (15.6 % of the total variance).

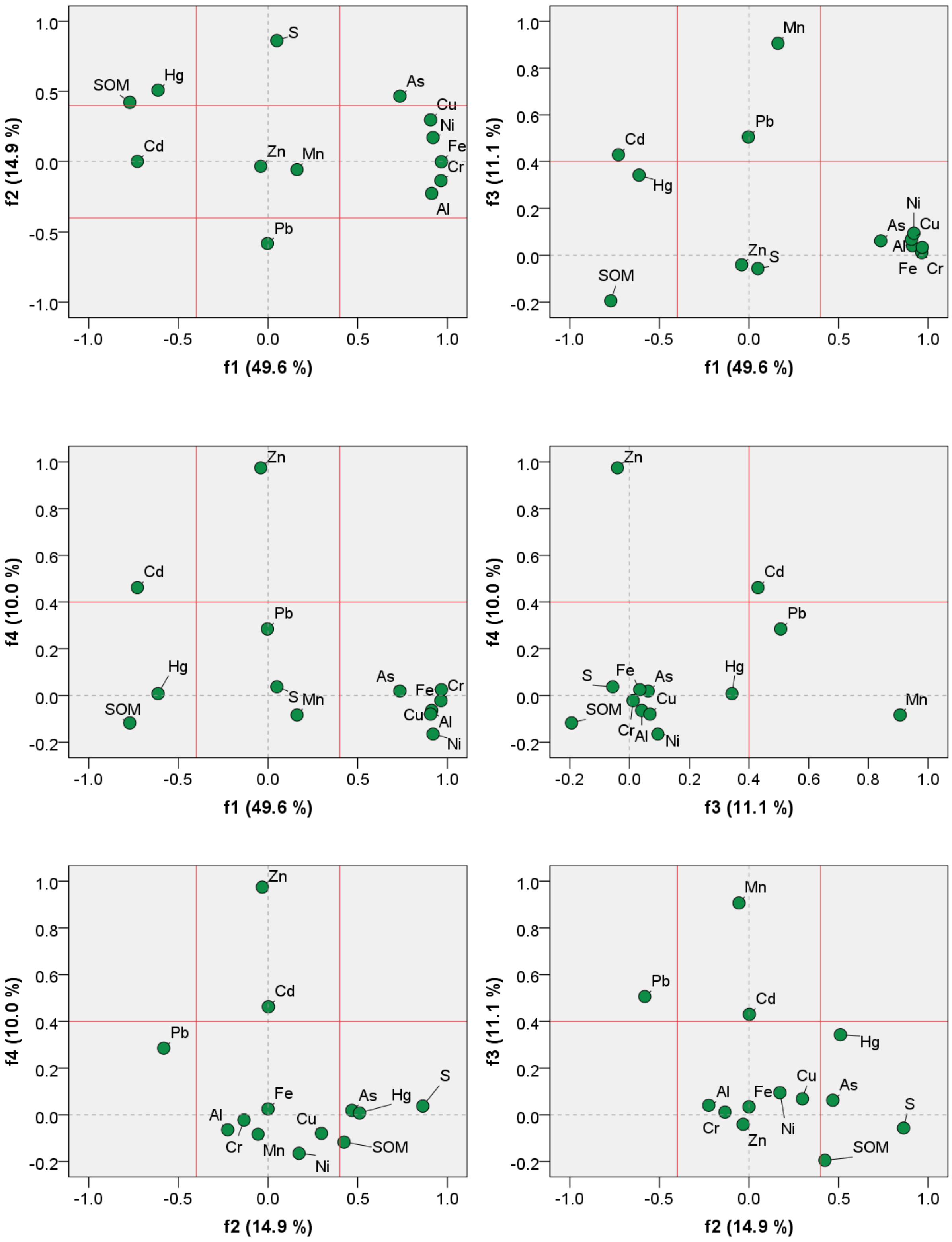

Figure 17. Loading plots of the factor analysis for surface soil samples for four extracted factors.

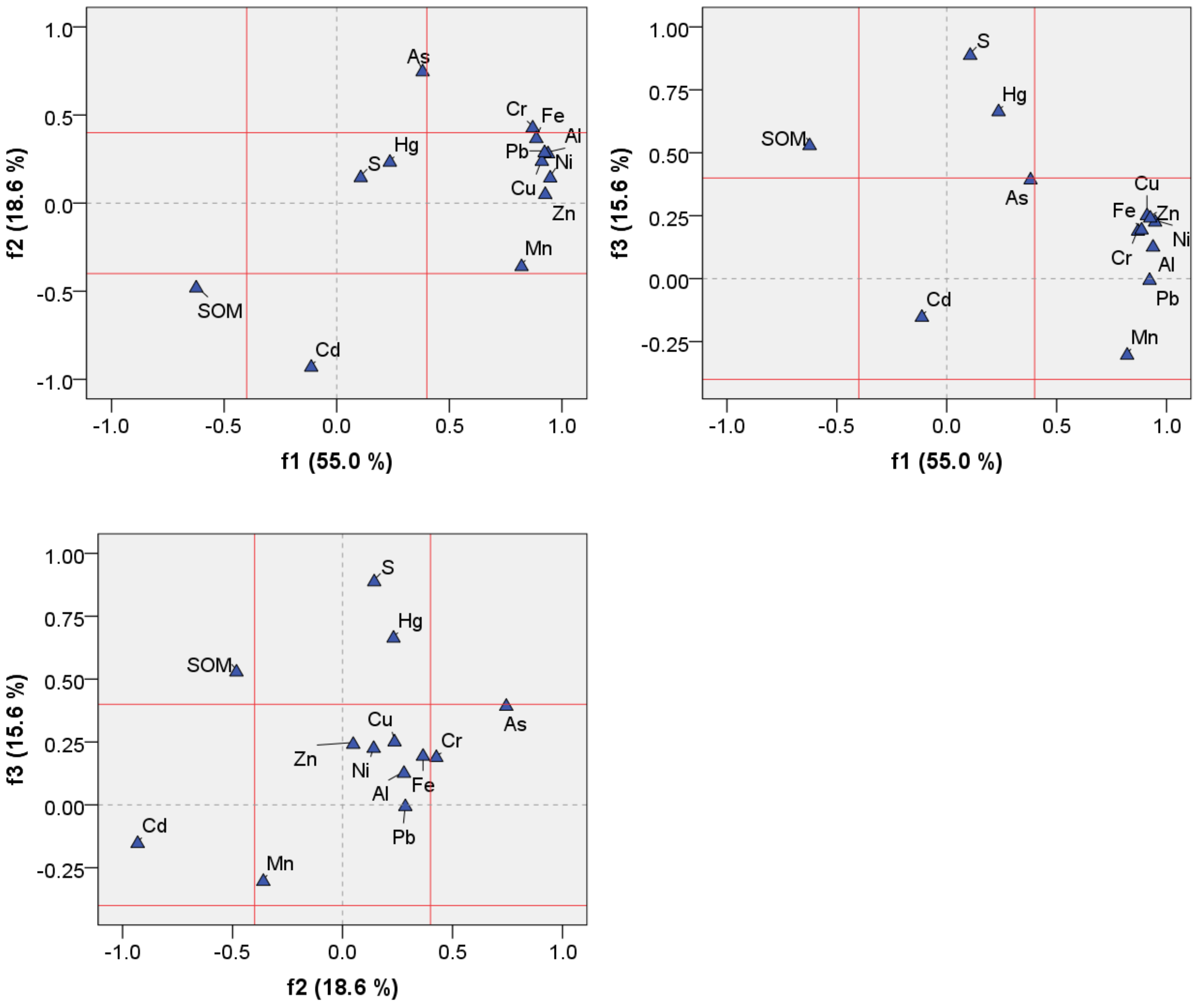

Figure 18. Loading plots of the factor analysis for mineral soil samples for three extracted factors.

To improve the statistics by increasing the ratio of samples to variables, the factor analysis was repeated with the samples from 2014 (n=35)[65] and 2015 (n=22). Based on the criterion Eigenvalue >1, the factor analysis for the surface soil samples extracted three factors. However, only 60.5 % of the variance among the Hg concentrations could be explained by these. The Eigenvalue of the forth factor is 0.987. Including this one, the communality of Hg improved (73.4 %). Regarding the scree plot, there might actually be four factors explaining the variances of the elements. Therefore, four extracted factors for the surface soils were chosen (Table 11). The loadings for the factors are plotted in Figure 19and Figure 20.

Table 11. Rotated component matrix for surface soil samples (left) and mineral soil samples (right) in Svalbard. (Sum of samples from 2014 and 2015) Surface soils: f1 explains 46.7 %, f2 13.2 %, f3 13.2 % and f4 11.8 % of the total variance. Mineral soils: f1 explains 51.5 %, f2 17.3 % and f3 15.1 % of the total variance.

	f1	f2	f3	f4
SOM	-0.776			0.472
Al	0.922			
As	0.871			
Cd			0.742	
Cr	0.955			
Cu	0.887			
Fe	0.952			
Hg				0.770
Mn		0.877		
Ni	0.957			
Pb		0.804	0.417	
S	-0.453			0.666
Zn			0.840	

	f1	f2	f3
Al	0.927		
As	0.457	0.622	
Cd			0.844
Cr	0.863		
Cu	0.899		
Fe	0.928		
Hg		0.733	
Mn			0.729
Ni	0.935		
Pb	0.883		
S		0.871	
Zn	0.911		

F1 (46.7 % of the total variance) for the surface soils shows high loadings for Al, As, Cr, Cu, Fe and Ni and a negative loading for SOM and S. Mn and Pb appear in f2 (13.2 %). Cd, Pb and Zn are affected by f3 (13.2 % of the total variance). F4 explains 11.8 % of the total variance and the loadings are high for SOM, Hg and S. Three factors were extracted for the mineral soils for the increased dataset. F1 exhibits high loadings for Al, As, Cr, Cu, Fe, Ni, Pb and Zn and explains 51.5 % of the total variance. As, Hg and S have high loadings of f2 (17.3 % of the total variance) and Cd and Mn of f3 (15.1 % of the total variance).

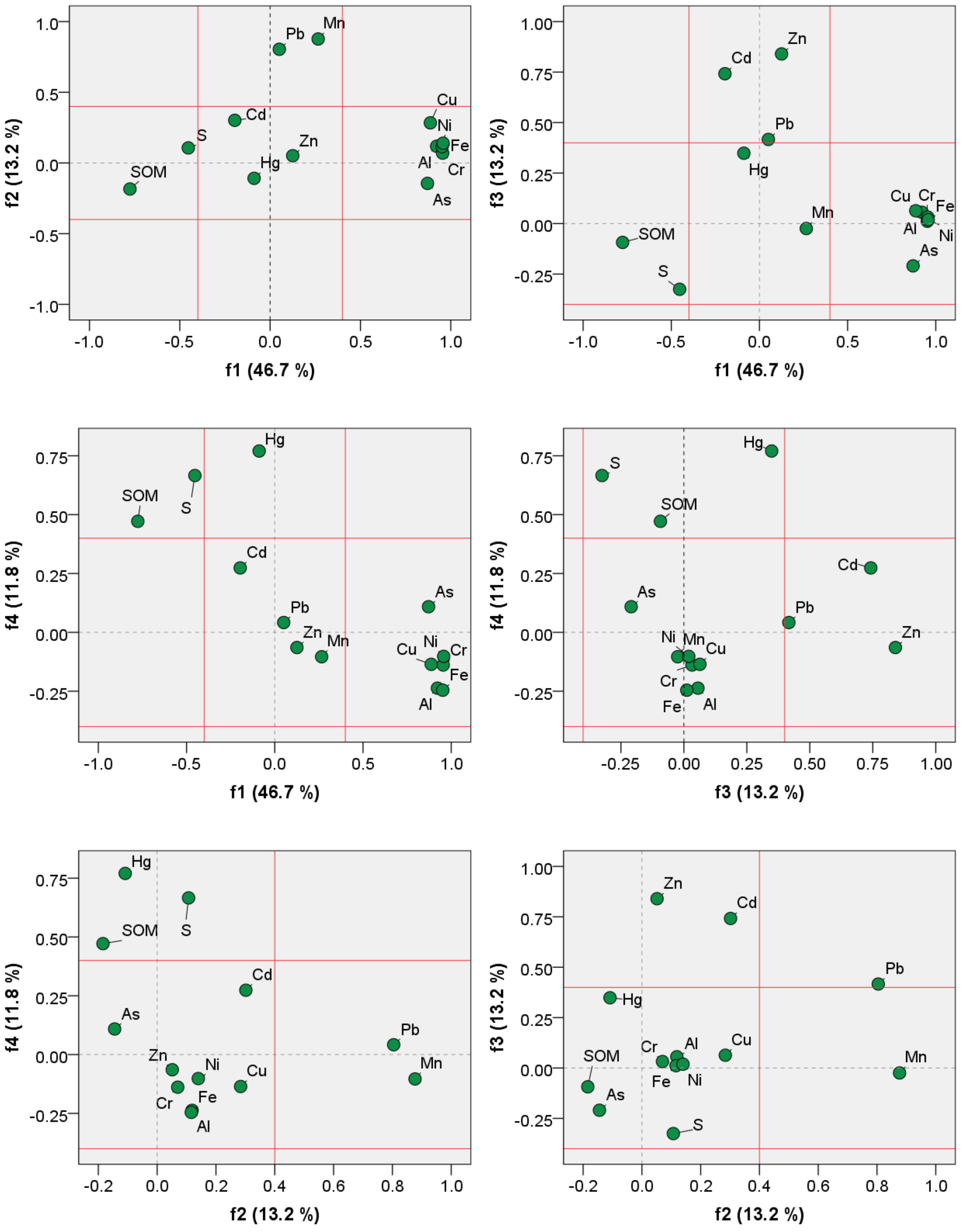

Figure 19. Loading plots of the factor analysis for surface soil samples for four extracted factors (including samples from 2014).

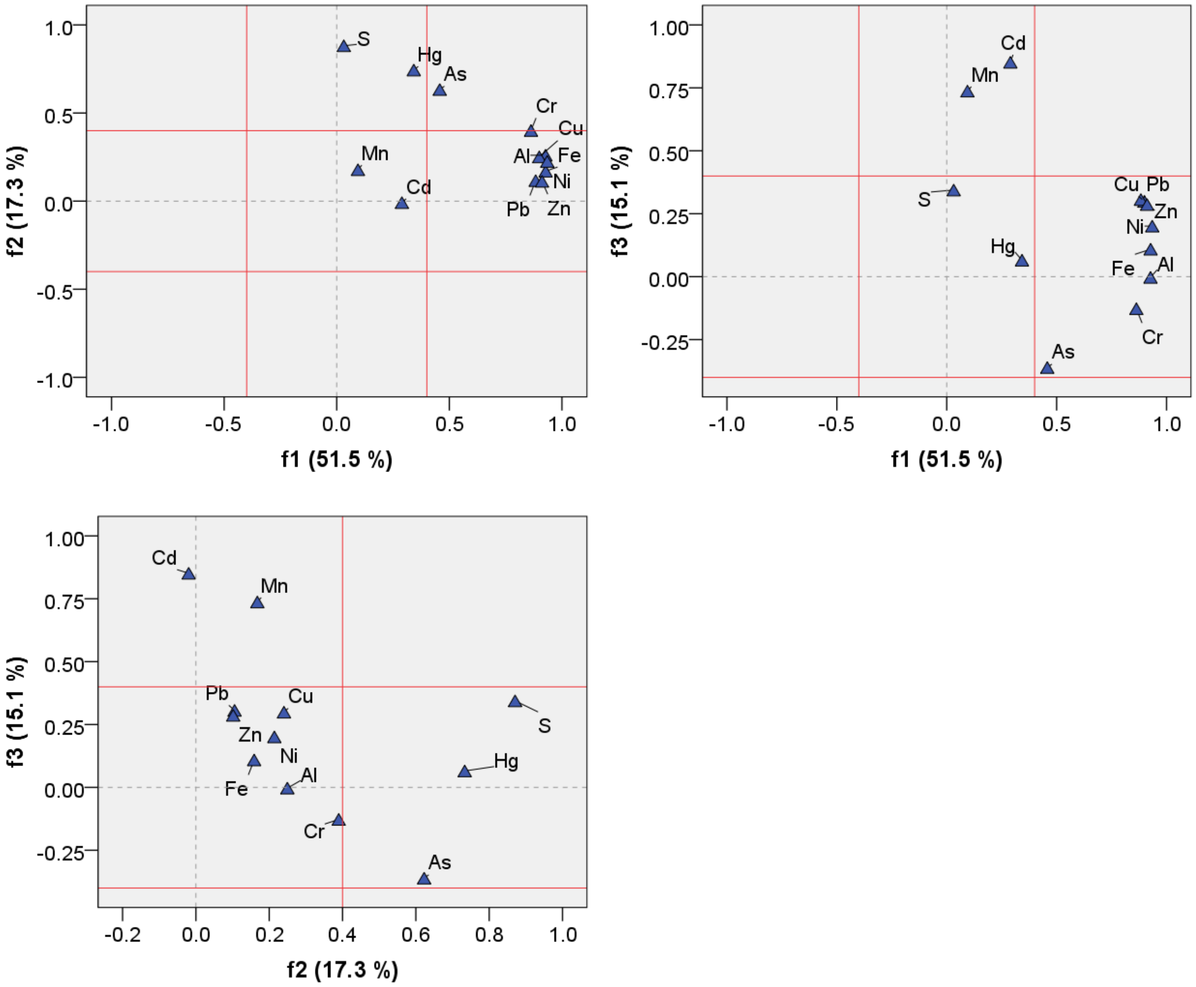

Figure 20. Loading plots of the factor analysis for mineral soil samples for three extracted factors (including samples from 2014).

4.7 Water extraction of surface soils

The results from the water extraction experiment are presented in Table 12. The SUVA values, Hg and S content for the 5 different sampling sites are shown in Figure 21. The highest SUVA was observed for soils from Endalen, the lowest from Bayelva B. SUVA values $\geq$4 are often evaluated as high, indicating high amounts of hydrophobic, aromatic and high molecular weight NOM fractions. In contrast, SUVA values $\leq$3 indicate non-humic, hydrophilic and low molecular weight compounds.[70] Hg concentrations significantly correlate with S content ($\rho=1$, $p=2.2\cdot10^{-16}$).

Table 12. Parameters determined for the water extraction experiment of surface soils in Svalbard: Total organic carbon (TOC in ppmC), absorbance (A_{254} in m^{-1}), pH, conductivity (σ in µS cm^{-1}).

	TOC (ppmC)	A_{254} (m^{-1})	pH	σ (µS cm^{-1})
Foxdalen A	71	1.90	5.9	189
Foxdalen B	111	2.09	6.1	327
Endalen	123	4.08	5.7	217
Bayelva A	78	0.99	6.9	341
Bayelva B	228	2.86	6.1	468

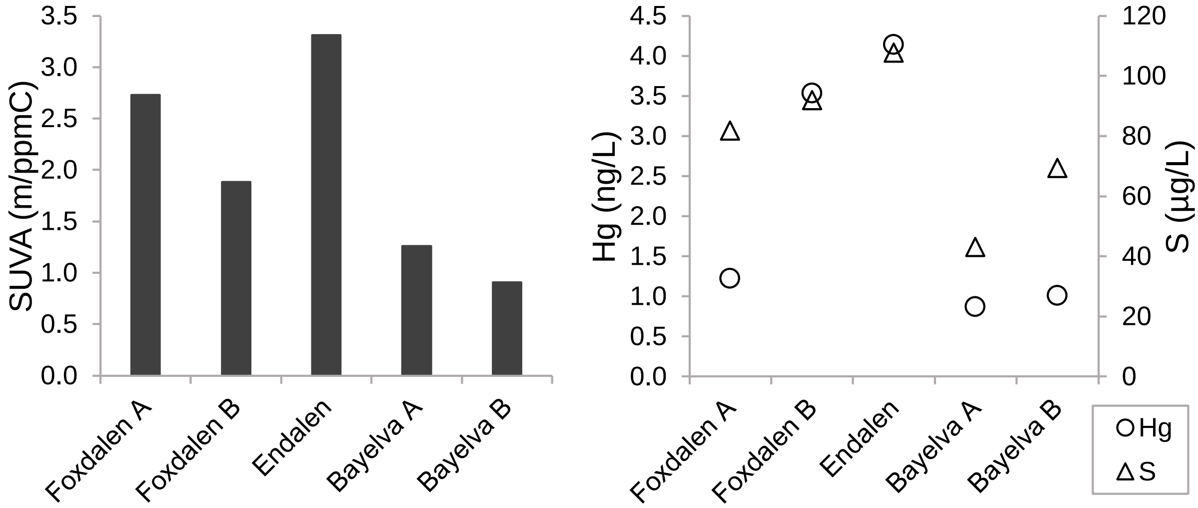

Figure 21. Specific ultraviolet absorbance (SUVA) (left), mercury (Hg) and sulfur (S) content (right) for the filtered (0.45 µm) water extraction of surface soils in Svalbard.

5 Discussion

In the first section (5.1) of this chapter, an overview about the elemental concentrations, their magnitudes and the SOM content are discussed in comparison with Norwegian topsoils and the samples from 2014. The sections 5.2-5.4 will further examine the Hg levels in connection with relevant previous studies, the obtained correlation of Hg and other variables and their relevance for the Hg cycling in Svalbard. The results of the factor analysis are discussed under 5.5. The last section (5.6) evaluates the differences among the sampling sites in Adventdalen and the Bayelva area.

5.1 General characteristics of soils in Svalbard

The mean concentrations of As, Cd, Hg, Cu, Zn, Ni and Pb of all samples (Table 3) in surface soils are in the range of unpolluted soils in Norway and classified as very good “Tilstandsklasse 1: Meget god”[71]. A classification of Cr is difficult because levels cannot be distinguished into Cr(III) and Cr(VI). Only the As concentrations in mineral soils can be assigned to the second grade “Tilstandsklasse 2: God”[71]. Since it is the mineral soil featuring these magnitudes of As, this indicates an origin from geology characteristics.

The SOM content in all samples is rather low and no lower limit (e.g. SOM>70 %[27]) can be applied for discussion of surface soils. Reasons for the low content can be attributed to the permafrost and climate influences. Cryosols can have thin organic layers and be mixed with underlying mineral soils.[18,72] The vegetation cover is sparsely and microbial activity is low. This is in accordance with the observations during sampling. Most of the SOM was ignited at 250 C (Figure 14 right) and the proportions of the litter, HA and FA cannot be clearly distinct as proposed by Ratnayake et al.[64] Weight loss at higher temperature may also originate from structural water-loss. This approach may not be suitable for Arctic tundra soils.

Significant differences in the samples from 2014 and ours both taken in the Bayelva area can indicate heterogeneous soil characteristics/development at this site. As seen from Figure 13 the vicinity to the glacier in the Bayelva area introduces also differences among Bayelva A and Bayelva B samples. The significant variations of the elemental concentration comparing the whole dataset from 2014 and 2015 are probably connected to different sampling sites. In particular, the differences in the mineral soil suggest strong geological differences. A different geological background is given in Adventdalen and the Bayelva area (Figure 13, Figure 22, Figure 23). In addition, different sample handling and contamination during the laboratory work can have introduced variations in them between the samples taken in 2014 and 2015.

Furthermore, soil studies conducted in Norway and presenting background values can be used to assess the concentrations in Svalbard soils.[27,31,73–75] Elemental composition of organic surface soils in Norway was published by Nygård et al.[27] in 2012. Mean concentrations of Pb, Hg and Mn in surface soils in Svalbard are lower than the mean of Norwegian soils[27,73]. Cd, Cu and Zn are comparable to surface soils concentrations in Norway, whereas the levels of Cr, Ni and As in Svalbard are higher than mean concentrations in Norwegian soils.[27] Cr and Ni are not reported to be among those elements which are long-range transported (as e.g. As).[27,76,77] Their concentrations may be attributed to local geological conditions in Svalbard.

5.2 Comparison of Hg levels with relevant previous work

The Hg concentrations in surface soils ranged from 0.0540 to 0.180 µg/g with a mean of 0.110 µg/g. The levels of Hg sampled in the Bayelva area in 2015 are in the same range as those from 2014[65] (mean of all samples 0.109 µg/g) and show no significant differences.

Beldowski et al.[15] conducted a study on sedimentary Hg in Isfjorden and Hornsund. They took shore soil samples and observed similar concentrations in sediments and soil (2 – 65 ng/g). Sedimentary THg was observed to be influenced by the organic matter content. Organic-rich sediments had elevated THg concentrations and an increased contribution of mobile Hg as part of the solid speciation. Soil samples were taken along the beaches at different tides. A baseline value of 0.27 mg/kg (range 0.21 – 0.38 mg/kg) for Hg among other heavy metals in surface soils around Ny-Ålesund were presented by Hao et al.[78] Our values are higher than the ones reported from Beldowski et al.[15] in Hornsund and Isfjorden (Billefjord) and lower than the ones reported by Hao et al.[78] around Ny-Ålesund. The levels published in the latter study included also sampling sites presumably more influenced by local activities, e.g. vicinity to the airport. Therefore, higher Hg levels are expected. In the case of the study by Beldowski et al.[15], the sampling sites along the beach contained probably only very low SOM contents explaining the low levels compared to ours.

Total Hg (THg) of the humus layer in wetland soils in the Canadian High Arctic ranged between 10 and 250 ng/g (average 46 ng/g).[79] They determined also the OM content by LOI. OM content ranged from high (75 %) to low (5 %) and the mean was 30 %. A correlation analysis among THg and OM content was not performed. Riget et al.[80] reported Hg levels in the humus and mineral layer (down to 15 cm after removal of the humus) in soils in Greenland. The geometric mean of the Hg concentrations of 4 different locations in the mineral layer varied from <0.01 to 0.03 µg/g dw in four different sample areas and from 0.0199 to 0.117 µg/g dw in the organic layer. A study on THg and MeHg contents of lichens and underlying soil in the Canadian High Arctic was conducted by St. Pierre et al.[72] They reported THg contents in surface soil ranging from 0.98 to 86.4 ng/g. These concentrations were positively predicted by % organic carbon (OC), % $CaCO_3$ and soil crustal element composition. OC was noted as low (median: 6.20 %, range: 0.84 – 59.8 %).[72] The AMAP assessment in 2002[2] published levels for Hg in soils in the Russian Arctic. Concentrations between 0.04 and 0.15 µg/g dry weight (dw) were observed in 1998 and 2001. Allen-Gil et al.[45] evaluated possible effects of the heavy metal smelting complex in the Taimyr Peninsula (Siberian Arctic). They did not find indication for elevated levels in, e.g. freshwater fish, sediments and mosses. They noted their levels in the same orders of magnitude as in Alaska or in the Canadian Arctic. Therefore, this study can also be used for comparison. They reported Hg surface soil levels of 0.074 to 0.368 µg/g dw (median: 0.148 µg/g dw) with a median of 20 % TOC. Hg was enriched in these top increments of the soil cores compared to the bottom increment with a median of 0.7 % TOC (0.008 – 0.414 µg/g dw, median: 0.014 µg/g). A possible correlation between Hg and TOC was not part of the publication. The observed values in this study show the same magnitude as in the Russian Arctic[2], Canadian High Arctic[79] and Greenland[80]. All these sample sites were along the shore and it seems that there are only few variations of Hg in topsoils in the Arctic resulting from different SOM contents.

