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Essential and non-essential elements in feathers of Snow bunting nestlings of Longyearbyen and Adventdalen - Svalbard

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Abstract

One of the important anthropogenic stressors for the natural environment is pollution. The presence of contaminants, such as heavy metals presents great risks for all living organisms, including humans. Therefore, it is important to continuously monitor levels and impacts of pollutants in the environment. Levels of pollutants released to the environment due to anthropogenic activities like metal pollution from mining activities or urban development can be assessed by measuring bioavailable levels of pollutants in living organisms also known as biomonitors.

In this current study snow bunting nestlings (*Plectrophenax nivalis)* were used as biomonitors to assess local metal pollution due to the coal mining activities and urban settlement in Longyearbyen. This was done by measuring the levels of elements in feathers of snow bunting nestlings using high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). The hypothesis was that the coal power plant in Longyearbyen was the main source of local metal pollution and that there was a pollution gradient from the coal power plant towards mine 6 mines in Adventdalen.

Nestling feathers were collected from 147 nestlings, which were of 5-6 weeks old from 31 nests in the neighboring area around and along the old cable line between Longyearbyen town and coal mine 6 in Adventdalen between May and June 2014. Feathers from all nestlings in one nest were pooled together thus concentration of metals represents average concentration nestlings from one nest. The concentration of 74 elements in feathers was measured by HR-ICP-MS but only 38 elements were found to be within limits of detection (LOD), and only 20 elements of elements above LOD are discussed in this report. The elements discussed in this study are cadmium (Cd), cobalt (Co), tin (Sn), vanadium (V), mercury (Hg), lead (Pb), chromium (Cr), selenium (Se), barium (Ba), manganese (Mn), copper (Cu), strontium (Sr), zinc (Zn), iron (Fe), aluminum (Al), silicon (Si), sodium (Na), calcium (Ca), potassium (K) and magnesium (Mg).

The results showed that the essential metals Mg (606±350 µg/g dry weight (dw)), K (580±390 µg/g dw), Na (243±174 µg/g dw) and Ca (574±236 µg/g dw) were the most abundant elements while Cd (0.01±0.02 µg/g dw), Co (0.03±0.03 µg/g dw), Sn (0.08±0.22 µg/g dw) and V (0.21±0.18 µg/g dw) were the least abundant elements measured in this study. Thus the order of elements concentrations in the feathers was Mg > K > Ca > Na > S i > Al > Fe > Zn > Sr > Cu > Mn > Ba

> Ba > Se > Cr > Pb > Hg > V > Sn > Co > Cd. A pollution gradient, with the levels of elements increasing from the Power plant in Longyearbyen to Mine 6 in Adventdalen was identified for metals Cd (P=0.012), Mn (P=0.022) and Cr (P=0.028). Other elements like Si (P=0.056), Fe (P=0.075), Al (P=0.076), Co (P=0.083), Sn (P=0.094) and Ba (P=0.094) also showed tendencies of positive correlation (P value between 0.05 and 0.1) with distance from the power plant in Longyearbyen to mine 6 in Adventdalen. Also in a principle component analysis (PCA) the essential elements showed Mg, Na and K showed a positively close correlation and that the elements Mn, Co, Fe, Si, Ba and Al were very closely correlated. The results indicated that concentration of elements increased further away from the coal power plant but increased close to mine 6 in Adventdalen. Since mine 6 had not been active for a long time, the high levels of elements observed around mine 6 was attributed to a damping site of wastes from the coal power plant located close to mine 6 in Adventdalen. Thus the results disproved the hypothesis that the coal power plant in Longyearbyen was the main source of pollution.

The concentration of elements in feathers of snow bunting nestlings in this current study were low compared to those reported in other previous studies. Also the levels found in feathers of snow buntings in this current study were below threshold levels in feathers that have been found to cause adverse effects in birds. Therefore levels of elements in snow bunting of this current study may not be of environmental concern. However this being one of the first studies to measure levels of essential and non-essential elements in snow bunting, future biomonitoring studies of elements in feathers or other body parts are recommended, and also even though concentrations measured in this study were low, future studies on effects of toxic elements in snow buntings are highly recommended.