Låg and Steinnes[73] conducted a study on Hg concentrations in humus samples from Norwegian forest areas and obtained concentrations ranging from 0.02 – 0.55 µg/g (arithmetic mean: 0.188 µg/g) with a mean of 65 % OM. Steinnes and Andersson[75] reported levels of 0.14 to 0.20 µg/g of Hg in the humus layer in Norway. They found a slightly higher concentration in the south-east compared to the north. The magnitude of our concentrations is comparable or to some extent lower to those in topsoils in Norway.[73,75] This may be attributed to the higher SOM content in Norwegian topsoils.

The ratio of the Hg concentrations in surface soils to mineral soils is 4.4 (Table 5). This indicates that Hg accumulates in the surface soil and predominantly derives from atmospheric deposition, although there has probably always been an accumulation in the surface soil. With the given information it is not possible to assess the extent of contribution from anthropogenic or natural sources. Studies on peat cores from ombrotrophic bogs[31], however, indicate that levels of Hg are higher than pre-industrial levels in the Northern Hemisphere and the enrichment of Hg in surface soils is strongly associated with long-range transport of anthropogenic Hg.[1] The peat bog investigations in 2000 by Steinnes and Sjøbakk.[31] showed a 15 times higher Hg accumulation over the last 100 years than the pre-industrial level (net annual accumulation of 0.3 – 0.9 µg/m^2). This increase was attributed to be of anthropogenic origin.

Levels of Hg in surface soils in Svalbard are comparable to Norwegian topsoils[73,75] to remote areas in other parts of the Arctic considering the varying SOM contents. This, however, implies that the SOM content is the main factor driving the ability of the soil to retain Hg after deposition. St. Pierre et al.[72] observed also a positive predication with % $CaCO_3$ and distance to the sea. The latter is very interesting since an accumulation in soils linked with the AMDEs would indicate the opposite. Spatial patterns in atmospheric transport and deposition may also account for these observations. Ca was not among the selected elements. However, a possible correlation in surface soils with Hg was tested and was not significant (ρ=0.020, p=0.89). Though the Ca concentration determined by ICP-MS may also be present in other minerals not only as $CaCO_3$.

Our levels of Hg in the mineral soil are very low and range from 0.0174 to 0.0401 µg/g with a mean of 0.0279 ± 0.0073 µg/g and are probably attributed to the SOM content in the mineral soil. Levels in the mineral layer in Greenland[80] were reported to be of the same order of magnitude.

5.3 Correlation among Hg, SOM and other elements

Hg levels were found to be highly significant correlated ($p<0.001$) with the SOM content (Figure 15) indicating the importance of SOM as a ligand for Hg. No correlation was found with the S content. This may be due to the thin surface soil layer, comparably low SOM content and other possible S-containing molecules and precipitates. Furthermore, the water extraction of the soil revealed generally low to moderate aromaticity of the DOM and a significant correlation ($p<0.001$) between Hg and S indicates the importance of the S-donor atom for Hg as part of the DOM. There was no standard addition used to quantify the Hg loss during the experiment. Therefore, these data should only be used as an estimate. A significant positive correlation between Hg and Cd (Figure 15) can indicate a similar source of these elements. Cd is, like Hg, prone to be long-range transported in the atmosphere (but particle-bound) and also highly enriched in the surface soil (ratio 6.5 in Table 5). The distribution of Cd is highly influenced by anthropogenic emission. Cadmium levels are reported to be enriched in Norwegian surface soils and show a south-north decline.[1] Moss surveys in Norway showed that Cd and Hg are among the elements which are long-range transported.[1] The AMAP assessment 2002[2] discussed the possible similar fates based on snowpack observations. However, the gaseous and particle-bound elements are unlikely to share a similar input pathway to the Arctic but atmospheric deposition is important for both of them.[2] These two positive correlations are also supported with the samples from 2014. One can argue that the significantly negative correlation of Hg with Al, Cr and Fe suggests that Hg is not originating from the bedrock. These elements are more abundant in the mineral part of the soil (Figure 9 and Figure 12) and are typical lithophilic elements.[77] This expresses the importance of OM as ligand for Hg and the accumulation in the surface soil after atmospheric deposition. The reported inverse correlation with the elements associated with the mineral soil is in particularly important. This suggests that Hg is presumably derived from atmospheric deposition. The organic-rich surface soil layer in Svalbard is very thin and when sampling a mixing with underlying mineral soil can alter the surface soil composition and also induce this negative correlation.

Unfortunately, bromine and chlorine concentrations were not measured in the soil samples. Concentrations of these elements would provide more information about the deposition of Hg and its association with halogens derived presumably from the sea ice.

5.4 Biogeochemical cycling of Hg in the Arctic

The Hg levels reported in the present study show clear indications of an accumulation of Hg in the surface soils in Svalbard from atmospheric deposition after long-range transport. This is supported by the enrichment of Hg in the surface soil compared to the mineral soil, the significant positive correlation with SOM and Cd and the significant negative correlation with Al, Cr and Fe which are strongly associated with the mineral soil. The colder climate facilitates also the abilities of the SOM to retain dry deposited GEM. The fact that there are no significant differences between Adventdalen and the Bayelva area indicates that there is no Hg deposition in vicinity to the settlements and local sources. However, the extent of the possible pathways of deposition in the snow-free periods or of Hg stored in the snow, and being released during snow melting, and their contribution to the observed levels cannot be assessed.

In the context of the AMDEs and the fate of deposited Hg, which is not directly re-emitted from the snowpack, other studies indicated that riverine transport during melting period appears to be more important than an accumulation in soil. Studies on Hg levels in the Bayelva river, Londonelva and some small streams around Ny-Ålesund reported significantly higher levels of Hg in late June/begin of July compared to August. Mean concentrations of 4.05 ng/L in the first period and 2.50 ng/L in the second period were observed. The decrease of 38.3 % was suggested to be derived by the AMDEs connected with the spring melting period.[81] A study by Søndergaard et al.[82] reported Hg loadings in a river in Greenland in 2009 and 2010. The authors suggested that transports of Hg during summer periods are likely to originate from Hg deposited in the winter and released during melting period. The present levels and the ones from 2014[65] are to some extent lower than Norwegian topsoils. This may be due to the lower SOM content, shorter snow-free periods with an observed GEM maximum during the summer after the minimum in spring time[10,30] or that Hg deposited in the winter or during AMDEs on the snow is further transported with the melted snow to the rivers and further to the ocean. The levels of Hg in surface soil may also be attributed to other environmental parameters or soil characteristics (low aromaticity of SOM, pH) in the sampling areas. More information about the soil texture and properties can give further explanations for the observed Hg levels in Svalbard.

More data are needed, especially on Hg concentrations in Arctic soil to gain more information about the role of the soil in the biogeochemical cycling of Hg. Soil parameters such as pH and cation exchange capacity can provide new insights as they are reported to influence the adsorption of Hg[83]. These can lead to further conclusions about Hg accumulation in soils in the Arctic. Transects to detect possible variations in the Hg concentrations with distance to the sea are also a possibility for further research and may be linked to the AMDEs. Our data on the Hg concentrations in surface soils in Svalbard indicate that soils can be an important sink in the Hg cycling.

5.5 Factor analysis

5.5.1 Surface soils

F1 (-SOM, Al, As, -Cd, Cr, Cu, Fe, -Hg, Ni; Table 10, left) displays probably local influence of bedrock geology or deposition of mineral dust. This factor explains about 50 % of the variance. In particular, the negative association of SOM, Cd and Hg with the elements (Al, As, Cr, Cu, Fe, Ni) which are significantly more abundant in the mineral soil (see Figure 9) indicates that Cd and Hg are presumably not originating from underlying mineral soil. Cd and Hg are presumably derived from atmospheric deposition and accumulate in the organic-rich surface soil. The same grouping of the elements which are more associated with the mineral soil Al, As, Cr, Cu, Ni and Fe can also be seen in the plots f2-f1, f3-f1 and f4-f1 in Figure 17. F2 (SOM, As, Hg, -Pb, S) is strongly dominated by S and can be interpreted as chemical influence of SOM and S and their association with Hg and As. A positive correlation of S and TOC was reported before in European top- and subsoils (low in OM because humus layer was removed from topsoil).[84] As is strongly associated with S and present as sulfides and sulpharsenides. Notably is the negative association of Pb with Hg since they are both reported to be long-range transported and Pb also correlated in European humus samples with Hg.[84] Therefore, f2 displays probably chemical characteristics and associations in the soil rather than the source of these elements. F3 (Cd, Mn, Pb) is predominated by Mn. Mn in moss samples was reported to be among those elements associated with higher plants.[76,77] However, there are only few vascular plants in Svalbard and the vegetation is dominated by mosses and lichens. In surface soils Mn was reported to be described by a factor indicating elements which are easily available for plant uptake[27]. In the latter case an association with Zn was described by the same factor which is not observed in our factor analysis case. Zn predominates f4 (Cd, Zn) which could reflect long-range transport.

The factor analysis of the surface soil samples from 2014 and 2015 shows similar association between the elements and their sources simplified by the factors (Table 11). Though, the explained variances differ slightly. F1 (Al, As, Cr, Cu, Fe, Ni, -S) likely reflects again the influence from underlying bedrock. This factor explains 45.8 % of the total variance and corresponds to f1 from the previous factor analysis. F3 (Cd, Zn) corresponds to f4 from the previous analysis. F4 (Hg, S) could reflect the same geochemical association as seen in f2 from the previous analysis. As is not explained by f4. This can be due to the spatial pattern of the As concentrations. In 2014 samples were taken near Ny-Ålesund and significant lower concentrations of As in the surface soils were obtained compared to the samples in 2015 (see 5.1). Samples from Adventdalen exhibit higher levels of As (see also 5.6). With the inclusion of the samples 2014 the effect of these high levels is to some extent suppressed. This could explain the missing appearance of As in factor 4 and shifted geochemical associations of As. F2 (Mn, Pb) corresponds to f3 from the previous analysis.

Notably is that Hg is not associated with the same factors as, e.g. Cd, Pb and Zn which are also reported to be long range transported and an association of these elements was seen in moss studies.[76,77] Hg is the only metal among them which is transported in its gaseous elemental form and shows a evenly distribution in the northern hemisphere explaining the missing association here.

5.5.2 Mineral soils

For the discussion of the factor analysis of the mineral soil it is important to point out that only 54.9 % of Hg variance (Table 24 in Appendix D) can be explained by the extracted factors. 65.8 % when samples from 2014 were included. The factor analysis of the mineral soil samples mostly reflects geological background and chemical association between the elements. There should be no influence from the airborne supply or plant activities.

F1 (-SOM, Al, Cr, Cu, Fe, Mn, Ni, Pb, Zn) is dominated by elements deriving from the geological background. As seen also in f1 for the surface soils Al, Cr, Cu, Fe Ni are strongly explained by this factor. There is also again a negative association with SOM. Furthermore, Mn, Pb and Zn are explained by this factor. As did not meet the criterion ≥0.4 in f1 (loading: 0.381) and dominates f2 (-SOM, As, -Cd). F3 (SOM, Hg, S) most likely represents geochemical associations in the soil as seen also in f2 for the surface soils (and in f4 with the enlarged dataset). Hg is strongly associated with SOM and S. As (loading: 0.391) is to some extent also explained by f3.

F1 (Al, As, Cr, Cu, Fe, Ni, Pb, Zn) of the enlarged sample set (n=57) is presumably driven by local bedrock influences (see Figure 20). In addition to the previous analysis, As concentrations can be explained by this factor and Mn not. As discussed before, the reduced impact of the samples taken in Adventdalen to the whole sample number can be suggested as the reason for the different grouping of As. F2 (As, Hg, S) explains presumably geochemical characteristics of the association of As and Hg with S.

5.6 Spatial variations: Adventdalen and Bayelva area

Important factors explaining regional differences in Svalbard are the geological background and local deposition in vicinity to the emission source (e.g. airport, mine, power plant).[25] As mentioned in 3.1 there are different geological conditions in Adventdalen and the Bayelva area on which the soil develops. The ratios in Figure 13 in Bayelva B samples differ from Bayelva A, especially in the Mg/Al ratio. The vicinity to the Brøggerbreen glacier can be one reason for this. These soils developed probably later than in Bayelva A.

For the discussion of the differences between the sample sites, the extended sample set included in this work and the 15 samples from 2014 from the Bayelva area were used. Differences between the concentration data could be explained by the small sample amount in the Bayelva area. Figure 10 and Figure 11 indicate that elements which are significantly higher in the mineral soil also lead to significant differences in the surface soil compared to the other sites. For Adventdalen As, Cr, Fe and Ni show this trend. These elements have significantly higher concentrations in the mineral soil, are more associated with the crustal components and may be derived from weathering of rocks in Adventdalen. Migration processes in the soil may also enrich these elements in the surface soil. Additional input may be from anthropogenic activities. As described under 2.3 Cr and Ni are not among those elements which are likely to be long-range transported[1,77,85] and contamination occurs usually in vicinity to point sources[1]. Coal-fired power plants, coal mining or local traffic can be among those sources. As discussed under 5.1, the present As concentrations also exceed levels in topsoils in Norway. The comparison of the surface soil and mineral soil also suggests that the high levels in the surface soil may be attributed to bedrock geology. As is enriched in coal[86] and coal mining activities occur in Adventdalen. Shale is one present rock in the Adventdalen group and attributed with enhanced levels of As compared to sandstone and carbonates.[84] This indicates that local geology circumstances may account for natural enhancement in the mineral soil and their weathering can enrich As in surface soils. There may be also an additional input from the coal-firing power plant in Longyearbyen and mining operations[25].

Significant higher concentration of Cd, Pb and Zn in the surface soils in the Bayelva area compared to Adventdalen are also notable as they are reported to be long-range transported.[2] A study by Singh et al.[57] on heavy metals in lichens and cryoconite (windblown dust in holes on the surface of glaciers) near Ny-Ålesund also reported an accumulation of Cd, Ni, Pb and Zn in these remote areas and discussed probable anthropogenic sources of these.[57]

5.6.1 Comments to the sampling site in Endalen

Only two samples were taken in Endalen. Therefore, no statistical comparison could be done. However, it appears that surface soils in Endalen are subjected to higher values of Cd, Hg and Mn and lower of Cr, Cu and Ni than the sites Foxdalen A and B. There are possible explanations, e.g. the vicinity to Longyearbyen and the (now closed) mine Gruve 5 and difference in spatial deposition patterns. More samples are needed to draw conclusions. A transect of sampling points with distant Longyearbyen to exclude local anthropogenic influences should be further investigated.

6 Conclusion

In this work surface soil samples were investigated for possible Hg accumulation. Furthermore, the elemental concentrations of Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, S and Zn were determined. Mineral soil samples were investigated to detect crustal influences.

The presented results showed clear indications that atmospheric Hg deposition is associated with an accumulation in the soil in Svalbard. In comparison with other reported Hg levels in soils in the Arctic, it seems that there are only small spatial variations resulting from different SOM contents.[2,6,15,45,72,78,80]

The factor analysis of the surface soil samples showed that half of the variations between the elemental concentrations may be explained by crustal influence. Hg was associated with SOM and S and not with the crustal elements. Therefore, the atmospheric deposition is presumably the pathway for Hg to enter terrestrial ecosystems. It can either occur in the snow-free periods or on the snow cover. The latter one would result in transfer to the soil during the snow melt. Both pathways are possible and should be part of further research. The factor analysis also showed that Hg features a different deposition pathway from Cd, Pb and Zn (and also to some extent from As). Hg concentrations positively correlated with the SOM contents and Cd concentrations. Again, this supports the importance of the SOM content as a predominant factor for Hg accumulation in soil.

Significant differences of the element concentration of As, Cd, Cr, Mn and S in the mineral soils were observed between Adventdalen and the Bayelva area. These may originate from geological differences or from the still present SOM content in the mineral soil. The former one may also explain variations between the two sites in the surface soils. However, local influences from the settlements cannot be excluded. In addition, the thickness of the organic-rich surface layer in the Arctic is important to consider when sampling surface soils. Portions of the mineral layer, which cannot be clearly distinguished from the surface layer, can alter the elemental composition when analyzing the surface soils.

For future studies on Hg levels in soils in Svalbard transects of sampling sites can help to evaluate the influence of the distance to the ocean. A determination of halogen concentrations (especially Br) may give further knowledge on the Hg cycling. Furthermore, transects with distance to Longyearbyen may be used for a local pollution assessment.

7 References

(1) Steinnes, E.; Friedland, A. J. Metal contamination of natural surface soils from long-range atmospheric transport: Existing and missing knowledge. *Environ. Rev.* **2006**, *14*, 169–186.

(2) AMAP. *AMAP Assessment 2002 : Heavy Metals in the Arctic.*; Arctic Monitoring and Assessment Programme (AMAP), 2005.

(3) AMAP. *AMAP Assessment Report: Arctic Pollution Issues*; Arctic Monitoring and Assessment Programme (AMAP), 1998.

(4) Lantzy, R. J.; Mackenzie, F. T. Atmospheric trace metals: global cycles and assessment of man's impact. *Geochim. Cosmochim. Acta* **1979**, *43*, 511–525.

(5) Mason, R.; Fitzgerald, W.; Morel, F. The biogeochemical cycling of elemental mercury: Anthropogenic influences. *Geochim. Cosmochim. Acta* **1994**, *58*, 3191–3198.

(6) AMAP. *AMAP Assessment 2011: Mercury in the Arctic*; Arctic Monitoring and Assessment Programme (AMAP), 2011.

(7) Slemr, F.; Brunke, E. G.; Ebinghaus, R.; Kuss, J. Worldwide trend of atmospheric mercury since 1995. *Atmos. Chem. Phys.* **2011**, *11*, 4779–4787.

(8) Lamborg, C. H.; Fitzgerald, W. F.; O'Donnell, J.; Torgersen, T. A non-steady-state compartmental model of global-scale mercury biogeochemistry with interhemispheric atmospheric gradients. *Geochim. Cosmochim. Acta* **2002**, *66*, 1105–1118.

(9) Selin, N. E.; Javob, D. J.; Park, R. J.; Yantosca, R. M.; Strode, S.; Jaegle, L.; Jaffe, D. Chemical cycling and deposition of atmospheric mercury: Global constraints from observations. *J. Geophys. Res. Atmos.* **2007**, *112*, 1–14.

(10) Berg, T.; Pfaffhuber, K. A.; Cole, A. S.; Engelsen, O.; Steffen, A. Ten-year trends in atmospheric mercury concentrations, meteorological effects and climate variables at Zeppelin, Ny-Alesund. *Atmos. Chem. Phys.* **2013**, *13*, 6575–6586.

(11) Gamberg, M.; Chételat, J.; Poulain, A. J.; Zdanowicz, C.; Zheng, J. Mercury in the Canadian Arctic Terrestrial Environment: An Update. *Sci. Total Environ.* **2015**, *509-510*, 28–40.

(12) Schroeder, W. H.; Anlauf, K. G.; Barrie, L. a; Lu, J. Y.; Steffen, A. Arctic Springtime Depletion of Mercury. *Nature* **1998**, *394*, 331–332.

(13) Steffen, A.; Douglas, T.; Amyot, M.; Ariya, P.; Aspmo, K.; Berg, T.; Bottenheim, J.; Brooks, S.; Cobbett, F. A synthesis of atmospheric mercury depletion event chemistry in the atmosphere and snow. *Atmos. Chem. Phys.* **2008**, *8*, 1445–1482.

(14) Poissant, L.; Zhang, H. H.; Canário, J.; Constant, P. Critical review of mercury fates and contamination in the arctic tundra ecosystem. *Sci. Total Environ.* **2008**, *400*, 173–211.

(15) Bełdowski, J.; Miotk, M.; Zaborska, A.; Pempkowiak, J. Distribution of sedimentary mercury off Svalbard, European Arctic. *Chemosphere* **2015**, *122*, 190–198.

(16) Paré, M. C.; Bedard-haughn, A.; Pare, M. C. Surface Soil Organic Matter Qualities of Three Distinct Canadian Arctic Sites. *Arctic, Antarct. Alp. Res.* **2013**, *45*, 88–98.

(17) Paré, M. C.; Bedard-Haughn, A. Soil organic matter quality influences mineralization and GHG emissions in cryosols: A field-based study of sub- to high Arctic. *Glob. Chang. Biol.* **2013**, *19*, 1126–1140.

(18) Jones, A. V; Stolbovoy, V.; Tarnocai, C.; Broll, G.; Spaargaren, O.; Montanarella (eds.), L. *Soil Atlas of the Northern Circumpolar Region*; European Commission, Office for Official Publications of the European Communities, Luxembourg, 2009.

(19) Report, A. A. Amap 1998 appendix. **1994**, 616–619.

(20) Kimble, J. M. *Cryosols - Permafrost-Affected Soils*; Springer, 2004.

(21) Soils of Canada - Orders - Cryosolic http://www.soilsofcanada.ca/orders/cryosolic/ (accessed Mar 1, 2016).

(22) Nieder, R.; Benbi, D. K. *Carbon and Nitrogen in the Terrestrial Environment*; 2008.

(23) Sumner, M. E. *Handbook of Soil Science*; CRC Press, 1999.

(24) Dai, X. Y.; Ping, C. L.; Michaelson, G. J. Characterizing soil organic matter in Arctic tundra soils by different analytical approaches. *Org. Geochem.* **2002**, *33*, 407–419.

(25) Alloway, B. J. *Heavy Metals in Soils: Trace Metals and Metalloids in Soils and their Bioavailability*; Springer, 2013.

(26) Wild, B.; Schnecker, J.; Alves, R. J. E.; Barsukov, P.; Barta, J.; Capek, P.; Gentsch, N.; Gittel, A.; Guggenberger, G.; Lashchinskiy, N.; et al. Input of easily available organic C and N stimulates microbial decomposition of soil organic matter in arctic permafrost soil. *Soil Biol. Biochem.* **2014**, *75*, 143–151.

(27) Nygård, T.; Steinnes, E.; Røyset, O. Distribution of 32 elements in organic surface soils: Contributions from atmospheric transport of pollutants and natural sources. *Water. Air. Soil Pollut.* **2012**, *223*, 699–713.

(28) Sonke, J. E.; Heimbürger, L.-E.; Dommergue, A. Mercury biogeochemistry: Paradigm shifts, outstanding issues and research needs. *Comptes Rendus Geosci.* **2013**, *345*, 213–224.

(29) Pacyna, E. G.; Pacyna, J. M.; Steenhuisen, F.; Wilson, S. Global anthropogenic mercury emission inventory for 2000. *Atmos. Environ.* **2006**, *40*, 4048–4063.

(30) Steffen, A.; Schroeder, W.; Macdonald, R.; Poissant, L.; Konoplev, A. Mercury in the Arctic atmosphere: An analysis of eight years of measurements of GEM at Alert (Canada) and a comparison with observations at Amderma (Russia) and Kuujjuarapik (Canada). *Sci. Total Environ.* **2005**, *342*, 185–198.

(31) Steinnes, E.; Sjøbakk, T. E. Order-of-magnitude increase of Hg in Norwegian peat profiles since the outset of industrial activity in Europe. *Environ. Pollut.* **2005**, *137*, 365–370.

(32) UNEP. *Global Mercury Assessment 2013: Sources, Emissions, Releases, and Environmental Transport*; UNEP Chemicals Branch, Geneva, Switzerland, 2013.

(33) Steffen, A.; Lehnherr, I.; Cole, A.; Ariya, P.; Dastoor, A.; Durnford, D.; Kirk, J.; Pilote, M. Atmospheric mercury in the Canadian Arctic. Part I: A review of recent field measurements. *Sci. Total Environ.* **2015**, *509-510*, 3–15.

(34) Fisher, J. A.; Jacob, D. J.; Soerensen, A. L.; Amos, H. M.; Steffen, A.; Sunderland, E. M. Riverine source of Arctic Ocean mercury inferred from atmospheric observations. *Nat. Geosci.* **2012**, *5*, 499–504.

(35) Douglas, T. A.; Loseto, L. L.; MacDonald, R. W.; Outridge, P.; Dommergue, A.; Poulain, A.; Amyot, M.; Barkay, T.; Berg, T.; Chetelat, J.; et al. The fate of mercury in Arctic terrestrial and aquatic ecosystems, a review. *Environ. Chem.* **2012**, *9*, 321–355.

(36) Leitch, D. R.; Carrie, J.; Lean, D.; Macdonald, R. W.; Stern, G. A.; Wang, F. The delivery of mercury to the Beaufort Sea of the Arctic Ocean by the Mackenzie River. *Sci. Total Environ.* **2007**, *373*, 178–195.

(37) Dommergue, A.; Larose, C.; Faïn, X.; Clarisse, O.; Foucher, D.; Hintelmann, H.; Schneider, D.; Ferrari, C. P. Deposition of mercury species in the Ny-Ålesund area (79°N) and their transfer during snowmelt. *Environ. Sci. Technol.* **2010**, *44*, 901–907.

(38) Schuster, E. The behavior of mercury in the soil with special emphasis on complexation and adsorption processes - A review of the literature. *Water Air Soil Pollut.* **1991**, *56*, 667–680.

(39) Skyllberg, U.; Xia, K.; Bloom, P. R.; Nater, E. A.; Bleam, W. F. Binding of Mercury(II) to Reduced Sulfur in Soil Organic Matter along Upland-Peat Soil Transects. *J. Environ. Qual.* **2000**, *29*, 855–865.

(40) Grigal, D. F. Mercury Sequestration in Forests and Peatlands: A Review. *J. Environ. Qual.* **2003**, *32*, 393–405.

(41) Oiffer, L.; Siciliano, S. D. Methyl mercury production and loss in Arctic soil. *Sci. Total Environ.* **2009**, *407*, 1691–1700.

(42) Gu, B.; Bian, Y.; Miller, C. L.; Dong, W.; Jiang, X.; Liang, L. Mercury reduction and complexation by natural organic matter in anoxic environments. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 1479–1483.

(43) Poulain, A. J.; Roy, V.; Amyot, M. Influence of temperate mixed and deciduous tree covers on Hg concentrations and photoredox transformations in snow. *Geochim. Cosmochim. Acta* **2007**, *71*, 2448–2462.

(44) Grigal, D. F. Inputs and outputs of mercury from terrestrial watersheds: a review. *Environ. Rev.* **2002**, *10*, 1–39.

(45) Allen-Gil, S. M.; Ford, J.; Lasorsa, B. K.; Monetti, M.; Vlasova, T.; Landers, D. H. Heavy metal contamination in the Taimyr Peninsula, Siberian Arctic. *Sci. Total Environ.* **2003**, *301*, 119–138.

(46) Thomas, R. *Practical Guide to ICP-MS: A Tutorial for Beginners*; CRC Press 2008, 2008.

(47) Starr, M.; Lindroos, A.-J.; Ukonmaanaho, L.; Tarvainen, T.; Tanskanen, H. Weathering release of heavy metals from soil in comparison to deposition, litterfall and leaching fluxes in a remote, boreal coniferous forest. *Appl. Geochemistry* **2003**, *18*, 607–613.

(48) Braun, J.-J.; Ngoupayou, J. R. N.; Viers, J.; Dupre, B.; Bedimo, J.-P. B.; Boeglin, J.-L.; Robain, H.; Nyeck, B.; Freydier, R.; Nkamdjou, L. S.; et al. Present weathering rates in a humid tropical watershed: Nsimi, South Cameroon. *Geochim. Cosmochim. Acta* **2005**, *69*, 357–387.

(49) Fitzgerald, W. F.; Engstrom, D. R.; Lamborg, C. H.; Tseng, C. M.; Balcom, P. H.; Hammerschmidt, C. R. Modern and historic atmospheric mercury fluxes in northern Alaska: Global sources and arctic depletion. *Environ. Sci. Technol.* **2005**, *39*, 557–568.

(50) Banica, F.-G. Lecture notes: Analytical Methods for Industrial- and Environmental Monitoring (KJ3053), 2014.

(51) Hoogsteen, M. J. J.; Lantinga, E. a.; Bakker, E. J.; Groot, J. C. J.; Tittonell, P. a. Estimating soil organic carbon through loss on ignition: effects of ignition conditions and structural water loss. *Eur. J. Soil Sci.* **2015**, *66*, 320–328.

(52) High Arctic http://global.britannica.com/place/High-Arctic (accessed Sep 10, 2015).

(53) Population of Svalbard - SSB https://www.ssb.no/en/befolkning/statistikker/befsvalbard/halvaar/2015-09-24 (accessed Nov 17, 2015).

(54) climate and daylight https://svalbard.nordicvisitor.com/travel-guide/climate-and-daylight/ (accessed Feb 11, 2016).

(55) Weather statistics for Longyearbyen (Svalbard) - yr.no http://www.yr.no/place/Norway/Svalbard/Longyearbyen/statistics.html (accessed Feb 11, 2016).

(56) Bekku, Y. S.; Kume, A.; Masuzawa, T.; Kanda, H.; Nakatsubo, T.; Koizumi, H. Soil respiration in a high arctic glacier foreland in Ny-Alesund, Svalbard. *Polar Biosci.* **2004**, *17*, 36–46.

(57) Singh, S. M.; Sharma, J.; Gawas-Sakhalkar, P.; Upadhyay, A. K.; Naik, S.; Pedneker, S. M.; Ravindra, R. Atmospheric deposition studies of heavy metals in Arctic by comparative analysis of lichens and cryoconite. *Environ. Monit. Assess.* **2013**, *185*, 1367–1376.

(58) Major, H.; Andresen, A.; Dallmann, W. K.; Kjaernet, T.; Nottvedt, A. *Temakart No. 31/32: Geological Map of Svalbard 1:100000*; Norsk Polarinstitutt, 2001.

(59) Westermann, S.; Wollschläger, U.; Boike, J. Monitoring of active layer dynamics at a permafrost site on Svalbard using multi-channel ground-penetrating radar. *Cryosphere* **2010**, *4*, 475–487.

(60) Monitoring active layer thickness and temperatures, a CALM-project http://www.unis.no/35_staff/staff_webpages/geology/ole_humlum/CALM.htm (accessed Nov 17, 2015).

(61) Brown, J.; Hinkel, K. M.; Nelson, F. E. The circumpolar active layer monitoring (calm) program: Research designs and initial results. *Polar Geogr.* **2000**, *24*, 166–258.

(62) Haldorsen, S.; Heim, M. An Arctic Groundwater System and its Dependence upon Climatic Change: An Example from Svalbard. *Permafr. Periglac. Process* **1999**, *10*, 137–149.

(63) Schumacher, B. A. Methods for the Determination of Total Organic Carbon (TOC) in Soils and Sediments, United States Environmental Protection Agency, 2002.

(64) Ratnayake, R. R.; Seneviratne, G.; Kulasooriya, S. A. A Modified Method of Weight Loss on Ignition to Evaluate Soil Organic Matter Fractions. *Int. J. Soil Sci.* **2007**, *2*, 69–73.

(65) Fors, M. E. Studie av kvikksølv , svovel og naturlig organisk materiale i jord i Ny-Ålesund, Svalbard., NTNU Trondheim, 2014.

(66) Weishaar, J.; Aiken, G.; Bergamaschi, B.; Fram, M.; Fujii, R.; Mopper, K. Evaluation of specific ultra-violet absorbance as an indicator of the chemical content of dissolved organic carbon. *Environ. Sci. Technol.* **2003**, *37*, 4702–4708.

(67) Norwegian Polar Institute: Map Data and Services http://geodata.npolar.no/ (accessed Apr 27, 2016).

(68) Gulińska, J.; Rachlewicz, G.; Szczuciński, W.; Barałkiewicz, D.; Kózka, M.; Bulska, E.; Burzyk, M. Soil contamination in high arctic areas of human impact, central Spitsbergen, Svalbard. *Polish J. Environ. Stud.* **2003**, *12*, 701–707.

(69) Schaug, J.; Rambæk, J. P.; Steinnes, E.; Henry, R. C. Multivariate analysis of trace element data from moss samples used to monitor atmospheric deposition. *Atmos. Environ. Part A. Gen. Top.* **1990**, *24*, 2625–2631.

(70) Świetlik, J.; Sikorska, E. Characterization of natural organic matter fractions by high pressure size-exclusion chromatography, specific UV absorbance and total luminescence spectroscopy. *Polish J. Environ. Stud.* **2006**, *15*, 145–153.

(71) Norwegian Environment Protection Agency. Helsebaserte tilstandsklasser for forurenset grunn. Report: TA-2553-2009. **2009**, 30.

(72) St. Pierre, K. A.; St. Louis, V. L.; Kirk, J. L.; Lehnherr, I.; Wang, S.; La Farge, C. Importance of open marine waters to the enrichment of total mercury and monomethylmercury in lichens in the canadian high arctic. *Environ. Sci. Technol.* **2015**, *49*, 5930–5938.

(73) Låg, J.; Steinnes, E. Regional Distribution of Mercury in Humus Layers of Norwegian Forest Soils. *Acta Agric. Scand.* **1978**, *28*, 393–396.

(74) Låg, J.; Steinnes, E. Regional Distribution of Selenium and Arsenic in Humus Layers of Norwegian Forest Soils. *Geoderma* **1978**, *20*, 3–14.

(75) Steinnes, E.; Andersson, E. M. Atmosperic deposition of mercury in Norway: temporal and spatial trends. *Water Air Soil Pollut.* **1991**, *56*, 391–404.

(76) Berg, T.; Steinnes, E. Recent trends in atmospheric deposition of trace elements in Norway as evident from the 1995 moss survey. *Sci. Total Environ.* **1997**, *208*, 197–206.

(77) Berg, T.; Royset, O.; Steinnes, E.; Vadset, M. Atmospheric trace element deposition: Principal component analysis of ICP-MS data from moss samples. *Environ. Pollut.* **1995**, *88*, 67–77.

(78) Hao, Z. L.; Wang, F.; Yang, H. Z. Baseline Values for Heavy Metals in Soils on Ny-Alesund, Spitsbergen Island, Arctic: The Extent of Anthropogenic Pollution. *Adv. Mater. Res.* **2013**, *779-780*, 1260–1265.

(79) Loseto, L. L.; Siciliano, S. D.; Lean, D. R. S. Methylmercury production in High Arctic wetlands. *Environ. Toxicol. Chem.* **2004**, *23*, 17–23.

(80) Riget, F.; Asmund, G.; Aastrup, P. Mercury in Arctic char (Salvelinus alpinus) populations from Greenland. *Sci. Total Environ.* **2000**, *245*, 161–172.

(81) Jenny, S.; Hald, K. Kartlegging og studie av metaller og naturlig organisk materiale i elver på Svalbard. **2014**.

(82) Søndergaard, J.; Rigét, F.; Tamstorf, M. P.; Larsen, M. M. Mercury Transport in a Low-Arctic River in Kobbefjord, West Greenland (64° N). *Water, Air, Soil Pollut.* **2012**, *223*, 4333–4342.

(83) Soares, L. C.; Egreja Filho, F. B.; Linhares, L. A.; Windmoller, C. C.; Yoshida, M. I. Accumulation and oxidation of elemental mercury in tropical soils. *Chemosphere* **2015**, *134*, 181–191.

(84) Salminen, R. *Geochemical Atlas of Europe - Part 1: Background Information, Methodology and Maps*; Geological Survey of Finland, 2005.

(85) Steinnes, E. Heavy metal contamination of the terrestrial environment from long-range atmospheric transport : Evidence from 35 years of research in Norway. **2010**, *35001*, 2003–2005.

(86) Wang, S.; Mulligan, C. N. Occurrence of arsenic contamination in Canada: Sources, behavior and distribution. *Sci. Total Environ.* **2006**, *366*, 701–721.

Appendix A: Geological Maps

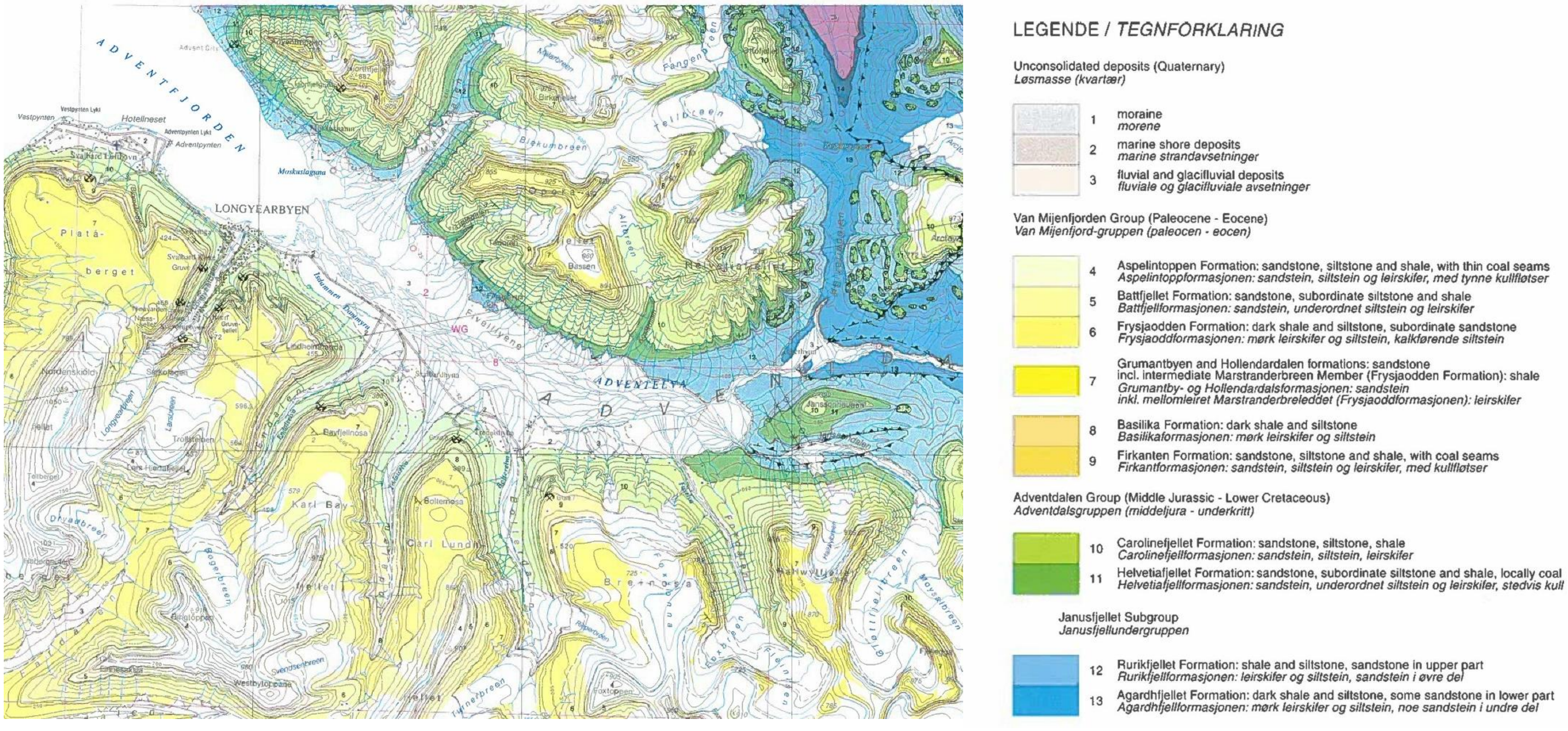

Figure 22. Geological Map Svalbard 1:100000. (changed after Major et al.[58])

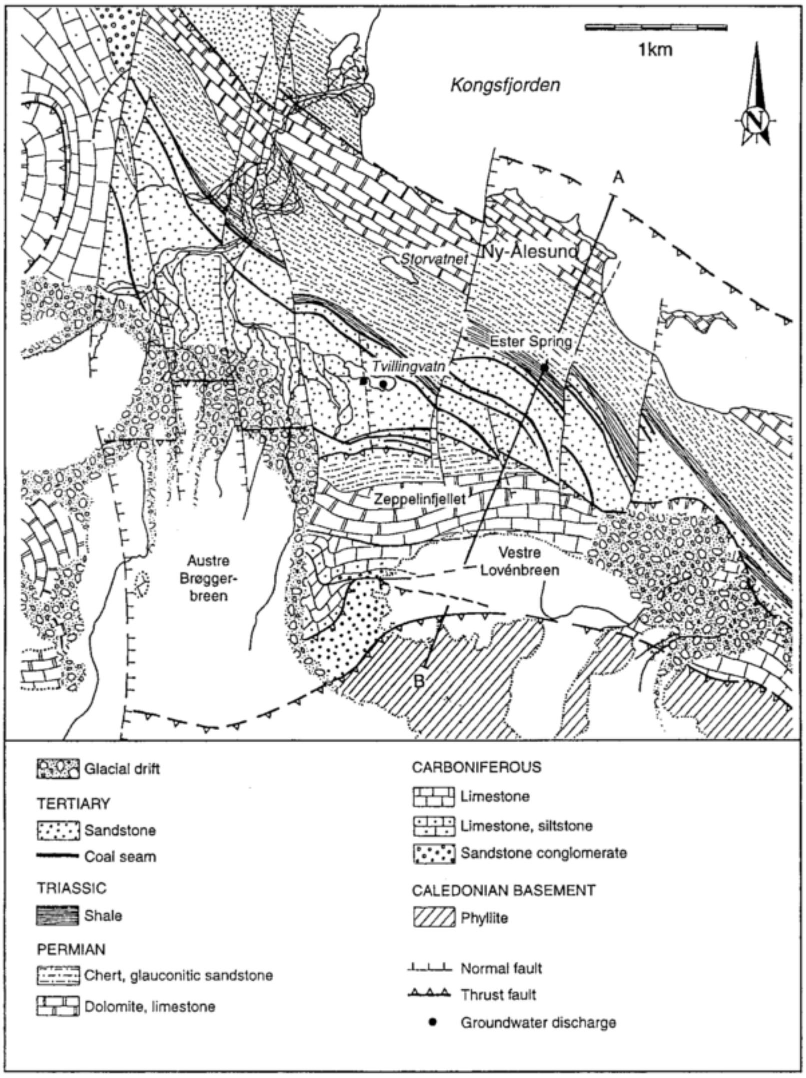

Figure 23. Geological Map of Ny-Ålesund.[62]

Appendix B: Soil composition data

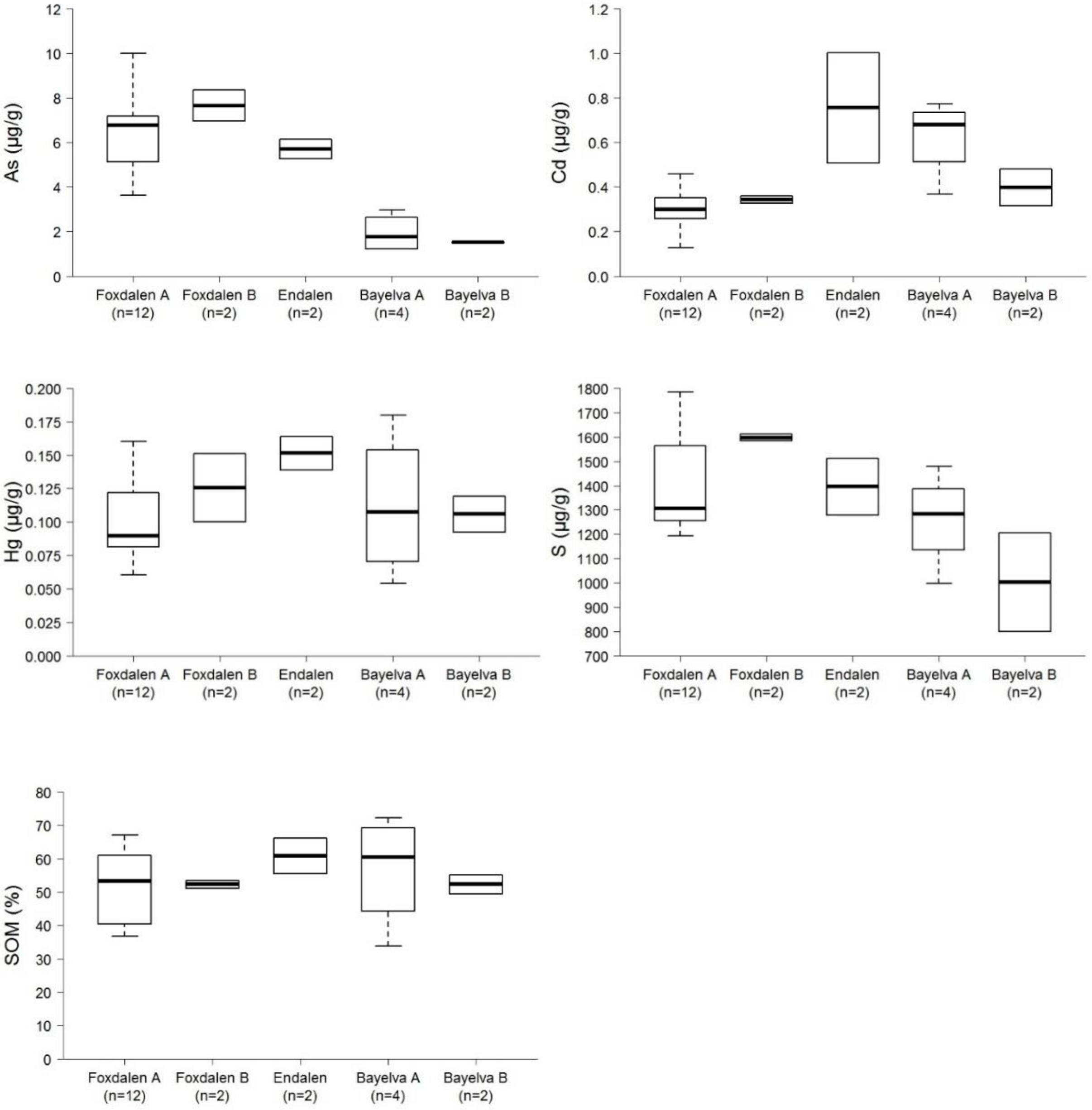

Figure 24. Arsenic (As), cadmium (Cd), mercury (Hg) and sulfur (S) concentrations (µg/g) in surface soils in Svalbard. Whiskers show the minimum and maximum value of the data, boxes indicate the lower and upper quartile from the median (bolt bar), respectively.

Table 13. Concentrations (µg/g) of 12 elements in surface soils of Svalbard. (mean and standard deviation)

Element	Foxdalen A (n=12)	Foxdalen B (n=2)	Endalen (n=2)	Bayelva A (n=4)	Bayelva B (n=2)
Al	$20.5\cdot10^3$ ± $7.3\cdot10^3$	$20.1\cdot10^3$ ± $0.5\cdot10^3$	$15.2\cdot10^3$ ± $0.4\cdot10^3$	$10.5\cdot10^3$ ± $4.6\cdot10^3$	$22.8\cdot10^3$ ± $5.7\cdot10^3$
As	6.41 ± 1.74	7.66 ± 0.98	5.70 ± 0.62	1.93 ± 0.86	1.52 ± 0.04
Cd	0.301 ± 0.083	0.343 ± 0.024	0.756 ± 0.350	0.625 ± 0.177	0.398 ± 0.116
Cr	28.6 ± 8.7	27.6 ± 0.5	22.3 ± 0.5	15.9 ± 7.5	25.0 ± 5.5
Cu	12.8 ± 2.5	13.1 ± 0.3	10.5 ± 0.8	6.67 ± 1.08	10.6 ± 1.2
Fe	$16.1\cdot10^3$ ± $4.5\cdot10^3$	$16.7\cdot10^3$ ± $0.6\cdot10^3$	$12.8\cdot10^3$ ± $0.6\cdot10^3$	$8.81\cdot10^3$ ± $4.87\cdot10^3$	$11.0\cdot10^3$ ± $0.2\cdot10^3$
Hg	0.101 ± 0.029	0.126 ± 0.036	0.151 ± 0.017	0.112 ± 0.054	0.106 ± 0.019
Mn	187 ± 60	211 ± 7	287 ± 70	187 ± 97	225 ± 24
Ni	18.0 ± 4.5	18.6 ± 1.4	14.1 ± 3.2	8.44 ± 3.92	15.4 ± 3.6
Pb	8.49 ± 1.67	9.14 ± 0.07	10.1 ± 0.8	10.7 ± 1.6	12.4 ± 1.2
S	$1.40\cdot10^3$ ± $0.22\cdot10^3$	$1.60\cdot10^3$ ± $0.02\cdot10^3$	$1.40\cdot10^3$ ± $0.16\cdot10^3$	$1.26\cdot10^3$ ± $0.20\cdot10^3$	$1.00\cdot10^3$ ± $0.29\cdot10^3$
Zn	63.2 ± 9.1	63.4 ± 0.2	64.0 ± 17.3	75.3 ± 11.0	51.7 ± 10.8

Table 14. Concentrations (µg/g) of 12 elements in mineral soils of Svalbard. (mean and standard deviation)

Element	Foxdalen A (n=12)	Foxdalen B (n=2)	Endalen (n=2)	Bayelva A (n=4)	Bayelva B (n=2)
Al	$33.9\cdot10^3$ ± $10.2\cdot10^3$	$43.9\cdot10^3$ ± $4.0\cdot10^3$	$26.3\cdot10^3$ ± $2.4\cdot10^3$	$20.8\cdot10^3$ ± $10.3\cdot10^3$	$37.4\cdot10^3$ ± $4.4\cdot10^3$
As	10.4 ± 3.0	10.4 ± 0.5	10.4 ± 0.8	3.48 ± 1.97	3.05 ± 0.99
Cd	0.0545 ± 0.0125	0.0584 ± 0.0207	0.0610 ± 0.0095	0.108 ± 0.039	0.0980 ± 0.0094
Cr	49.8 ± 13.2	59.5 ± 5.7	41.7 ± 1.6	31.4 ± 15.5	42.8 ± 5.9
Cu	15.2 ± 5.0	21.4 ± 3.1	11.3 ± 1.1	7.7 ± 3.4	15.9 ± 2.2
Fe	$26.7\cdot10^3$ ± $8.3\cdot10^3$	$36.9\cdot10^3$ ± $8.6\cdot10^3$	$23.1\cdot10^3$ ± $1.7\cdot10^3$	$16.2\cdot10^3$ ± $7.6\cdot10^3$	$23.3\cdot10^3$ ± $3.3\cdot10^3$
Hg	0.0322 ± 0.0059	0.0254 ± 0.0045	0.0209 ± 0.0048	0.0215± 0.0049	0.0243 ± 0.0973
Mn	240 ± 93	305 ± 51	175 ± 26	281 ± 117	427 ± 77
Ni	22.0 ± 7.5	30.9 ± 4.6	14.1 ± 1.6	13.0 ± 6.7	23.5 ± 3.9
Pb	10.7 ± 2.7	12.5 ± 0.8	8.51 ± 0.99	7.75 ± 3.29	12.6 ± 0.6
S	810 ± 247	687 ± 240	546 ± 137	448 ± 188	182 ± 0
Zn	51.6 ± 16.5	71.3 ± 11.1	43.7 ± 4.3	43.3 ± 8.6	49.9 ± 2.0

Table 15. ICP-MS results for 12 selected elements (in µg/g) and soil organic matter (SOM) content (in %) determined by loss-on-ignition (LOI) for surface soils in Svalbard.