List of abbreviations

Al	Aluminum
Au	Gold
Ba	Barium
Bi	Bismuth
Ca	Calcium
Cd	Cadmium
Ce	Cerium
Co	Cobalt
Cr	Chromium
Cs	Cesium
Cu	Copper
Er	Erbium
Fe	Iron
Hg	Mercury
K	Potassium
La	Lanthanum
Mg	Magnesium
Mn	Manganese
Na	Sodium
Nd	Neodymium
P	Phosphorous
Pb	Lead
Pr	Praseodymium
Rb	Rubidium
S	Sulphur
Sb	Antimony

Se	Selenium
Si	Silcon
Sm	Samarium
Sn	Tin
Sr	Strontium
Th	Thorium
Ti	Titanium
Tl	Thallium
U	Uranium
V	Vanadium
Y	Yttrium
Zn	Zinc

ANOVA	Analysis of variance
‘dw’	Dry weight
DL	Detection limit
Fig	Figure
HR- ICP-MS	High resolution inductively coupled plasma mass spectrometer
LOD	Limits of detection
µg/g	Microgram per gram
mg	Milligram
PCA	Principle component analysis

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1.0 Introduction

Currently pollution is a large challenge to the global population and the environment than it was in previous years, for instance in 2010 it was estimated that more than 100 million people were at risk from toxic pollution at levels above international health standards (Andrew and Dan 2010) and the risks to the natural environment are even greater. Metal pollution still remains a major concern with five of the six top toxic threats being metals that is lead (Pb), radionuclides, mercury (Hg), chromium (Cr) and cadmium (Cd) (Pure-Earth and Green-Cross 2015). In Europe emissions of heavy metals have been reduced greatly during the last three decades but due to several sources and persistence they remain an a big challenge to the environment (Frantz et al. 2012).

Living organisms are naturally exposed to several elements at tolerable levels, although high levels of elements can be toxic to biota, even for those elements essential for physiological functions (Puls 1994, García-Barrera et al. 2012). Anthropogenic activities like mining release high levels of contaminants into the environment in a shorter time than would be released through natural processes like volcanic eruption. Release from anthropogenic sources therefore becomes a burden to the local environments and even places far from original areas of release especially the polar regions. In the arctic sources of heavy metal have been identified as originating from fossil fuel combustion, non- ferrous metal production, waste incineration and long range transportation from warmer areas further south (Bard 1999, Burger and Gochfeld 2004).

Heavy metals accumulate in body parts like liver, kidney, bones, feathers, hairs and eggs in several bird species and some heavy metals have the potential to biomagnify leading to high levels in top predators (Atwell et al. 1998, Campbell et al. 2005), which can negatively affect wildlife and their populations (Sonne 2010, Dietz et al. 2013). In birds heavy metals have been found to affect various biological features such as bone mineralization degree (Gangoso et al. 2009), fledging success (Nam and Lee 2006, Evers et al. 2008), aberrant incubation behavior (Evers et al. 2008), plumage intensity (Eeva et al. 1998), genetic diversity (Eeva et al. 2006) and humoral immune responsiveness (Snoeijs et al. 2004).

Impacts of metal pollution from activities such as mining or urban development can be assessed by measurements of heavy metal levels in abiotic components of the ecosystem. These may include analyses of air, soils, water and water sediments, etc. However, due to difficulties to assess the impact on organisms by measuring concentrations in the abiotic environment only, using biomonitors is a commonly applied method. This technique is based on the use of living organisms to analyze concentrations of pollutants to determine their effects on organism and ecosystems (Markert and Wünschmann 2011).