Sampling site	Sample ID	SOM	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	S	Zn
Foxdalen A	1	60.7	$13.8\cdot10^3$	4.56	0.297	21.9	9.29	$11.6\cdot10^3$	0.0906	120	11.8	6.38	$1.29\cdot10^3$	51.7
Foxdalen A	2	64.4	$13.1\cdot10^3$	5.07	0.458	19.2	8.73	$11.0\cdot10^3$	0.160	159	10.3	6.82	$1.24\cdot10^3$	58.4
Foxdalen A	3	61.3	$17.6\cdot10^3$	6.66	0.258	24.7	11.2	$15.6\cdot10^3$	0.0827	145	16.4	7.39	$1.28\cdot10^3$	57.7
Foxdalen A	4	55.0	$18.3\cdot10^3$	7.29	0.366	25.0	12.0	$16.6\cdot10^3$	0.133	234	18.3	8.75	$1.36\cdot10^3$	55.7
Foxdalen A	5	51.6	$21.9\cdot10^3$	5.30	0.302	29.3	12.7	$16.8\cdot10^3$	0.0888	153	19.2	8.11	$1.27\cdot10^3$	78.8
Foxdalen A	6	40.3	$29.4\cdot10^3$	7.07	0.259	39.6	16.7	$22.9\cdot10^3$	0.0797	183	24.9	9.54	$1.20\cdot10^3$	75.4
Foxdalen A	7	40.1	$36.5\cdot10^3$	6.92	0.128	47.8	16.1	$22.9\cdot10^3$	0.0608	186	24.4	9.60	$1.19\cdot10^3$	71.6
Foxdalen A	8	40.7	$24.7\cdot10^3$	7.09	0.232	33.3	14.1	$19.0\cdot10^3$	0.0701	169	20.1	9.61	$1.65\cdot10^3$	64.0
Foxdalen A	9	59.4	$15.7\cdot10^3$	5.21	0.386	22.4	14.9	$12.6\cdot10^3$	0.127	342	22.0	8.66	$1.78\cdot10^3$	68.2
Foxdalen A	10	67.0	$11.3\cdot10^3$	3.64	0.278	18.0	11.6	$8.77\cdot10^3$	0.117	131	14.9	5.63	$1.79\cdot10^3$	52.0
Foxdalen A	11	36.8	$22.8\cdot10^3$	9.99	0.338	32.2	13.6	$18.5\cdot10^3$	0.0868	186	17.8	10.4	$1.48\cdot10^3$	68.0
Foxdalen A	12	42.3	$20.4\cdot10^3$	8.08	0.313	29.7	12.1	$16.6\cdot10^3$	0.111	232	15.9	11.1	$1.33\cdot10^3$	57.2
Foxdalen B	13	53.5	$20.5\cdot10^3$	6.97	0.326	27.2	13.3	$16.3\cdot10^3$	0.100	217	19.6	9.19	$1.58\cdot10^3$	63.6
Foxdalen B	14	51.1	$19.8\cdot10^3$	8.36	0.360	27.9	12.9	$17.1\cdot10^3$	0.151	206	17.6	9.09	$1.61\cdot10^3$	63.3
Endalen	15	66.2	$15.4\cdot10^3$	6.14	0.509	22.7	11.1	$13.2\cdot10^3$	0.139	238	16.4	9.51	$1.51\cdot10^3$	51.7
Endalen	16	55.5	$14.9\cdot10^3$	5.27	1.00	22.0	9.95	$12.4\cdot10^3$	0.164	337	11.9	10.7	$1.28\cdot10^3$	76.2
Bayelva A	17	54.8	$11.2\cdot10^3$	2.31	0.661	16.9	7.34	$8.44\cdot10^3$	0.0872	196	8.31	11.1	$1.27\cdot10^3$	83.4
Bayelva A	18	33.8	$16.7\cdot10^3$	2.96	0.368	26.1	7.82	$15.8\cdot10^3$	0.0540	319	14.0	10.7	998	59.8
Bayelva A	19	66.3	$6.67\cdot10^3$	1.23	0.772	10.2	6.02	$5.37\cdot10^3$	0.180	135	5.58	8.64	$1.29\cdot10^3$	75.2
Bayelva A	20	72.2	$7.32\cdot10^3$	1.22	0.697	10.5	5.51	$5.62\cdot10^3$	0.128	97.9	5.85	12.4	$1.48\cdot10^3$	82.7
Bayelva B	21	55.2	$26.8\cdot10^3$	1.55	0.317	28.9	11.4	$11.1\cdot10^3$	0.120	208	18.0	13.2	$1.21\cdot10^3$	44.1
Bayelva B	22	49.5	$18.8\cdot10^3$	1.50	0.480	21.2	9.77	$10.8\cdot10^3$	0.0925	241	12.8	11.5	800	59.3

Table 16. ICP-MS results for other elements (in µg/g) for surface soils in Svalbard. (Part I)

Sampling site	Sample ID	B	Be	Ca	Co	Hf	Li	Mg	Na	Rb	Sr	Ti	V	Zr
Foxdalen A	1	33.1	0.490	$10.6\cdot10^3$	3.83	0.0786	14.5	$3.23\cdot10^3$	298	23.6	114	101	38.4	1.19
Foxdalen A	2	30.3	0.449	$9.87\cdot10^3$	3.77	0.0652	13.1	$3.20\cdot10^3$	286	22.7	95.2	84.5	36.6	0.952
Foxdalen A	3	39.7	0.588	$12.3\cdot10^3$	5.12	0.0748	19.2	$3.60\cdot10^3$	294	27.9	143	88.8	52.0	1.18
Foxdalen A	4	41.3	0.623	$11.4\cdot10^3$	6.00	0.0862	19.2	$3.81\cdot10^3$	319	29.7	121	97.8	52.3	1.31
Foxdalen A	5	42.4	0.671	$9.92\cdot10^3$	6.10	0.0831	24.6	$4.09\cdot10^3$	367	34.2	119	91.9	57.9	1.39
Foxdalen A	6	55.6	0.914	$8.67\cdot10^3$	8.09	0.0772	34.3	$4.93\cdot10^3$	451	45.8	115	91.8	79.2	1.34
Foxdalen A	7	70.2	1.03	$9.35\cdot10^3$	7.70	0.110	40.2	$5.62\cdot10^3$	524	61.1	162	117	99.2	1.79
Foxdalen A	8	48.5	0.780	$10.2\cdot10^3$	6.56	0.117	26.5	$4.57\cdot10^3$	427	41.3	132	122	64.3	1.82
Foxdalen A	9	36.0	0.585	$12.4\cdot10^3$	5.20	0.0908	16.1	$3.44\cdot10^3$	348	25.0	152	95.6	42.5	1.42
Foxdalen A	10	36.1	0.413	$16.6\cdot10^3$	3.37	0.0658	11.8	$3.30\cdot10^3$	261	18.2	176	84.0	30.6	1.03
Foxdalen A	11	45.9	0.749	$10.5\cdot10^3$	6.03	0.113	25.0	$3.78\cdot10^3$	321	38.4	162	103	61.7	1.80
Foxdalen A	12	40.8	0.701	$9.91\cdot10^3$	5.92	0.111	21.0	$3.74\cdot10^3$	314	35.9	136	107	56.9	1.823
Foxdalen B	13	44.8	0.678	$11.2\cdot10^3$	6.35	0.0887	22.6	$3.75\cdot10^3$	381	34.2	138	93.2	55.4	1.430
Foxdalen B	14	43.3	0.676	$12.3\cdot10^3$	6.49	0.102	21.5	$3.87\cdot10^3$	429	32.9	136	101	54.1	1.590
Endalen	15	34.5	0.662	$11.4\cdot10^3$	6.50	0.120	13.6	$2.80\cdot10^3$	372	31.4	319	106	66.8	1.539
Endalen	16	25.5	0.581	$6.72\cdot10^3$	6.09	0.105	12.8	$2.77\cdot10^3$	371	30.4	159	113	53.2	1.526
Bayelva A	17	23.1	0.454	$16.9\cdot10^3$	3.46	0.0735	8.72	$3.79\cdot10^3$	246	28.5	37.3	220	22.3	1.658
Bayelva A	18	21.5	0.669	$11.7\cdot10^3$	5.33	0.106	14.8	$3.47\cdot10^3$	294	36.2	36.3	263	31.4	2.314
Bayelva A	19	14.8	0.262	$14.5\cdot10^3$	2.23	0.0561	4.65	$3.32\cdot10^3$	202	14.8	41.4	167	12.1	1.310
Bayelva A	20	18.0	0.324	$15.7\cdot10^3$	2.07	0.0706	4.80	$3.26\cdot10^3$	213	14.6	35.2	181	13.0	1.560
Bayelva B	21	23.4	0.863	$8.56\cdot10^3$	5.27	0.0863	16.9	$3.67\cdot10^3$	790	52.6	39.3	157	34.6	1.566
Bayelva B	22	19.4	0.597	$7.81\cdot10^3$	5.40	0.0740	13.7	$3.15\cdot10^3$	561	33.6	34.4	113	24.4	1.498

Table 17. ICP-MS results for other elements (in µg/g) for surface soils in Svalbard. (Part II)

Sampling site	Sample ID	Ag	Ba	Ce	Cs	Bi	Ge	La	Mo	Nd	Pr	Sb	Sm	Tl	Y
Foxdalen A	1	0.0368	136	20.6	1.37	0.0640	0.265	9.90	0.461	9.26	2.36	0.0160	1.72	0.146	4.09
Foxdalen A	2	0.0362	136	18.6	1.33	0.0679	0.264	8.92	0.511	8.32	2.17	0.0145	1.57	0.145	3.53
Foxdalen A	3	0.0331	215	22.1	1.65	0.0769	0.262	10.4	0.494	10.9	2.68	0.0153	2.20	0.159	5.26
Foxdalen A	4	0.0466	219	27.2	1.73	0.0776	0.301	12.1	0.527	13.6	3.36	0.0191	2.79	0.178	7.38
Foxdalen A	5	0.0388	243	24.8	1.92	0.0917	0.318	11.5	0.349	12.3	2.99	0.0134	2.55	0.177	6.01
Foxdalen A	6	0.0440	263	26.8	2.67	0.110	0.242	12.7	0.343	13.6	3.15	$7.73\cdot10^{-3}$	3.00	0.224	7.30
Foxdalen A	7	0.0476	313	30.3	4.05	0.105	0.426	14.9	0.360	15.3	3.64	$5.75\cdot10^{-3}$	3.28	0.317	7.79
Foxdalen A	8	0.0530	237	29.7	2.43	0.101	0.379	14.1	0.684	13.9	3.49	$8.15\cdot10^{-3}$	2.88	0.239	6.98
Foxdalen A	9	0.0487	251	30.1	1.61	0.0776	0.360	13.4	0.607	17.1	3.96	0.0237	3.91	0.181	10.5
Foxdalen A	10	0.0396	191	17.2	1.18	0.0530	0.256	8.16	0.778	8.52	2.12	0.0232	1.77	0.144	4.44
Foxdalen A	11	0.0683	215	31.3	2.41	0.0846	0.320	15.3	0.853	14.4	3.64	0.0124	2.84	0.266	6.52
Foxdalen A	12	0.0597	188	31.2	2.22	0.0860	0.329	15.3	0.943	13.7	3.51	0.0189	2.68	0.257	6.20
Foxdalen B	13	0.0570	297	28.2	2.08	0.0879	0.309	12.7	0.476	15.4	3.61	0.0166	3.39	0.201	8.42
Foxdalen B	14	0.0464	253	27.2	2.00	0.0894	0.337	12.2	0.535	13.0	3.22	0.0185	2.65	0.195	6.49
Endalen	15	0.0697	202	28.4	2.26	0.0701	0.355	12.6	0.633	14.1	3.49	0.0120	2.93	0.199	7.91
Endalen	16	0.0548	159	26.2	1.83	0.0757	0.357	12.2	0.596	11.6	3.03	0.0103	2.27	0.188	5.15
Bayelva A	17	0.0279	86.3	18.9	1.40	0.105	0.283	9.14	0.395	8.52	2.25	$9.24\cdot10^{-3}$	1.64	0.173	4.41
Bayelva A	18	0.0379	107	34.3	2.07	0.126	0.248	17.4	0.362	15.2	3.93	0.0167	2.95	0.197	8.17
Bayelva A	19	0.0354	68.6	15.9	0.758	0.0890	0.195	7.57	0.235	7.09	1.88	0.0197	1.34	0.107	3.51
Bayelva A	20	0.0358	70.3	16.8	0.860	0.0949	0.255	8.07	0.330	7.40	1.99	0.0296	1.45	0.135	4.66
Bayelva B	21	0.0650	234	34.2	1.91	0.110	0.420	17.5	0.204	17.0	4.27	0.0121	3.53	0.266	9.52
Bayelva B	22	0.0334	159	25.9	1.10	0.0822	0.261	12.2	0.259	10.9	2.96	0.0168	2.07	0.176	4.87

Table 18. ICP-MS results for 12 selected elements (in µg/g) and soil organic matter (SOM) content (in %) determined by loss-on-ignition (LOI) for mineral soils in Svalbard.

Sampling site	Sample ID	SOM	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	S	Zn
Foxdalen A	1m	18.6	$20.3\cdot10^3$	9.67	0.0444	31.9	9.06	$17.6\cdot10^3$	0.0334	144	12.1	8.73	656	32.1
Foxdalen A	2m	15.6	$27.9\cdot10^3$	8.24	0.0659	44.6	12.5	$21.6\cdot10^3$	0.0248	308	17.1	9.03	721	42.3
Foxdalen A	3m	12.6	$34.4\cdot10^3$	11.8	0.0589	52.1	16.6	$28.2\cdot10^3$	0.0292	323	24.6	9.96	730	57.8
Foxdalen A	4m	12.9	$42.3\cdot10^3$	11.8	0.0424	55.7	19.0	$32.9\cdot10^3$	0.0257	301	27.2	13.69	762	63.0
Foxdalen A	5m	27.6	$18.9\cdot10^3$	3.57	0.0526	26.5	9.26	$12.8\cdot10^3$	0.0285	113	14.0	5.93	947	25.3
Foxdalen A	6m	12.7	$33.4\cdot10^3$	7.89	0.0564	49.1	14.9	$24.1\cdot10^3$	0.0292	200	22.3	10.4	$1.15\cdot10^3$	49.4
Foxdalen A	7m	9.49	$52.0\cdot10^3$	12.7	0.0664	72.3	24.5	$39.1\cdot10^3$	0.0390	381	35.3	15.1	$1.17\cdot10^3$	80.2
Foxdalen A	8m	7.79	$47.1\cdot10^3$	14.1	0.0502	67.0	21.9	$40.1\cdot10^3$	0.0380	365	33.6	14.7	$1.18\cdot10^3$	75.9
Foxdalen A	9m	12.0	$35.0\cdot10^3$	11.1	0.0439	52.5	16.1	$28.4\cdot10^3$	0.0243	218	22.8	10.6	556	54.0
Foxdalen A	10m	9.53	$37.9\cdot10^3$	8.49	0.0561	57.5	17.1	$31.3\cdot10^3$	0.0369	219	23.4	11.3	761	55.1
Foxdalen A	11m	20.0	$24.0\cdot10^3$	10.2	0.0809	39.3	9.77	$19.6\cdot10^3$	0.0372	186	14.9	8.12	690	38.1
Foxdalen A	12m	6.43	$33.9\cdot10^3$	13.7	0.0359	48.5	12.0	$24.8\cdot10^3$	0.0401	123	16.2	11.3	412	45.5
Foxdalen B	13m	12.8	$41.0\cdot10^3$	10.0	0.0438	55.5	19.2	$30.9\cdot10^3$	0.0222	269	27.7	11.9	857	63.4
Foxdalen B	14m	8.07	$46.7\cdot10^3$	10.7	0.0730	63.5	23.6	$43.0\cdot10^3$	0.0285	340	34.2	13.1	517	79.1
Endalen	15m	7.03	$24.6\cdot10^3$	9.84	0.0543	40.6	10.5	$21.9\cdot10^3$	0.0176	157	13.0	7.80	449	40.6
Endalen	16m	11.4	$28.0\cdot10^3$	10.9	0.0677	42.9	12.1	$24.3\cdot10^3$	0.0243	193	15.2	9.21	643	46.7
Bayelva	17m	8.31	$30.4\cdot10^3$	5.33	0.0962	43.7	11.2	$20.8\cdot10^3$	0.0188	310	16.4	10.1	316	46.2
Bayelva	18m	8.75	$25.6\cdot10^3$	4.02	0.127	38.5	9.35	$20.7\cdot10^3$	0.0275	398	19.5	9.46	422	53.9
Bayelva	19m	4.93	$20.5\cdot10^3$	3.89	0.0602	34.4	7.08	$18.4\cdot10^3$	0.0165	275	12.2	8.56	334	38.2
Bayelva	20m	50.1	$6.64\cdot10^3$	0.689	0.148	8.78	3.26	$4.87\cdot10^3$	0.0234	122	4.01	2.92	721	34.7
Bayelva	21m	5.47	$34.3\cdot10^3$	2.42	0.105	38.6	14.4	$21.0\cdot10^3$	0.0174	373	20.7	12.1	182	48.5
Bayelva	22m	5.89	$40.4\cdot10^3$	3.68	0.0913	47.0	17.5	$25.6\cdot10^3$	0.0311	481	26.2	13.0	183	51.3

Table 19. ICP-MS results for other elements (in µg/g) for mineral soils in Svalbard. (Part I)

Sampling site	Sample ID	B	Be	Ca	Co	Hf	Li	Mg	Na	Rb	Sr	Ti	V	Zr
Foxdalen A	1m	27.6	0.632	$2.83\cdot10^{3}$	4.57	0.131	18.9	$2.88\cdot10^{3}$	292	31.5	46.8	126	53.2	1.65
Foxdalen A	2m	38.4	0.884	$2.98\cdot10^{3}$	8.17	0.174	26.5	$3.98\cdot10^{3}$	367	45.9	59.8	147	76.6	2.23
Foxdalen A	3m	50.4	0.991	$3.21\cdot10^{3}$	11.4	0.197	37.1	$4.80\cdot10^{3}$	446	52.3	72.2	155	93.9	2.60
Foxdalen A	4m	59.0	1.29	$2.89\cdot10^{3}$	11.7	0.182	47.4	$5.74\cdot10^{3}$	505	64.5	74.1	133	108	2.49
Foxdalen A	5m	35.6	0.585	$5.52\cdot10^{3}$	3.96	0.109	19.3	$2.71\cdot10^{3}$	307	30.7	81.6	119	49.3	1.50
Foxdalen A	6m	50.8	1.01	$3.80\cdot10^{3}$	8.29	0.182	35.5	$4.48\cdot10^{3}$	518	52.1	92.5	143	86.9	2.39
Foxdalen A	7m	74.8	1.55	$3.30\cdot10^{3}$	14.3	0.239	60.1	$7.23\cdot10^{3}$	776	79.5	106	156	133	3.14
Foxdalen A	8m	65.5	1.45	$2.43\cdot10^{3}$	14.7	0.218	54.6	$6.62\cdot10^{3}$	735	73.8	91.1	137	130	3.04
Foxdalen A	9m	47.2	1.15	$2.21\cdot10^{3}$	8.78	0.184	36.1	$4.69\cdot10^{3}$	439	52.2	70.0	136	93.2	2.66
Foxdalen A	10m	51.6	1.21	$2.88\cdot10^{3}$	8.73	0.200	42.0	$5.36\cdot10^{3}$	504	56.9	80.3	163	97.8	2.82
Foxdalen A	11m	33.5	0.709	$4.49\cdot10^{3}$	5.73	0.154	26.3	$3.15\cdot10^{3}$	292	35.6	84.8	136	69.1	2.31
Foxdalen A	12m	42.4	1.03	$2.01\cdot10^{3}$	6.18	0.197	43.5	$3.28\cdot10^{3}$	321	46.0	63.8	128	84.1	2.45
Foxdalen B	13m	60.2	1.27	$3.13\cdot10^{3}$	11.2	0.172	47.2	$5.72\cdot10^{3}$	531	63.4	80.7	135	106	2.62
Foxdalen B	14m	62.9	1.60	$3.07\cdot10^{3}$	12.8	0.214	59.1	$6.76\cdot10^{3}$	554	64.2	80.3	1780	127	3.17
Endalen	15m	33.6	1.09	$1.31\cdot10^{3}$	7.15	0.248	22.8	$3.26\cdot10^{3}$	364	44.4	60.0	120	111	2.95
Endalen	16m	37.9	1.20	$1.88\cdot10^{3}$	8.07	0.258	25.4	$3.65\cdot10^{3}$	398	51.4	80.2	131	121	3.18
Bayelva	17m	26.5	1.21	$8.37\cdot10^{3}$	6.92	0.165	23.2	$7.99\cdot10^{3}$	487	67.9	35.6	394	52.4	3.31
Bayelva	18m	24.5	0.923	$4.74\cdot10^{3}$	7.04	0.171	22.1	$4.31\cdot10^{3}$	413	51.9	31.0	349	43.5	3.09
Bayelva	19m	15.8	0.911	$2.02\cdot10^{3}$	6.00	0.144	15.3	$3.59\cdot10^{3}$	327	40.0	28.3	436	38.0	2.81
Bayelva	20m	7.0	0.321	$6.74\cdot10^{3}$	2.10	0.060	3.49	$1.55\cdot10^{3}$	126	12.5	14.5	200	10.7	1.12
Bayelva	21m	19.3	1.11	$1.72\cdot10^{3}$	9.40	0.157	27.0	$4.74\cdot10^{3}$	805	58.7	29.5	243	43.0	2.76
Bayelva	22m	26.0	1.33	$2.08\cdot10^{3}$	11.1	0.156	32.3	$4.79\cdot10^{3}$	1153	64.9	37.4	141	50.2	3.08

Table 20. ICP-MS results for other elements (in µg/g) for mineral soils in Svalbard. (Part II)

Sampling site	Sample ID	Ag	Ba	Bi	Ce	Cs	Ge	La	Mo	Nd	Pr	Sb	Sm	Tl	Y
Foxdalen A	1m	0.0392	141	0.0895	28.6	2.02	0.268	13.8	0.714	12.2	3.30	0.0235	2.28	0.203	6.27
Foxdalen A	2m	0.0422	228	0.104	38.9	3.00	0.428	18.7	0.886	16.2	4.47	0.0242	2.89	0.286	7.81
Foxdalen A	3m	0.0372	245	0.144	47.1	3.13	0.517	21.8	0.575	21.3	5.48	0.0323	4.04	0.289	10.1
Foxdalen A	4m	0.0304	308	0.154	48.5	3.99	0.425	22.1	0.419	19.0	5.08	0.0266	3.52	0.323	8.61
Foxdalen A	5m	0.0466	171	0.0631	23.0	2.23	0.343	11.4	0.345	12.1	3.01	0.0462	2.61	0.187	7.25
Foxdalen A	6m	0.0335	256	0.114	41.3	3.26	0.489	19.6	0.404	18.8	4.95	0.0253	3.72	0.275	8.85
Foxdalen A	7m	0.0459	366	0.199	60.8	4.83	0.549	28.2	0.480	25.6	6.75	0.0141	4.85	0.411	11.1
Foxdalen A	8m	0.0327	325	0.179	53.2	4.12	0.549	24.7	0.548	21.8	5.86	0.0148	3.95	0.361	9.11
Foxdalen A	9m	0.0299	253	0.143	45.9	3.24	0.605	21.5	0.631	19.8	5.29	0.0213	3.45	0.284	8.89
Foxdalen A	10m	0.0657	302	0.148	47.1	4.10	0.497	22.3	0.717	22.1	5.68	0.0209	4.10	0.347	11.3
Foxdalen A	11m	0.0586	186	0.0746	33.1	2.46	0.361	15.7	0.630	14.0	3.80	0.0309	2.58	0.267	6.85
Foxdalen A	12m	0.0383	200	0.114	47.8	2.75	0.451	23.0	0.488	19.7	5.43	0.0146	3.28	0.284	6.98
Foxdalen B	13m	0.0400	299	0.171	47.5	3.94	0.438	22.8	0.554	21.1	5.54	0.0246	3.70	0.332	9.16
Foxdalen B	14m	0.0364	314	0.213	60.8	3.79	0.438	28.4	0.423	27.4	7.07	0.0135	4.95	0.334	11.6
Endalen	15m	0.0352	156	0.0946	46.4	2.83	0.401	20.5	0.652	20.9	5.36	0.0168	3.71	0.222	9.09
Endalen	16m	0.0577	192	0.107	50.2	3.51	0.363	22.2	0.674	23.0	5.84	0.0223	4.26	0.283	10.3
Bayelva	17m	0.0438	189	0.180	48.1	3.85	0.449	22.9	0.271	22.4	5.67	0.0167	3.91	0.355	11.9
Bayelva	18m	0.0539	154	0.127	51.3	3.14	0.328	25.0	0.337	24.5	6.24	0.0144	4.33	0.272	13.2
Bayelva	19m	0.0353	134	0.145	43.4	2.14	0.308	19.1	0.381	18.1	4.73	0.0124	3.03	0.266	9.68
Bayelva	20m	0.0168	59.9	0.0538	13.6	0.742	0.093	6.22	0.220	6.26	1.61	0.0216	1.17	0.0868	4.10
Bayelva	21m	0.0300	230	0.144	56.0	2.11	0.334	25.9	0.170	24.8	6.46	$9.88\cdot10^{-3}$	4.29	0.310	10.8
Bayelva	22m	0.0405	295	0.110	55.0	1.91	0.303	25.7	0.284	24.7	6.38	0.0136	4.15	0.332	10.0

Appendix C: Correlation

Table 21. Spearman's rank correlation coefficient for selected elements and soil organic matter (SOM) content in surface soils (n=22) in Svalbard. Elemental concentrations are given in µg/g and SOM in %. (Colors indicate level of significance: 🟩 p<0.05, 🟩 p<0.01 and 🟩 p<0.001)

	As	Pb	Cd	Hg	Cu	Zn	Cr	Ni	Fe	Al	Mn	S	SOM
As	1.00	-0.16	-0.48	-0.19	0.75	-0.088	0.74	0.64	0.86	0.61	0.19	0.34	-0.52
Pb	-0.16	1.00	0.29	-0.17	-0.13	0.23	0.16	-0.078	-0.029	0.24	0.40	-0.35	-0.40
Cd	-0.48	0.29	1.00	0.65	-0.65	0.26	-0.68	-0.65	-0.63	-0.66	0.34	-0.032	0.38
Hg	-0.19	-0.17	0.65	1.00	-0.35	-0.13	-0.54	-0.42	-0.49	-0.53	0.099	0.33	0.67
Cu	0.75	-0.13	-0.65	-0.39	1.00	0.037	0.81	0.94	0.83	0.80	0.18	0.27	-0.53
Zn	-0.088	0.23	0.26	-0.13	0.037	1.00	-0.028	-0.007	0.054	-0.053	-0.097	-0.12	-0.18
Cr	0.74	0.16	-0.68	-0.54	0.81	-0.028	1.00	0.82	0.93	0.95	0.19	-0.078	-0.78
Ni	0.64	-0.078	-0.65	-0.42	0.94	-0.007	0.82	1.00	0.81	0.84	0.24	0.14	-0.52
Fe	0.86	-0.029	-0.63	-0.49	0.83	0.054	0.93	0.81	1.00	0.83	0.18	0.038	-0.74
Al	0.61	0.24	-0.66	-0.53	0.80	-0.053	0.95	0.84	0.83	1.00	0.21	-0.18	-0.76
Mn	0.19	0.40	0.34	0.099	0.18	-0.097	0.19	0.24	0.18	0.21	1.00	-0.094	-0.38
S	0.34	-0.35	-0.03	0.33	0.27	-0.12	-0.078	0.14	0.038	-0.18	-0.094	1.00	0.34
SOM	-0.52	-0.40	0.38	0.67	-0.53	-0.18	-0.78	-0.52	-0.74	-0.76	-0.38	0.34	1.00

Table 22. Spearman's rank correlation coefficient for selected elements and soil organic matter (SOM) content in mineral soils (n=22) in Svalbard. Elemental concentrations are given in µg/g and SOM in %. (Colors indicate level of significance: 🟦 p<0.05, 🟦 p<0.01 and 🟦 p<0.001)

	As	Pb	Cd	Hg	Cu	Zn	Cr	Ni	Fe	Al	Mn	S	SOM
As	1.00	0.47	-0.56	0.51	0.56	0.55	0.72	0.48	0.70	0.58	0.043	0.37	-0.038
Pb	0.47	1.00	-0.18	0.36	0.89	0.87	0.83	0.90	0.85	0.96	0.66	0.14	-0.42
Cd	-0.56	-0.18	1.00	-0.26	-0.24	-0.12	-0.36	-0.13	-0.34	-0.23	0.40	-0.42	-0.13
Hg	0.51	0.36	-0.26	1.00	0.35	0.26	0.44	0.34	0.37	0.34	0.027	0.42	0.10
Cu	0.56	0.89	-0.24	0.35	1.00	0.91	0.94	0.96	0.95	0.97	0.56	0.37	-0.21
Zn	0.55	0.87	-0.12	0.26	0.92	1.00	0.89	0.96	0.91	0.94	0.67	0.30	-0.28
Cr	0.71	0.83	-0.36	0.44	0.94	0.89	1.00	0.90	0.97	0.93	0.44	0.42	-0.19
Ni	0.48	0.90	-0.13	0.34	0.96	0.96	0.90	1.00	0.90	0.96	0.69	0.34	-0.22
Fe	0.70	0.85	-0.34	0.37	0.95	0.91	0.97	0.90	1.00	0.95	0.46	0.32	-0.28
Al	0.58	0.96	-0.23	0.34	0.97	0.94	0.93	0.96	0.95	1.00	0.62	0.25	-0.34
Mn	0.043	0.66	0.40	0.027	0.56	0.67	0.44	0.69	0.46	0.62	1.00	-0.18	-0.52
S	0.37	0.14	-0.41	0.41	0.37	0.30	0.42	0.34	0.32	0.25	-0.18	1.00	0.59
SOM	-0.038	-0.42	-0.13	0.10	-0.21	-0.28	-0.19	-0.22	-0.28	-0.34	-0.52	0.59	1.00

Appendix D: Factor analysis

Table 23. Communalities surface (left) and mineral soils (right). (Extraction Method: Principal Component Analysis)

	Initial	Extraction
SOM	1.00	0.826
Al	1.00	0.889
As	1.00	0.765
Cd	1.00	0.930
Cr	1.00	0.949
Cu	1.00	0.922
Fe	1.00	0.937
Hg	1.00	0.755
Mn	1.00	0.858
Ni	1.00	0.914
Pb	1.00	0.676
S	1.00	0.753
Zn	1.00	0.954

	Initial	Extraction
SOM	1.00	0.901
Al	1.00	0.974
As	1.00	0.853
Cd	1.00	0.904
Cr	1.00	0.974
Cu	1.00	0.948
Fe	1.00	0.957
Hg	1.00	0.549
Mn	1.00	0.896
Ni	1.00	0.969
Pb	1.00	0.933
S	1.00	0.818
Zn	1.00	0.917

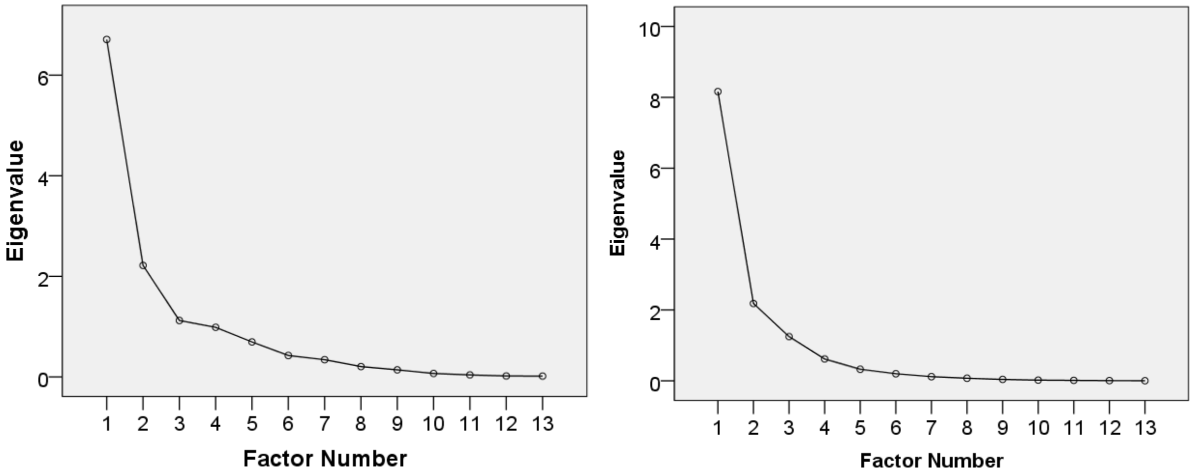

Figure 25. Scree plot for the factor analysis of the surface soils (left) and the mineral soils (right). For the surface soils four factors were extracted and for the mineral soils three based on the criterion Eigenvalue >1.

Table 24. Communalities of surface (left) and mineral (right) soils including samples from 2014. (Extraction Method: Principal Component Analysis)

	Initial	Extraction
SOM	1.00	0.867
Al	1.00	0.924
As	1.00	0.836
Cd	1.00	0.755
Cr	1.00	0.936
Cu	1.00	0.890
Fe	1.00	0.980
Hg	1.00	0.734
Mn	1.00	0.851
Ni	1.00	0.947
Pb	1.00	0.825
S	1.00	0.766
Zn	1.00	0.728

	Initial	Extraction
Al	1.00	0.922
As	1.00	0.732
Cd	1.00	0.796
Cr	1.00	0.914
Cu	1.00	0.951
Fe	1.00	0.896
Hg	1.00	0.658
Mn	1.00	0.569
Ni	1.00	0.957
Pb	1.00	0.880
S	1.00	0.872
Zn	1.00	0.919

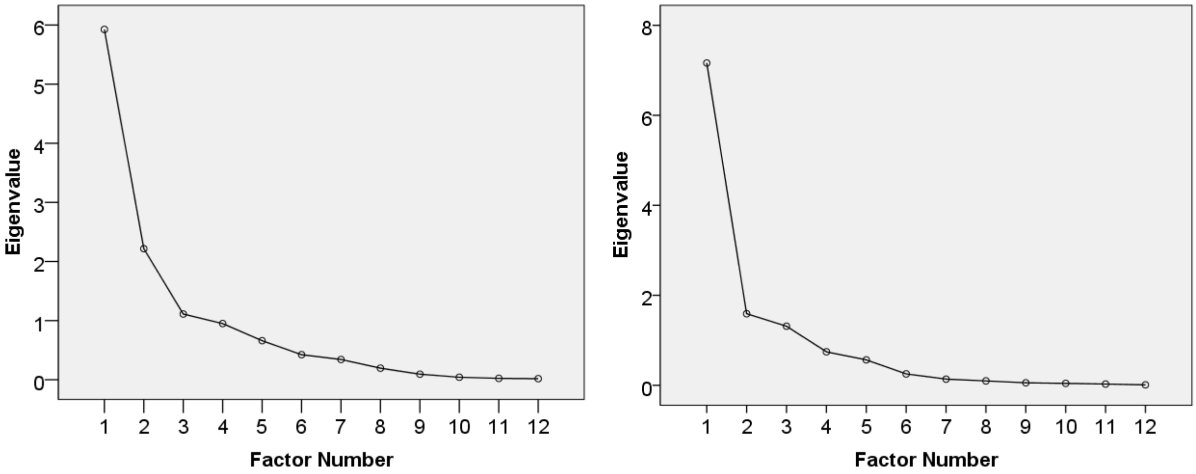

Figure 26. Scree plot for the factor analysis of the surface soils (left) and the mineral soils (right) of all samples from 2014 and 2015. For the surface soils four factors were extracted (factor 4: Eigenvalue=0.987) and for the mineral soils three based on the criterion Eigenvalue >1.

Appendix E: Mapping of soil composition

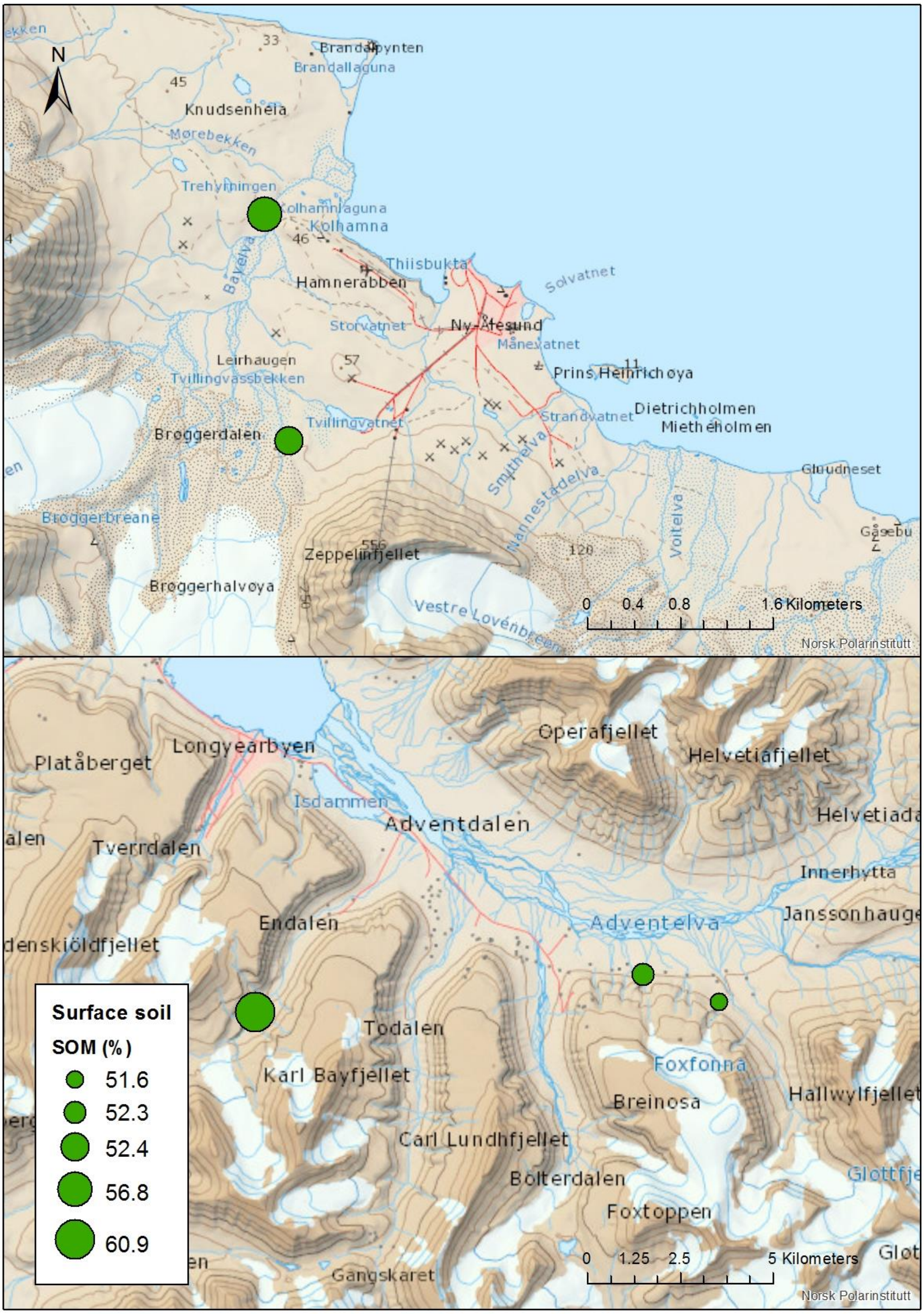

Figure 27. Mean of soil organic matter (SOM) amount (%) in surface soils in Svalbard.

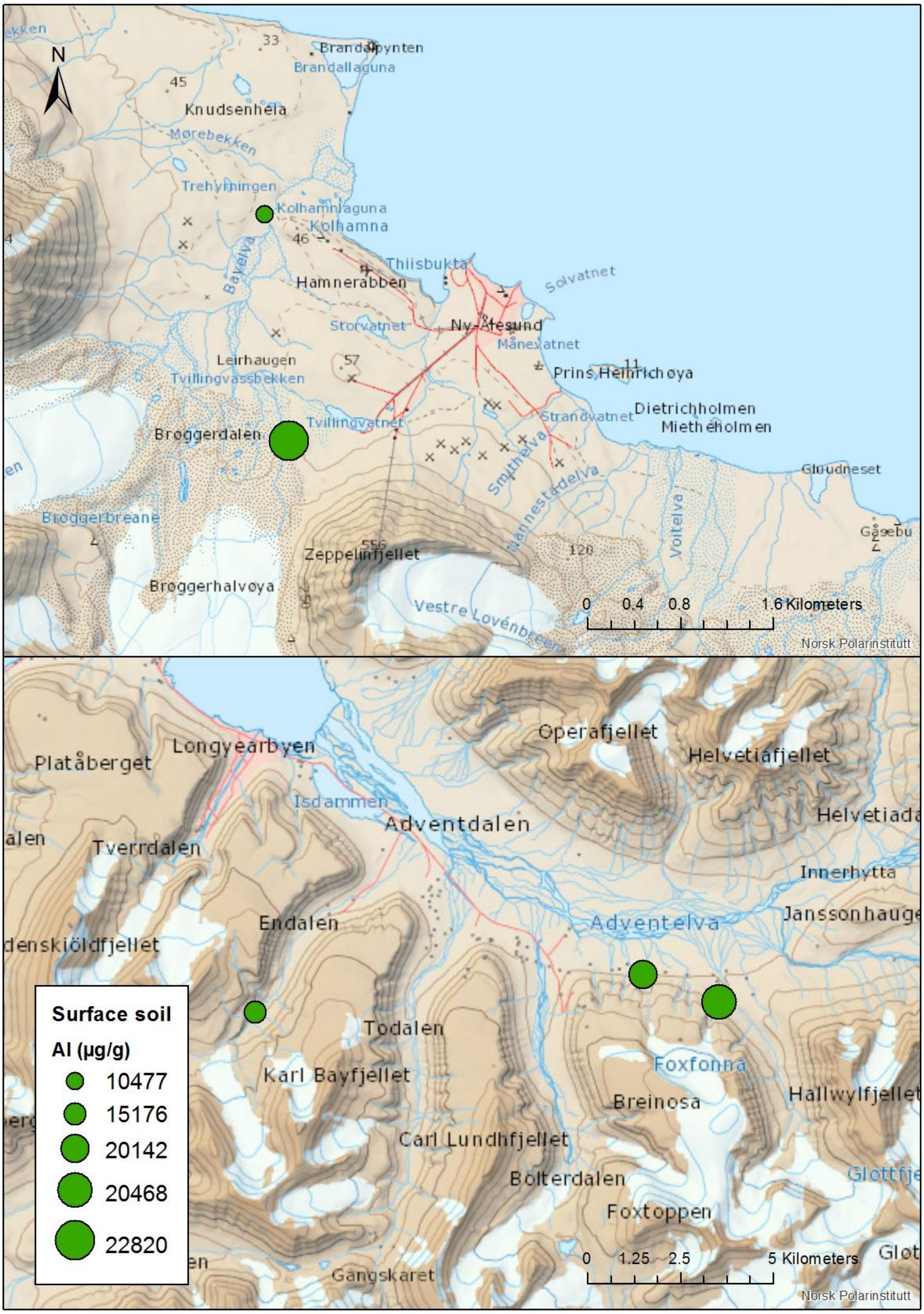

Figure 28. Mean concentrations (µg/g) of aluminum (Al) in surface soils in Svalbard.

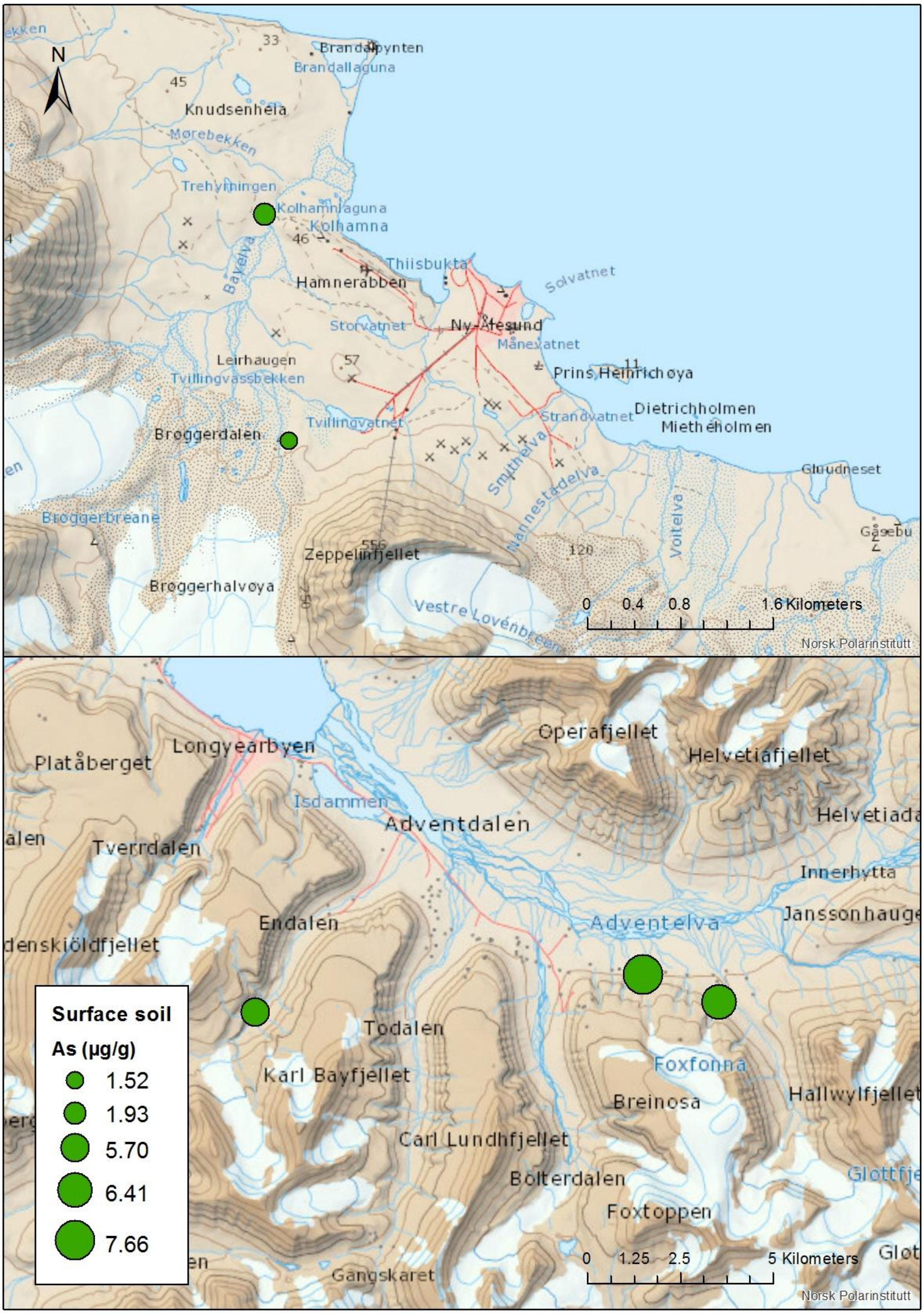

Figure 29. Mean concentrations (µg/g) of arsenic (As) in surface soils in Svalbard.

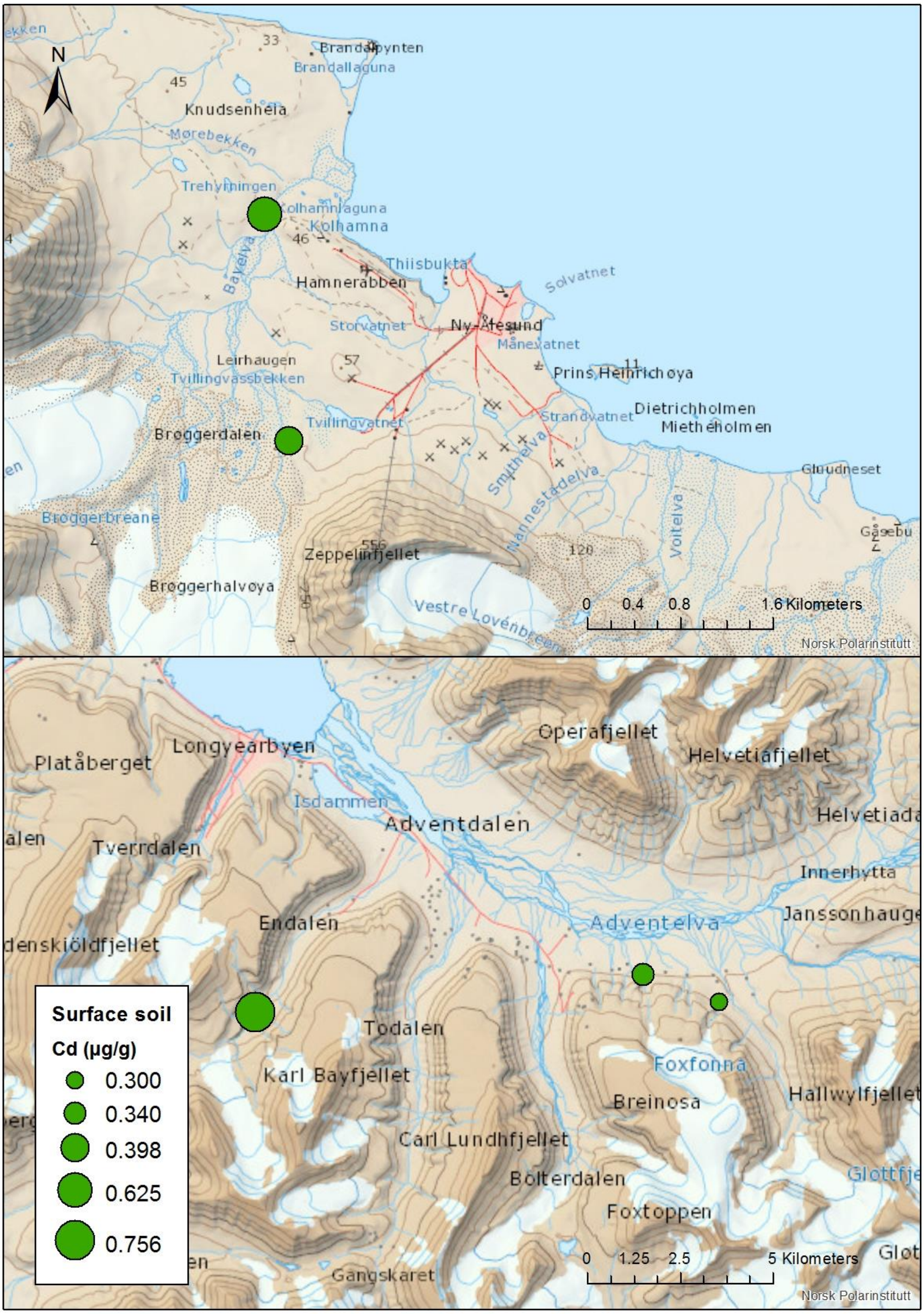

Figure 30. Mean concentrations (µg/g) of cadmium (Cd) in surface soils in Svalbard.

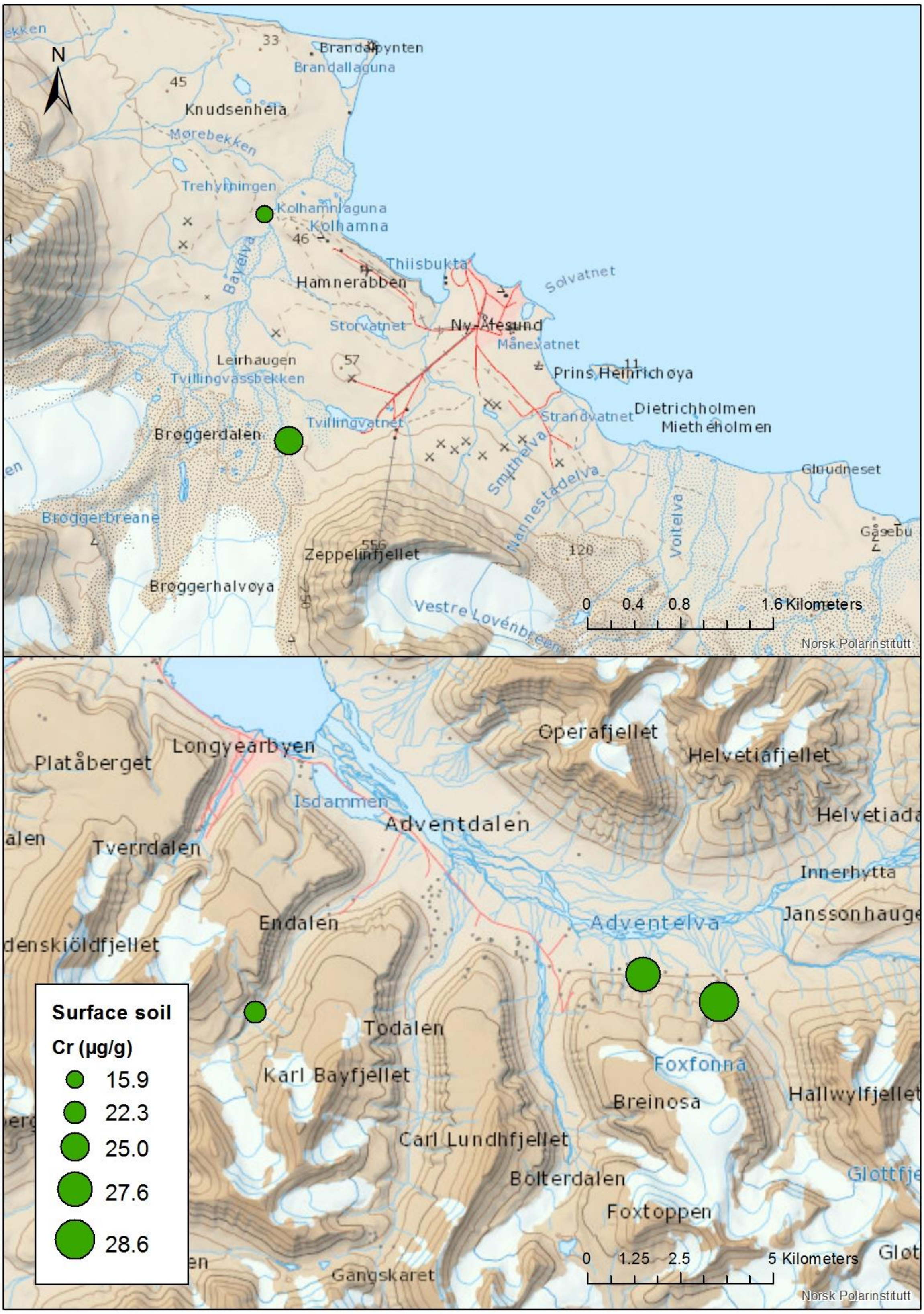

Figure 31. Mean concentrations (µg/g) of chromium (Cr) in surface soils in Svalbard.

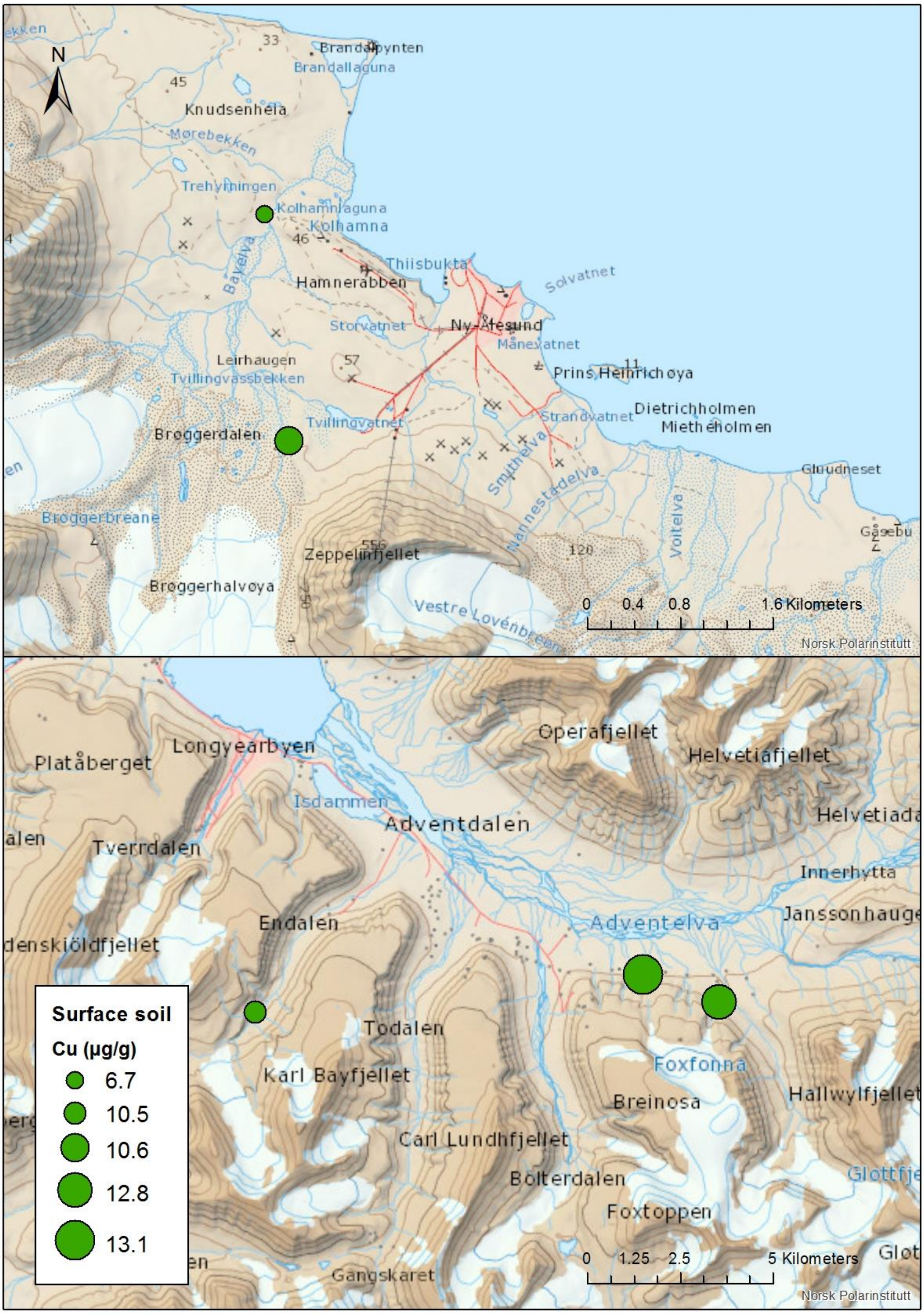

Figure 32. Mean concentrations (µg/g) of copper (Cu) in surface soils in Svalbard.

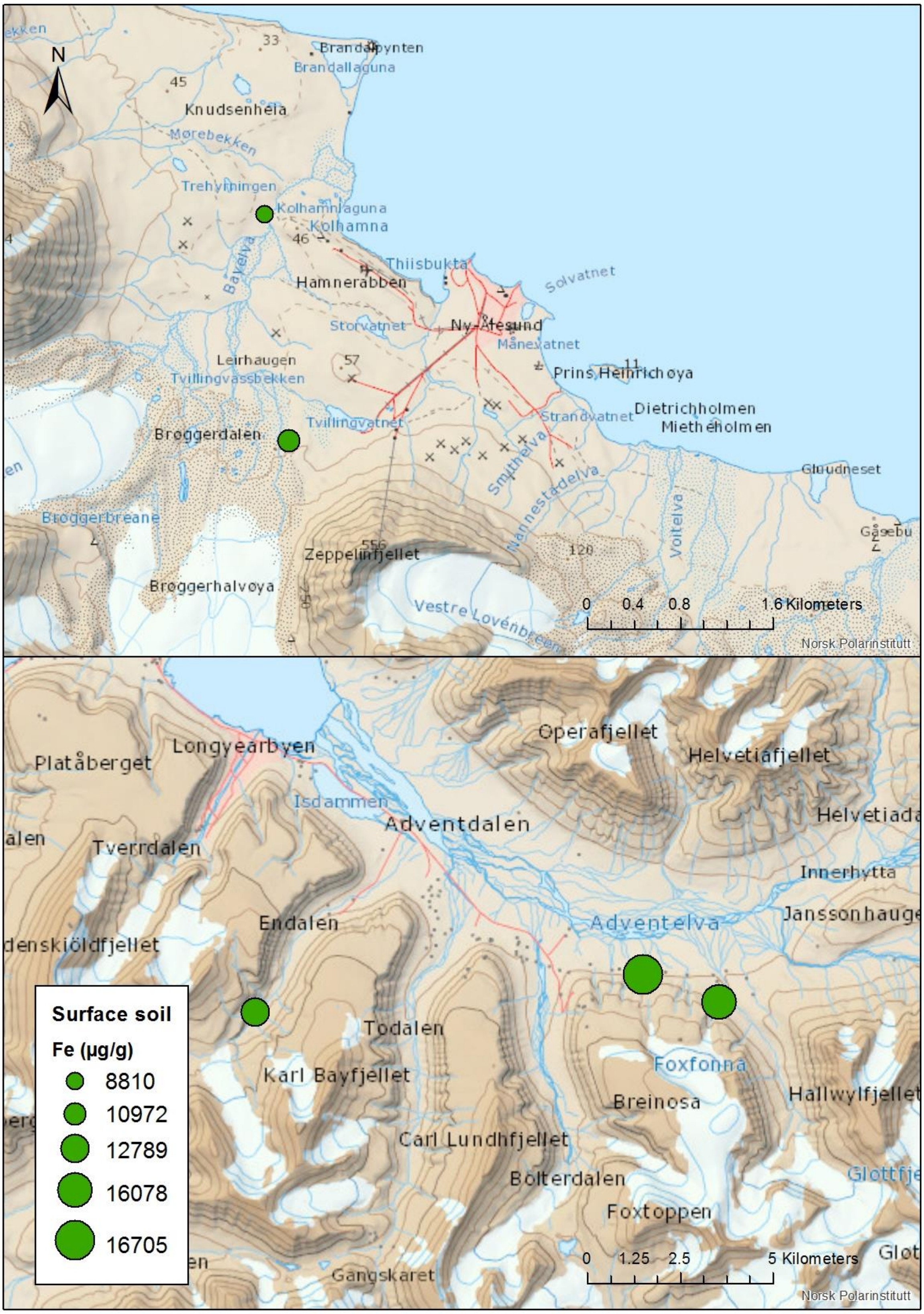

Figure 33. Mean concentrations (µg/g) of iron (Fe) in surface soils in Svalbard.

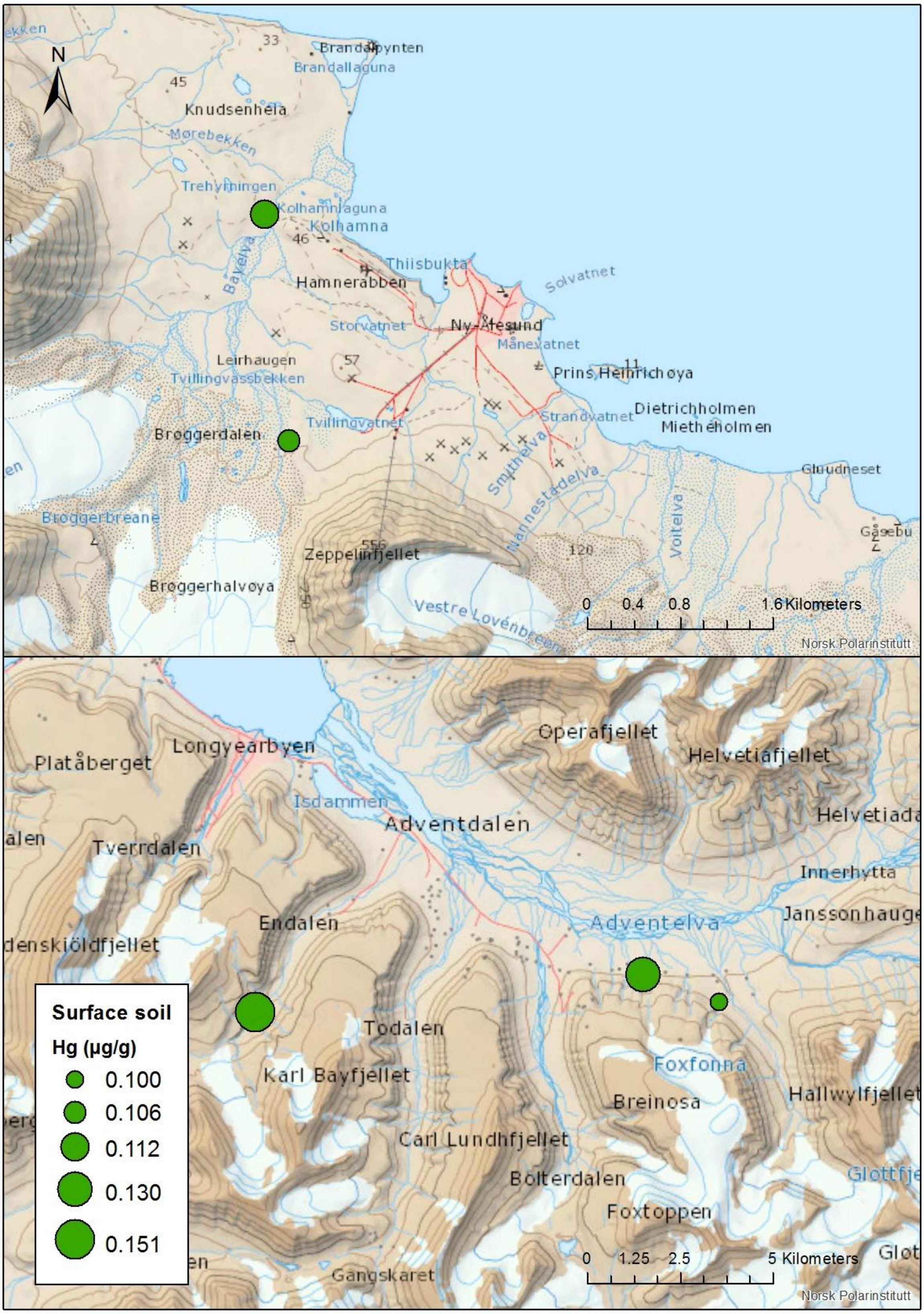

Figure 34. Mean concentrations (µg/g) of mercury (Hg) in surface soils in Svalbard.

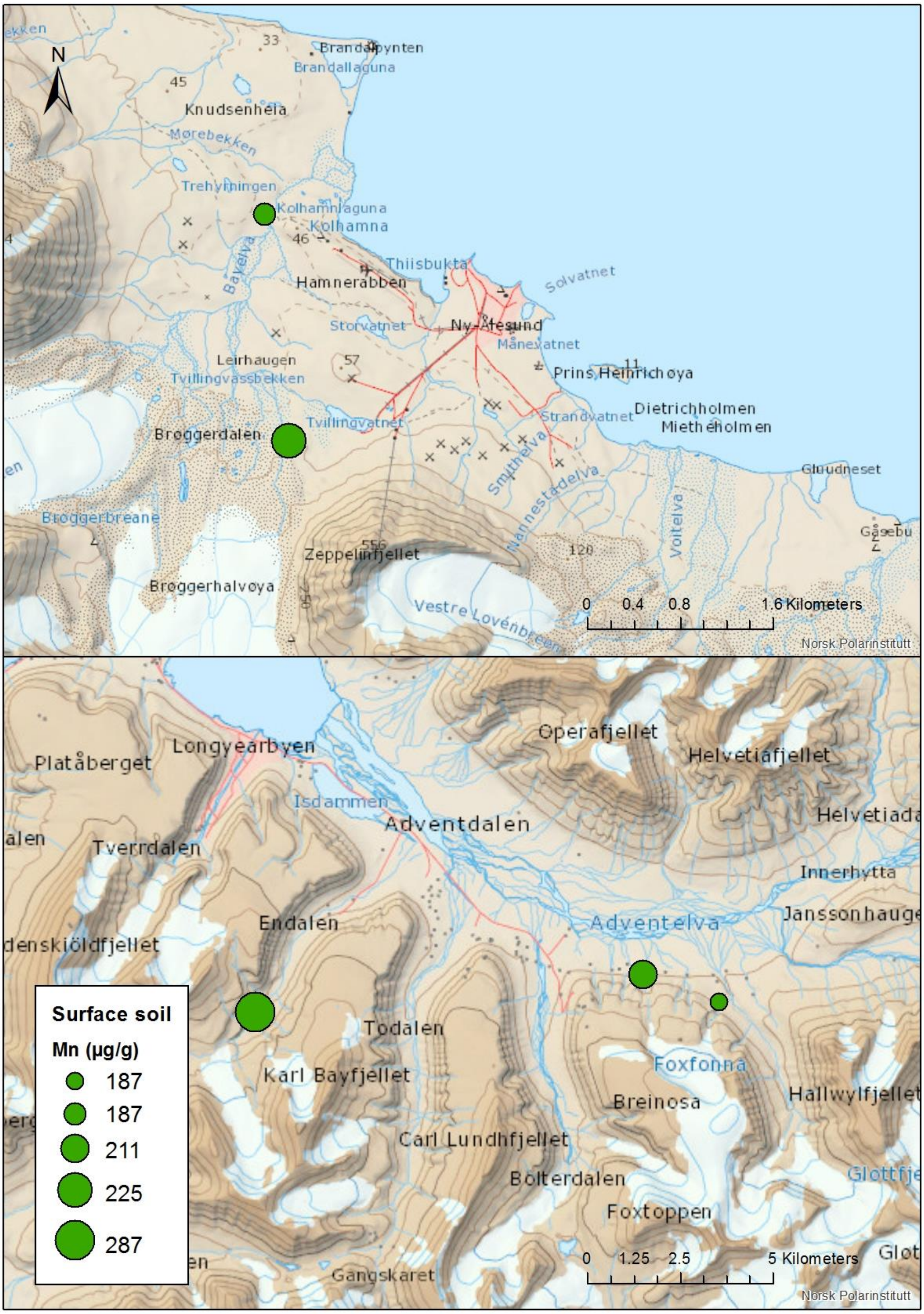

Figure 35. Mean concentrations (µg/g) of manganese (Mn) in surface soils in Svalbard.

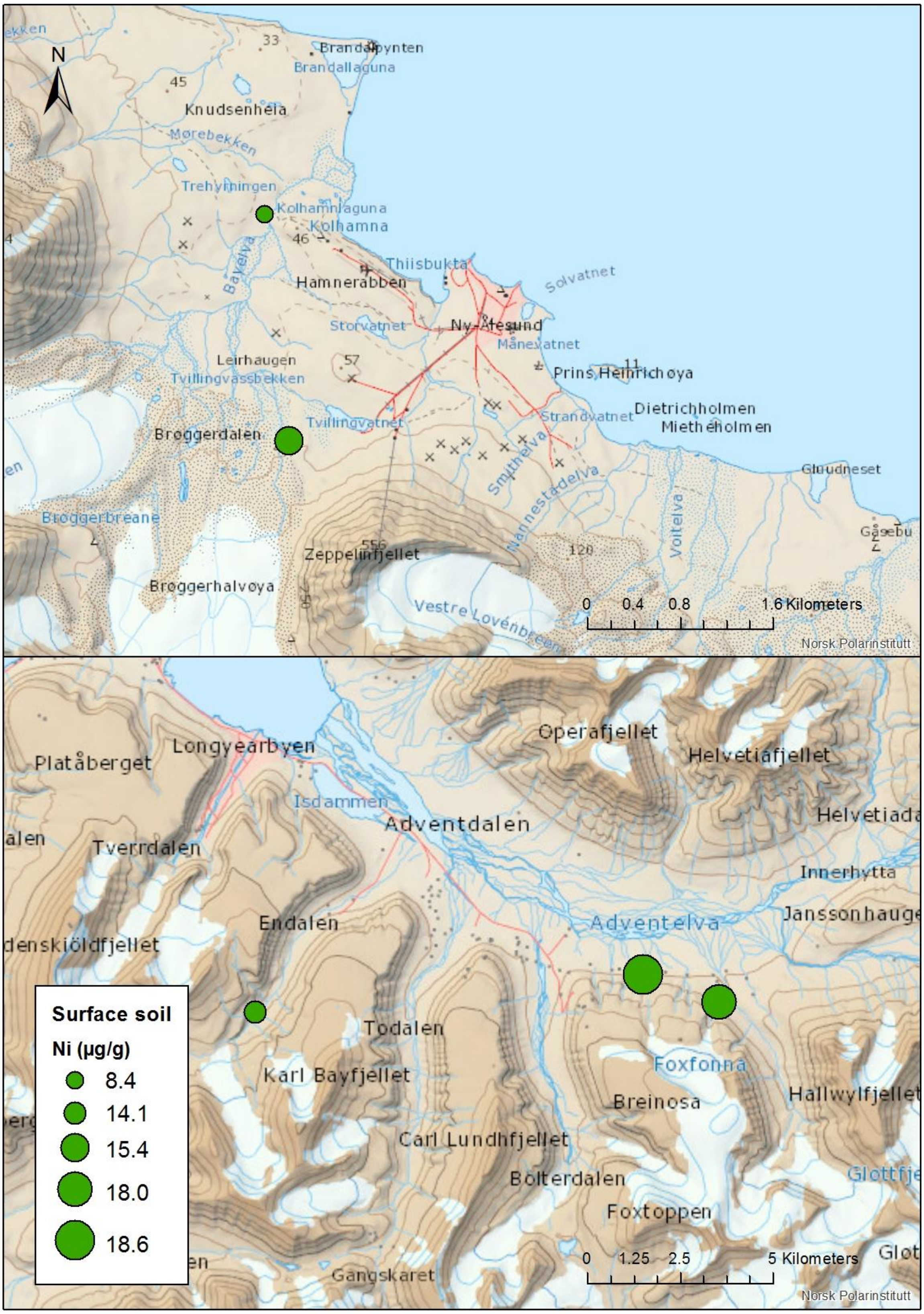

Figure 36. Mean concentrations (µg/g) of nickel (Ni) in surface soils in Svalbard.

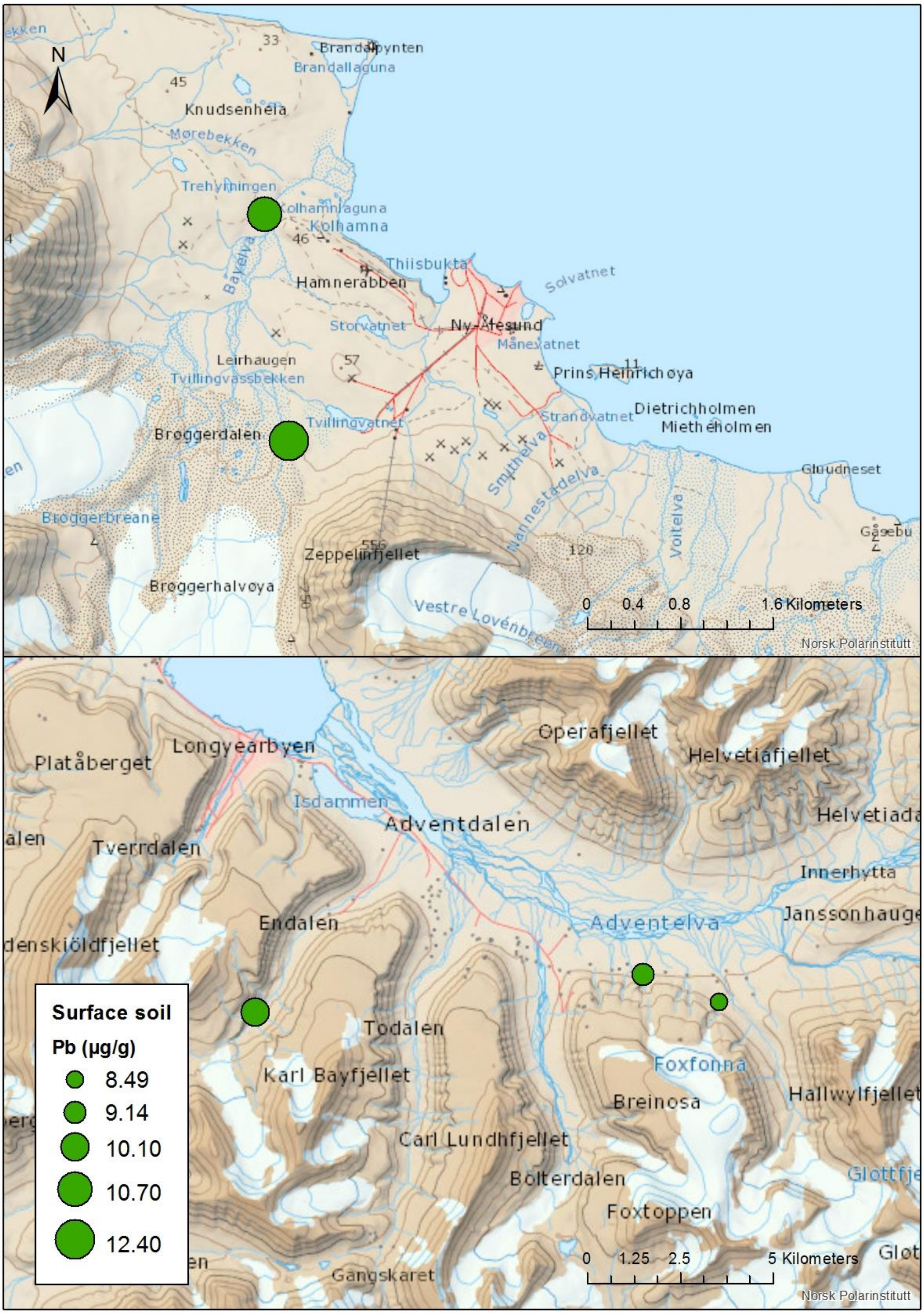

Figure 37. Mean concentrations (µg/g) of lead (Pb) in surface soils in Svalbard.

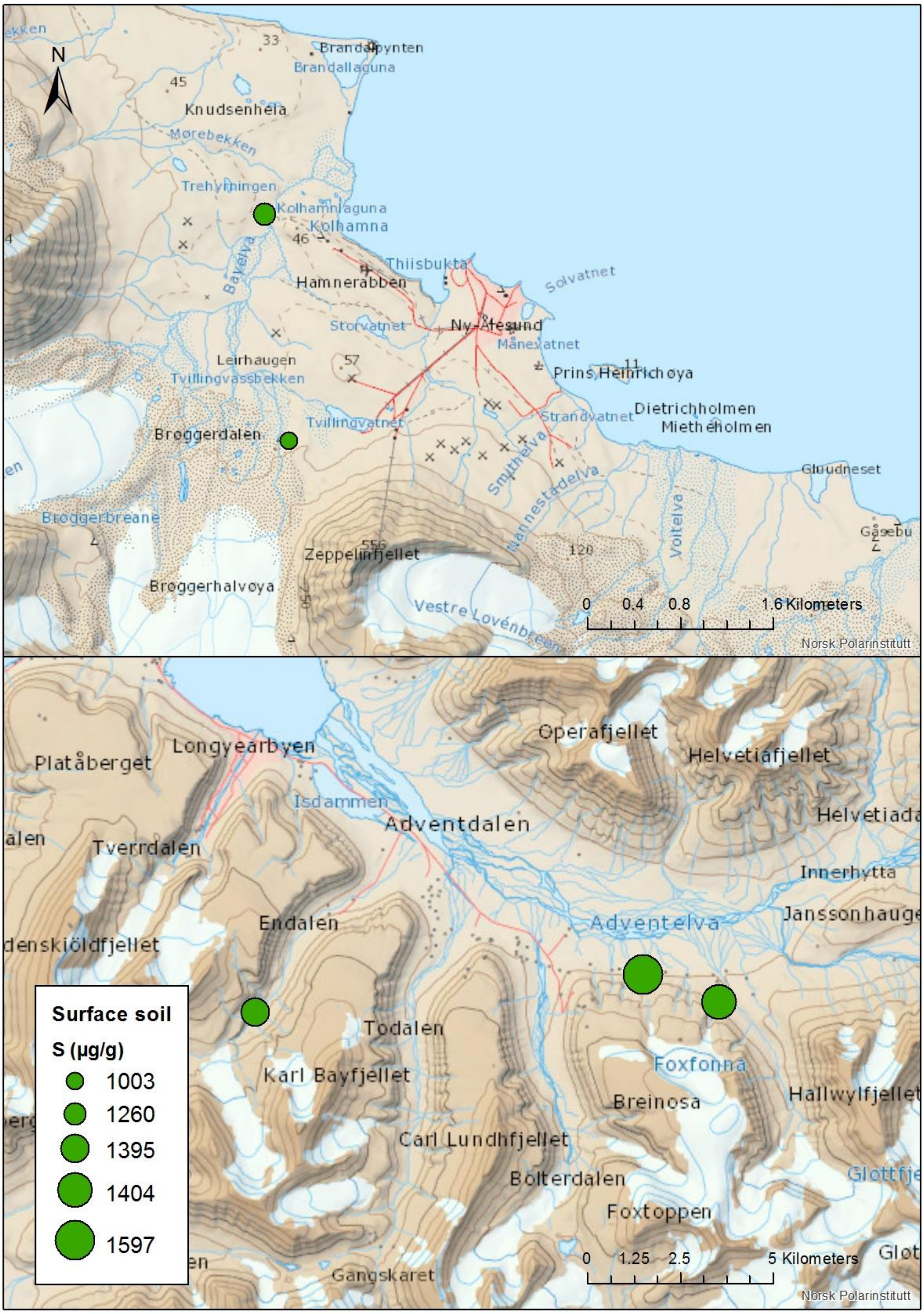

Figure 38. Mean concentrations (µg/g) of sulfur (S) in surface soils in Svalbard.

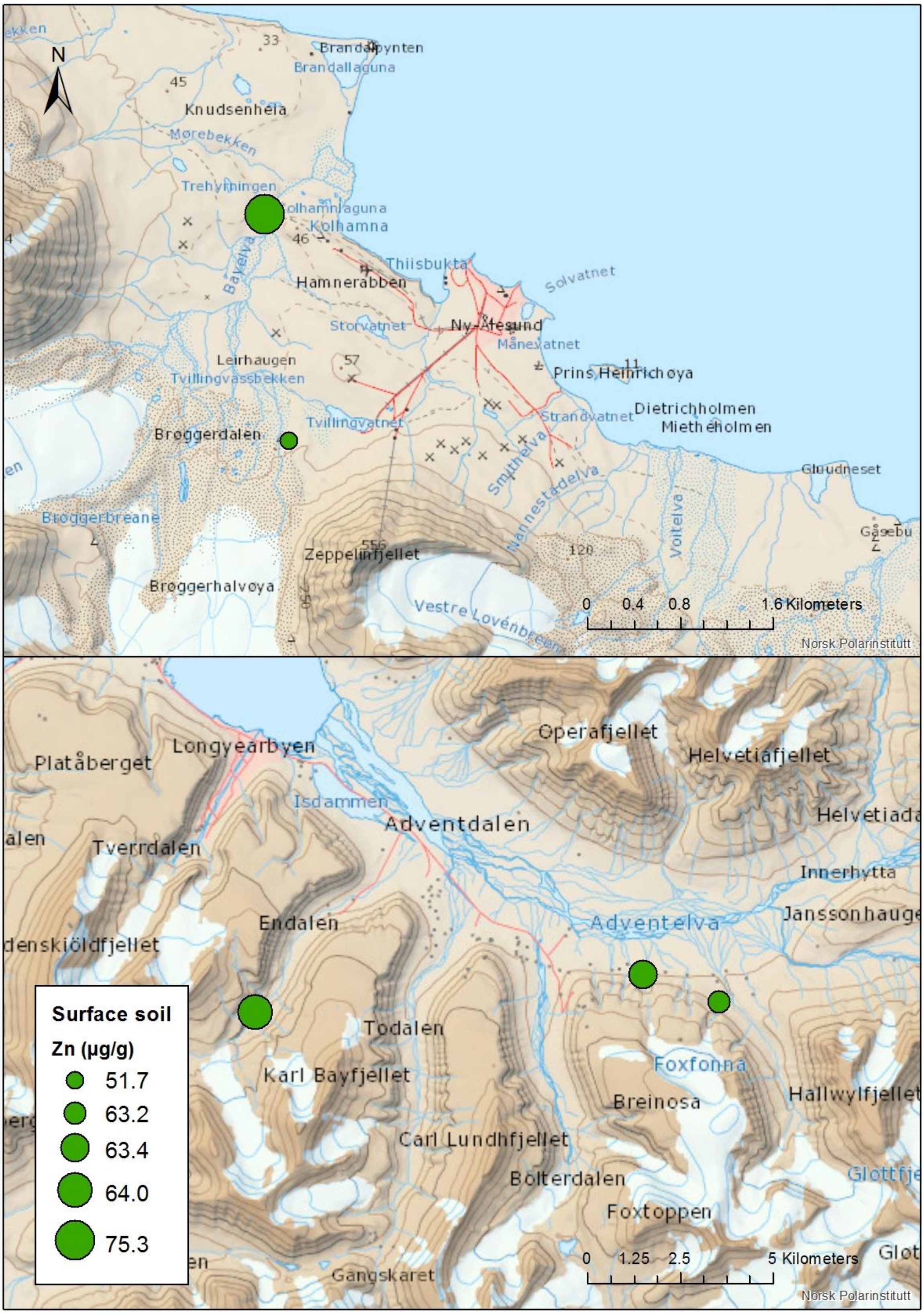

Figure 39. Mean concentrations (µg/g) of zinc (Zn) in surface soils in Svalbard.

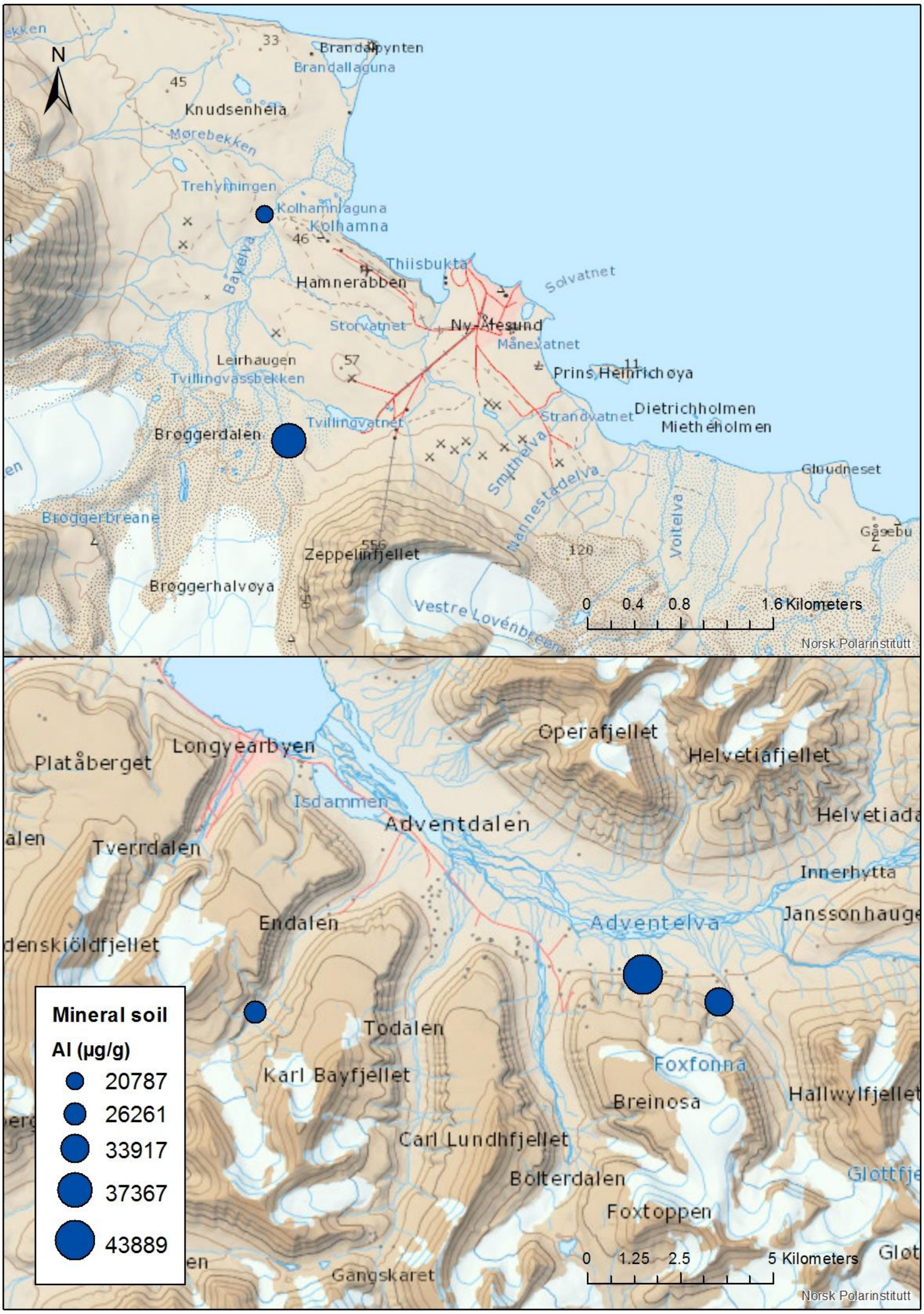

Figure 40. Mean concentrations (µg/g) of aluminum (Al) in mineral soils in Svalbard.

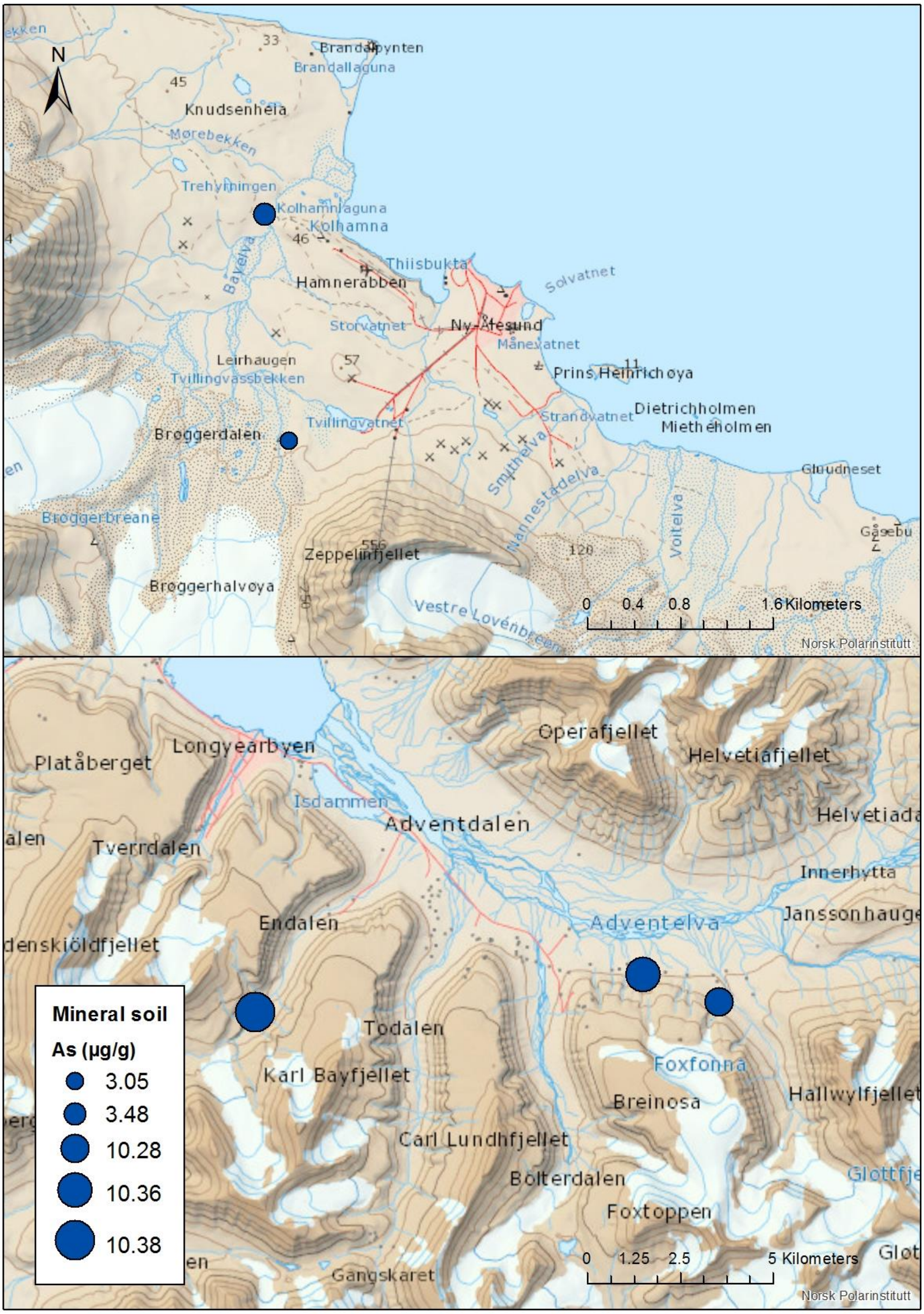

Figure 41. Mean concentrations (µg/g) of arsenic (As) in mineral soils in Svalbard.

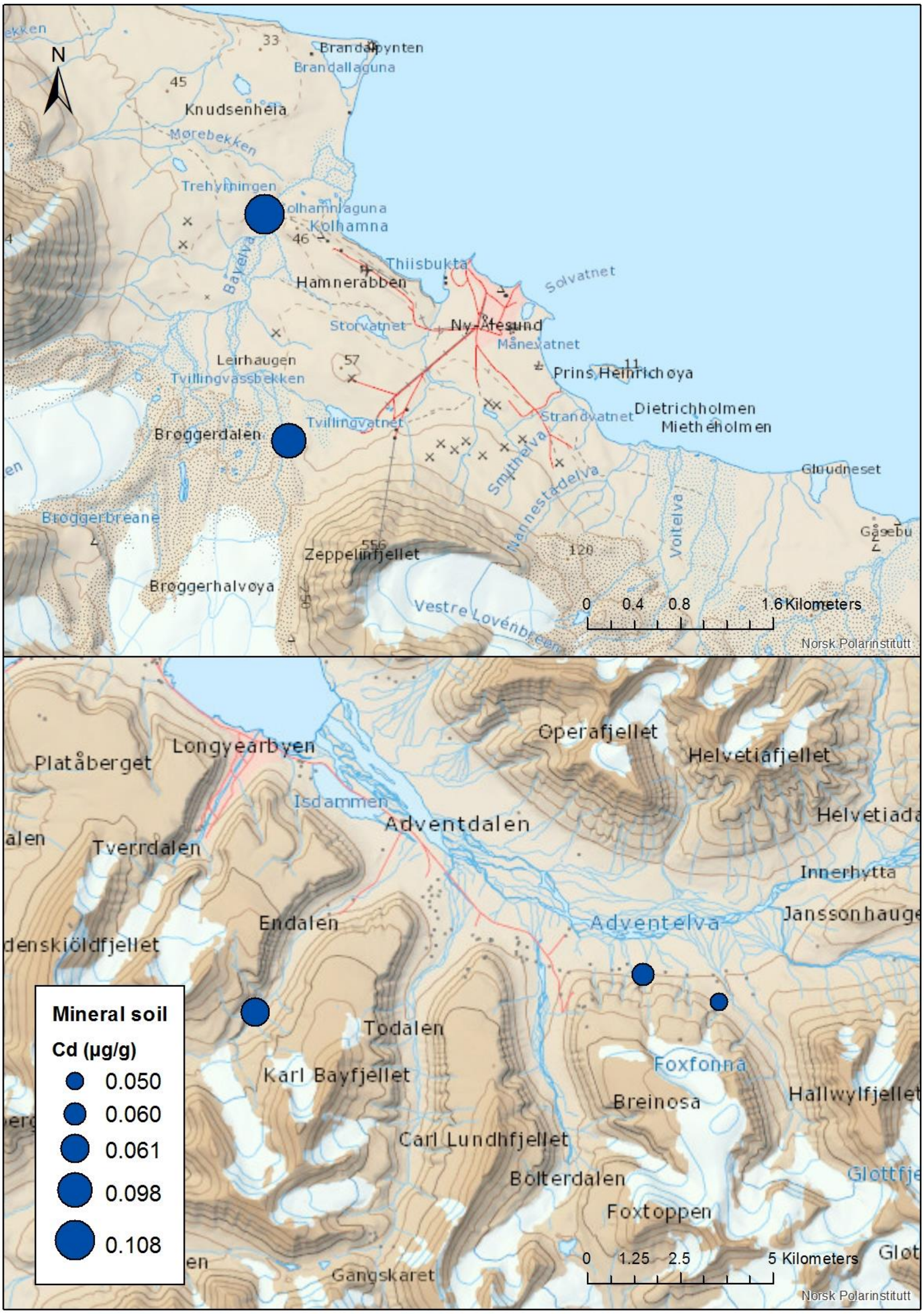

Figure 42. Mean concentrations (µg/g) of cadmium (Cd) in mineral soils in Svalbard.

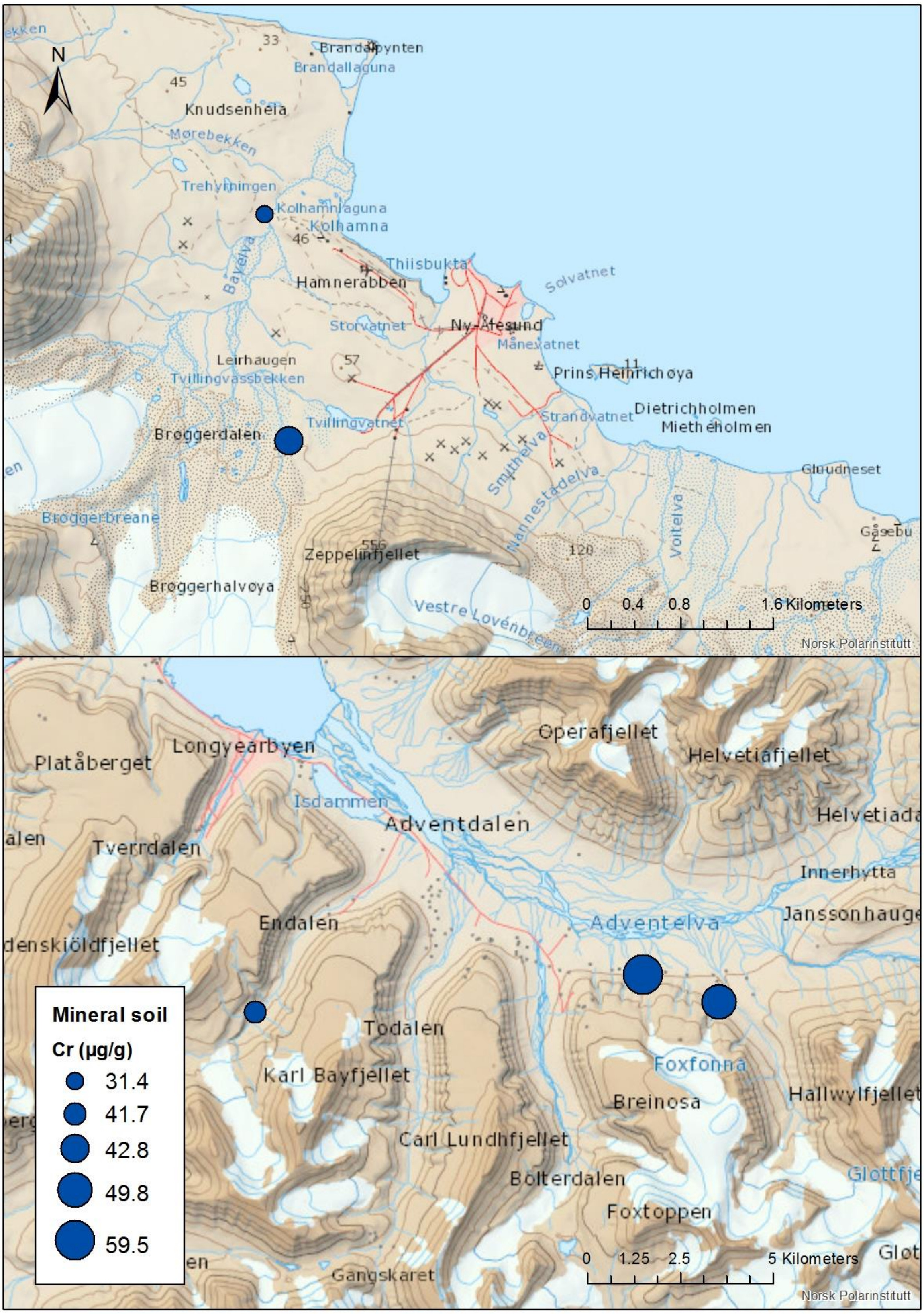

Figure 43. Mean concentrations (µg/g) of chromium (Cr) in mineral soils in Svalbard.

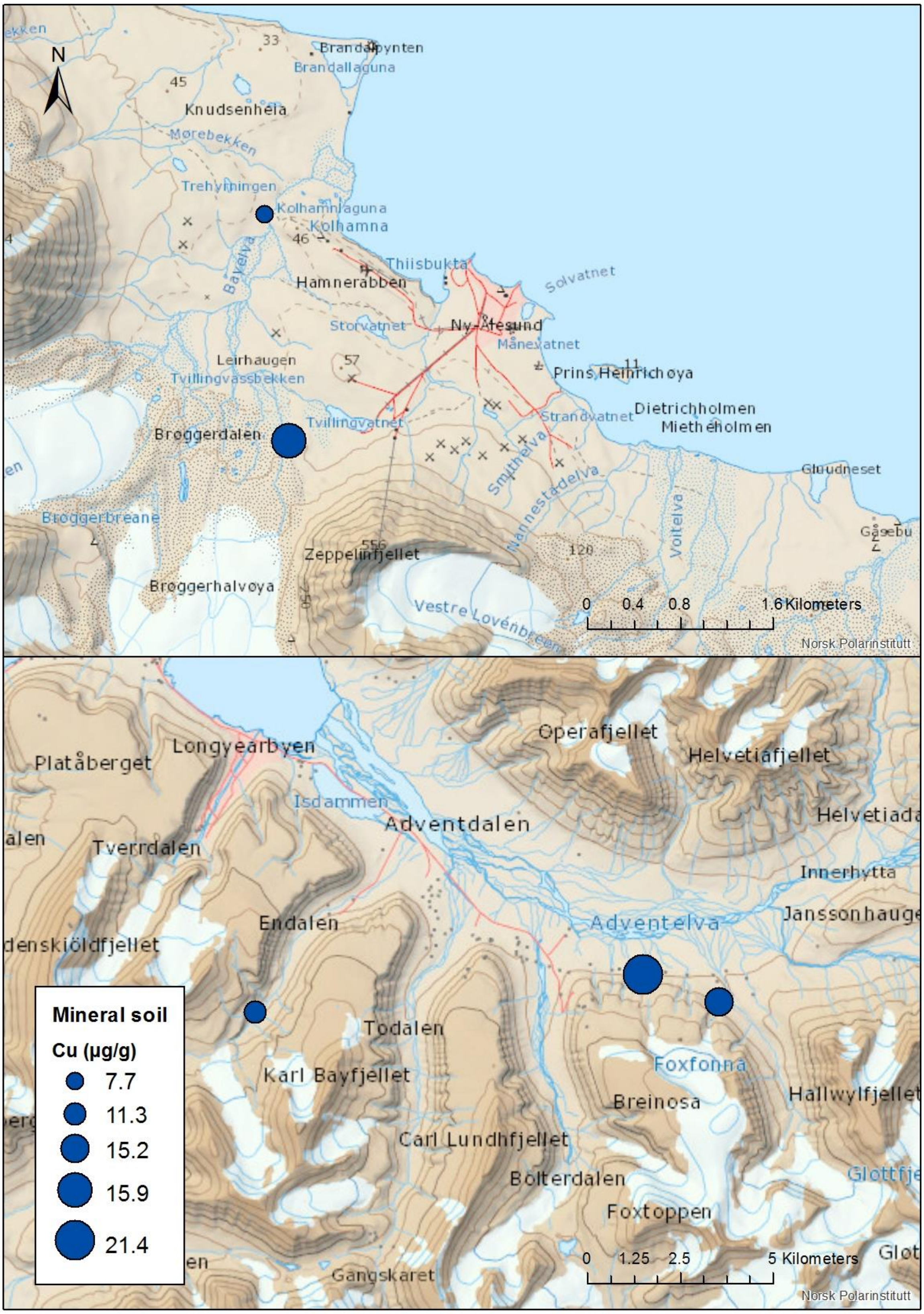

Figure 44. Mean concentrations (µg/g) of copper (Cu) in mineral soils in Svalbard.

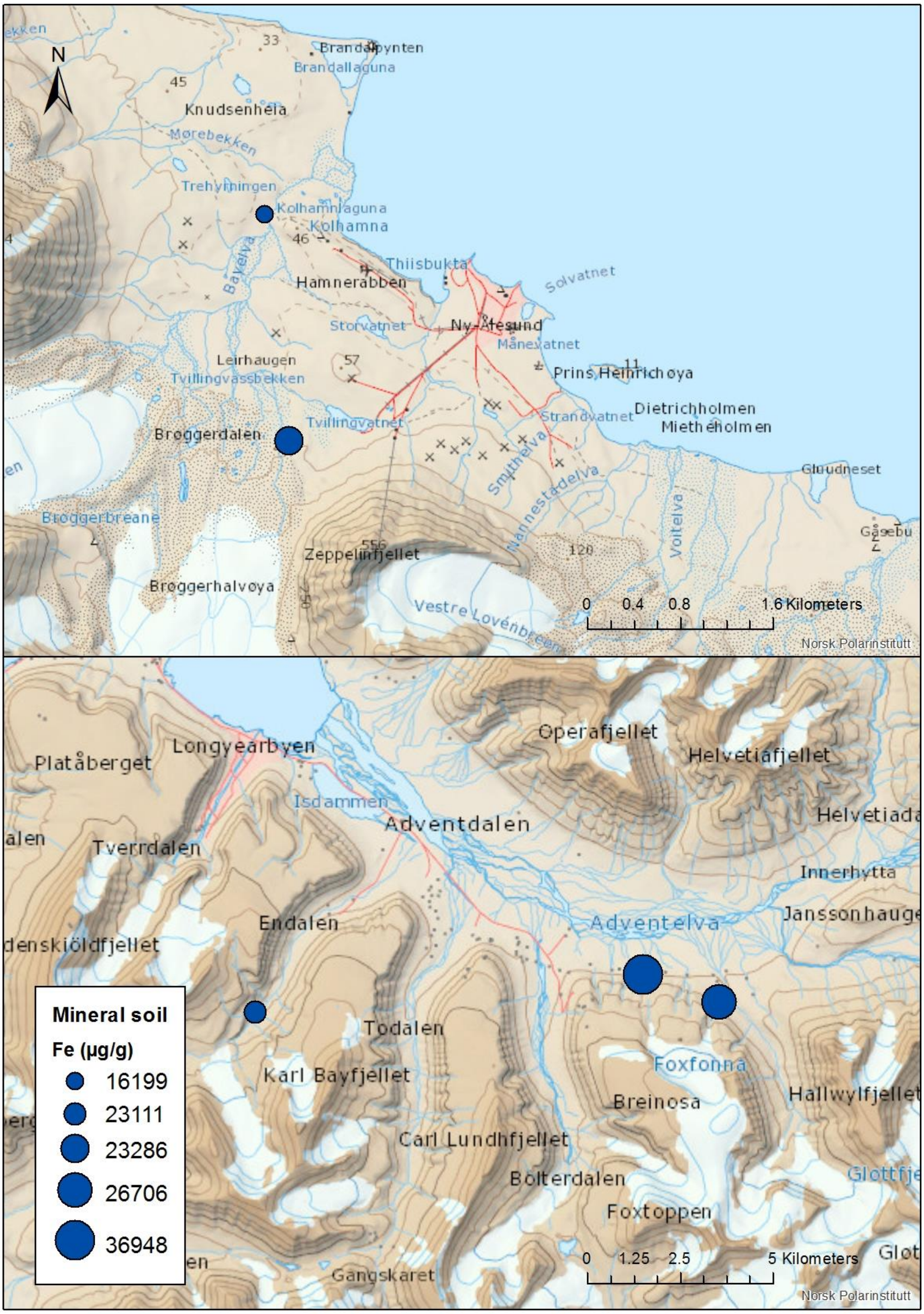

Figure 45. Mean concentrations (µg/g) of iron (Fe) in mineral soils in Svalbard.

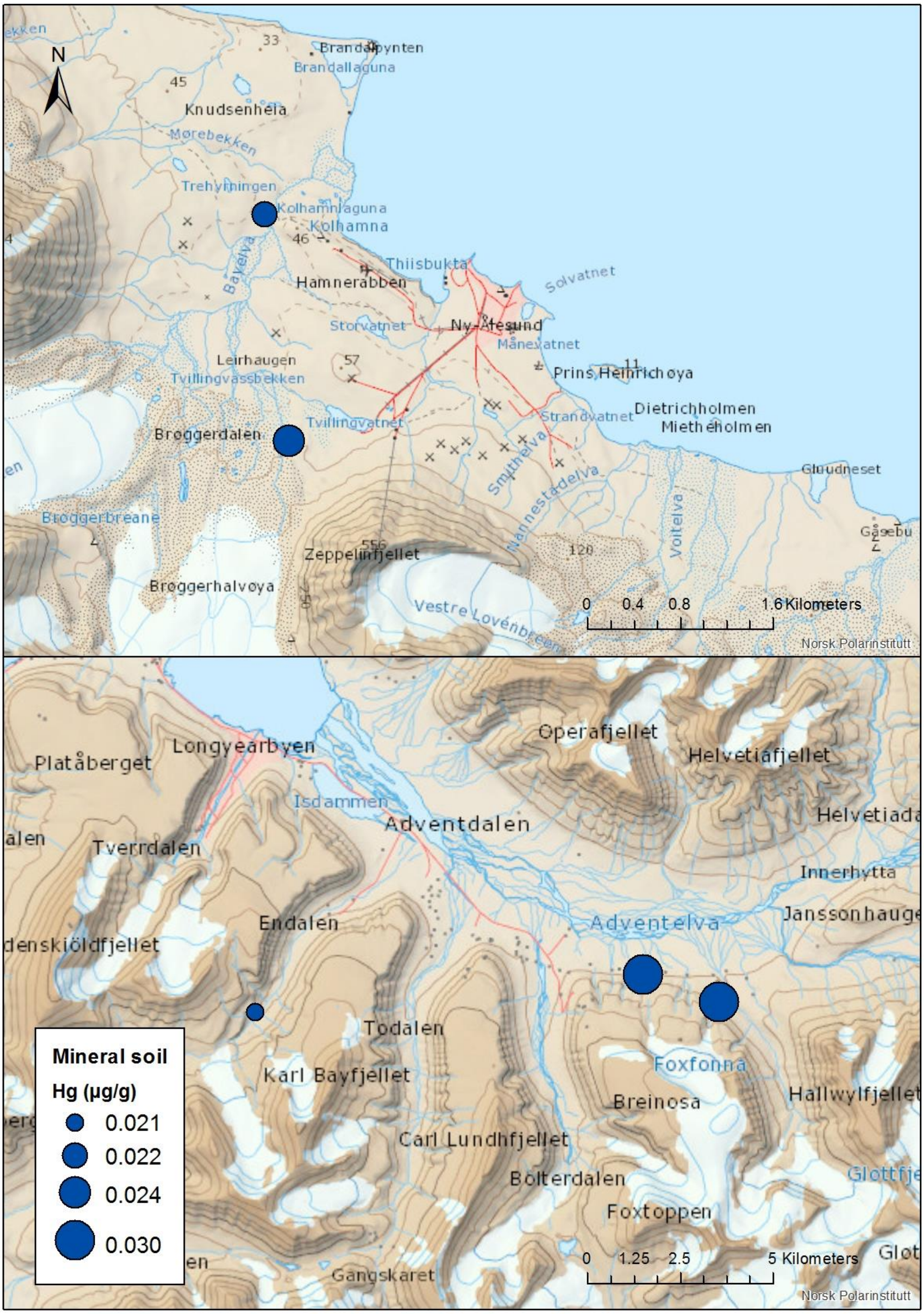

Figure 46. Mean concentrations (µg/g) of mercury (Hg) in mineral soils in Svalbard.

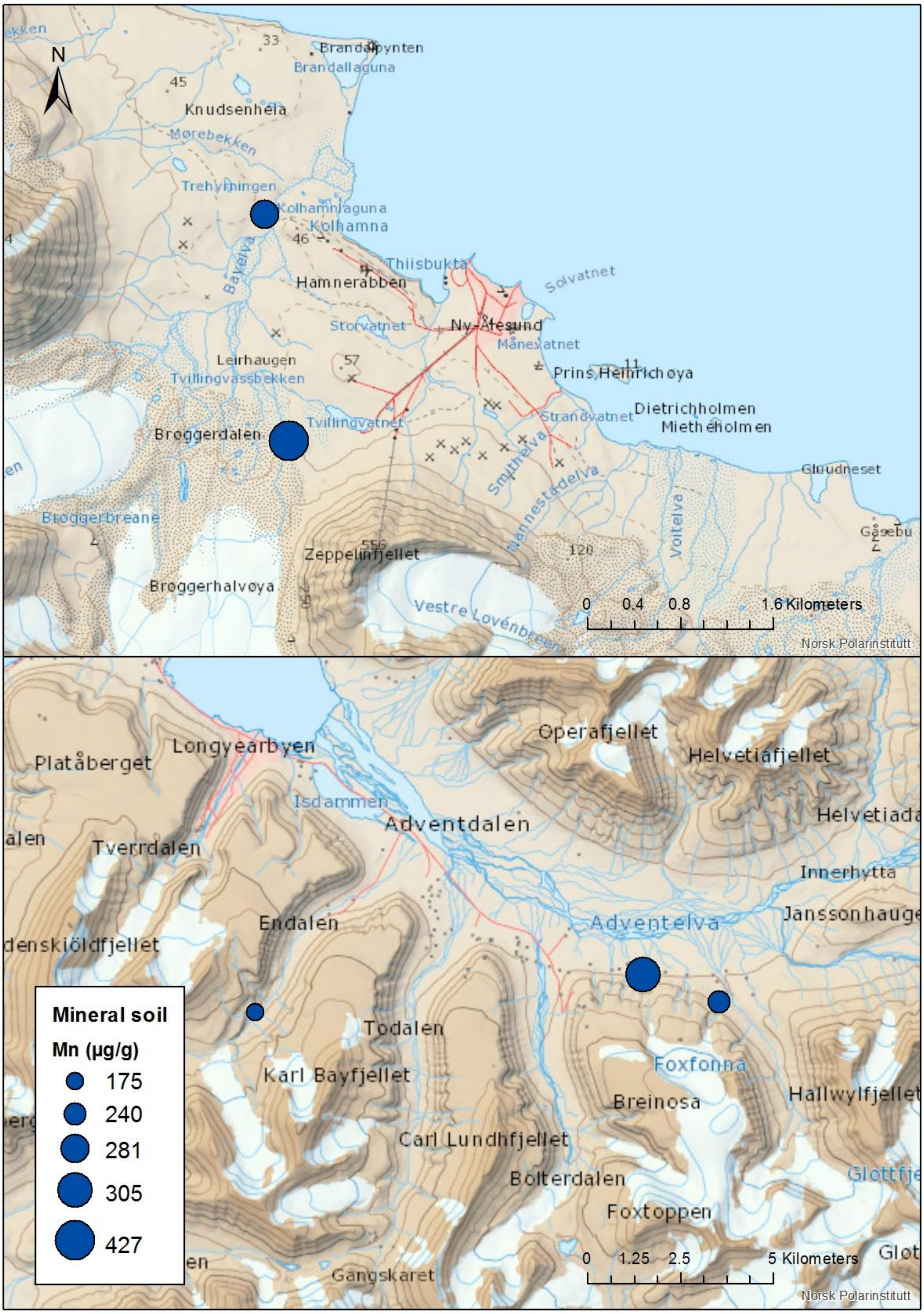

Figure 47. Mean concentrations (µg/g) of manganese (Mn) in mineral soils in Svalbard.

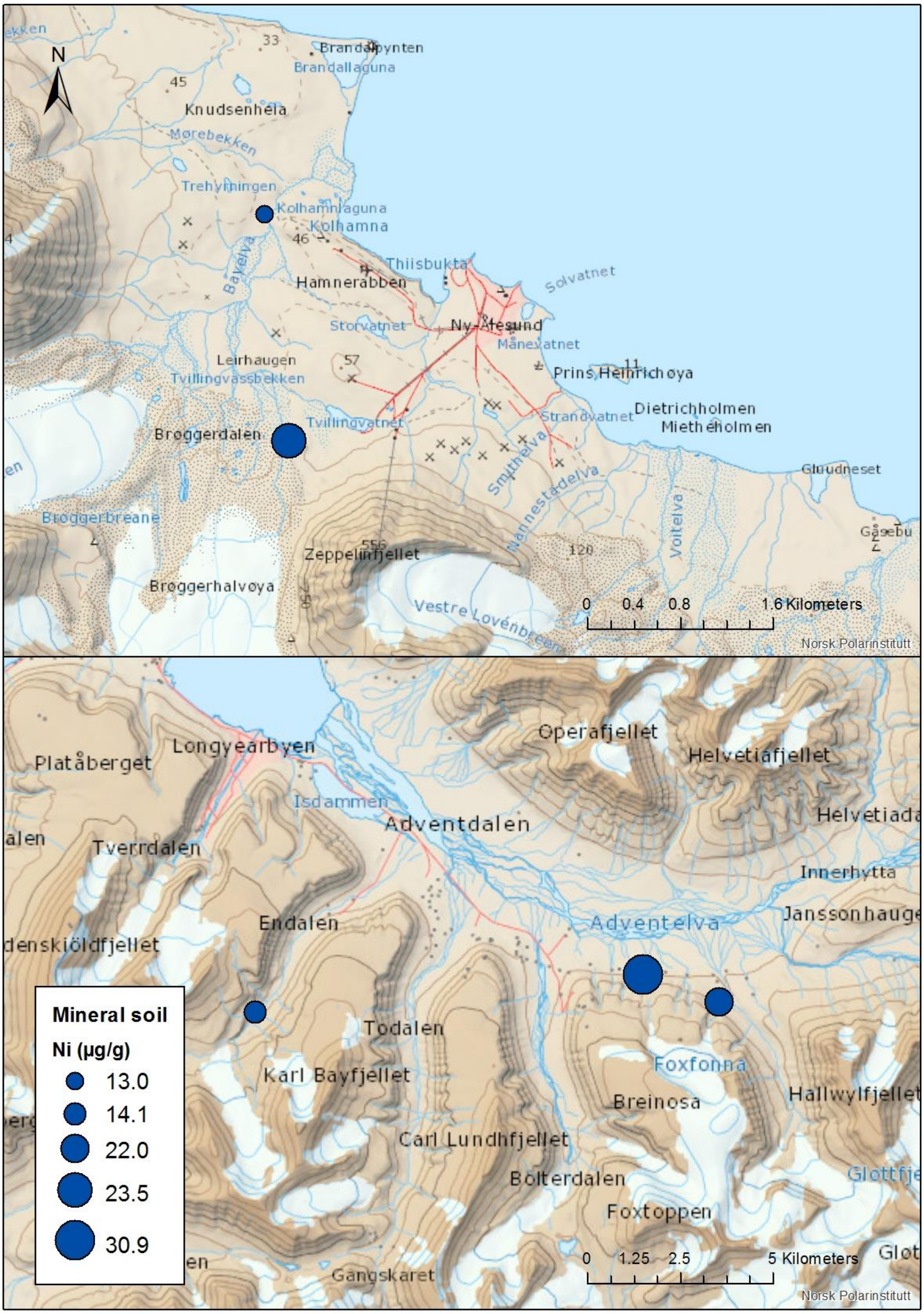

Figure 48. Mean concentrations (µg/g) of nickel (Ni) in mineral soils in Svalbard.

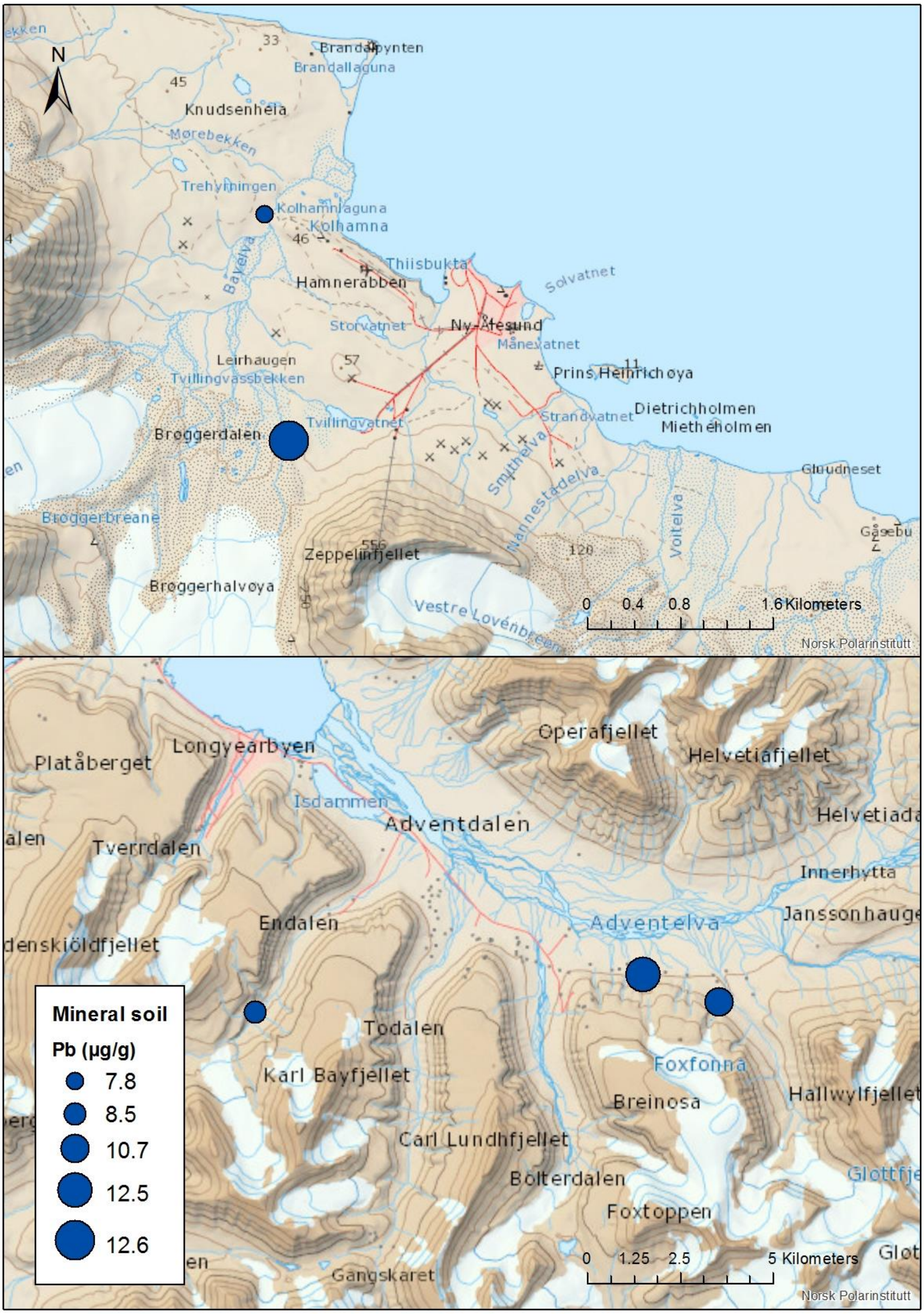

Figure 49. Mean concentrations (µg/g) of lead (Pb) in mineral soils in Svalbard.

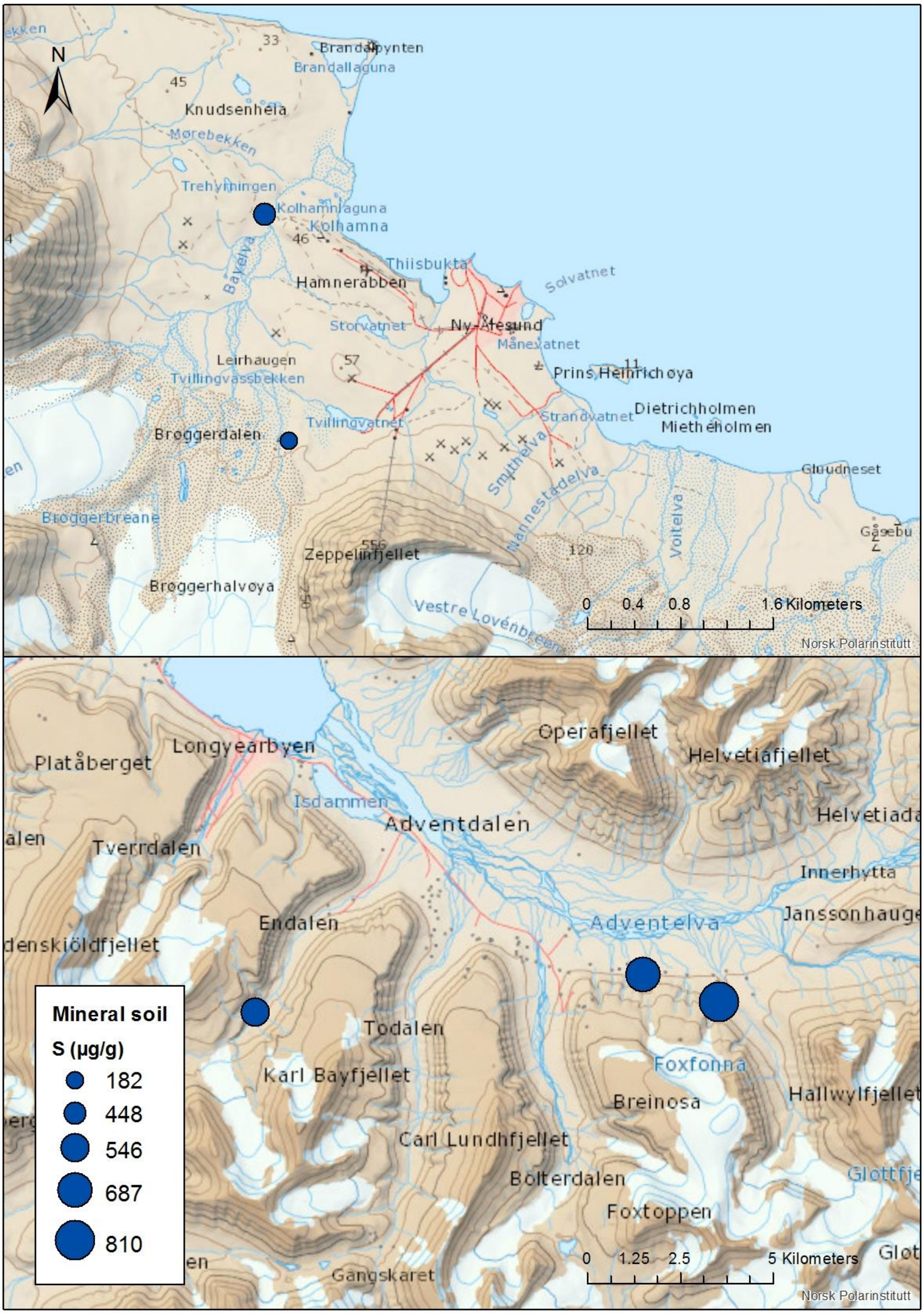

Figure 50. Mean concentrations (µg/g) of sulfur (S) in mineral soils in Svalbard.

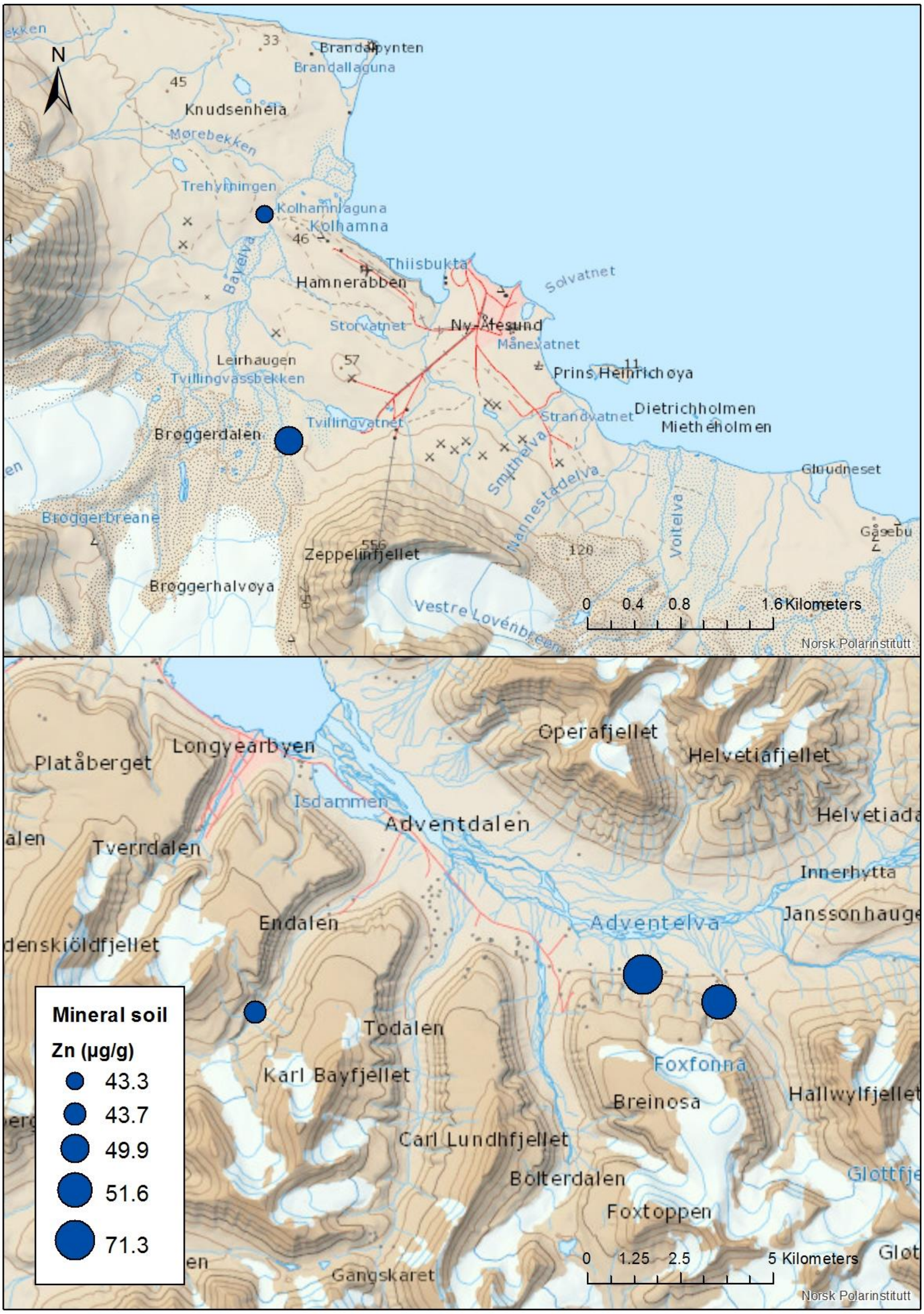

Figure 51. Mean concentrations (µg/g) of zinc (Zn) in mineral soils in Svalbard.