Biomonitors make it possible to integrate the results of the analysis in an overall biological system which is scarcely possible by direct physical/chemical measurements of single abiotic compartments of the environment. Moreover, measurements of heavy metal concentrations in for example soil provide an assessment of total metal concentration present, not of that portion which is bioavailable, that is available for uptake and accumulation by terrestrial organisms. It is only the bioavailable fraction of heavy metals that is potentially toxic and of ecotoxicological relevance.

1.1 Birds as sentinels for Pollution

The potential to use of birds as monitors of environmental pollution was recognized in the 1960s due to increased evidence that bird populations are sensitive to the effects of anthropogenic activities on the environment (Denneman and Douben 1993). Several studies have employed different body organs (Horai et al. 2007), blood (Scheifler et al. 2006), eggshells (Ayaş 2007), feather (Burger et al. 1993, Dauwe et al. 2002, Jaspers et al. 2004, Malik and Zeb 2009, Pon et al. 2011, Tsipoura et al. 2011) and prey samples (Zhang et al. 2006) of different bird species to monitor heavy metal pollution.

Birds have been used as bioindicators because they are often high on the food-chain, exposed to a wide range of chemicals, susceptible to bioaccumulation and are geographically widespread (Burger 1995, Scheifler et al. 2006, Horai et al. 2007, Burger and Gochfeld 2009). Feathers are important for use in environmental biomonitoring of heavy metals because they are a non-destructive tool compared to use of blood, body parts and eggs, are easy to store and transport and can be collected from both live and dead specimens. Birds excrete heavy metals into growing feathers during molting and therefore the concentration in feathers reflects the concentration in the bloodstream during feather growth (Jaspers et al. 2004, Burger 2013).

1.2 Snow buntings (Plectrophenax nivalis)

The snow bunting is the most northern passerine bird in the world with a breeding area that ranges south to Scotland and Iceland, northern Scandinavia, Greenland, Svalbard, arctic parts of Russia and the northern parts of North America. It is the only passerine breeding regularly and widely in Svalbard. It is a migratory bird that winters in temperate areas. Recoveries of ring-marked birds suggest that Svalbard's snow buntings migrate in a south-easterly direction over northwest Russia, towards the Russian steppes north of the Caspian Sea and in Kazakhstan. Most snow buntings leave Svalbard in August-September. The males arrive from the wintering grounds late March to early April and females move north into the breeding areas some weeks later than the male (Strøm 2016).

Svalbard’s snow bunting population belongs to the nominate race *P. n. nivalis.* Adults weigh 25g to 40g with a length of 16-17 cm. The males establish breeding territories soon after their spring arrival and sing from high perches to attract females. Nests are normally built by females in rocky crevices, under rock slabs, in screes or in buildings, well out of sight. Svalbard snow buntings also use artificial nest boxes that are mounted on the trestles supporting the cableway. Their nests are well insulated with a variety of materials, mostly feathers and reindeer hair. Egg-laying usually takes place in late May or early June, they usually lay 5 to 6 eggs, which are incubated for 12 to 14 days. The timing of breeding is such that the peak of hatching corresponds with the initial emergence of adult insects. The young are fed on insects by both parents and leave the nest after 12 to 14 days before they are fully fledged.

The male's breeding plumage is predominantly white, with some black on the back, wing-tips and central tail-feathers. The females resemble the males, but have grey-brown heads and backs. The male winter plumage is brownish on upper-parts that have black streaks whereas the female winter plumage is more buff than in summer. Juvenile birds have a grey head and breast and they have brown-black upper-parts. Their regular calling is a soft "teen", while the male breeding song is a lark-like warble. The melodious song of the snow bunting, Svalbard’s only songbird, gives a special character to the arctic landscape in spring (Strøm 2016).

1.3 Aim

The aim of this study was to assess local metal pollution due to the coal mining activities and urban settlement in Longyearbyen using snow bunting nestlings as biomonitors. This was done by measuring the levels of elements in feathers of snow bunting nestlings using high resolution inductively coupled mass spectrometry. Originally I probed the concentration of 74 elements in feathers but only 38 elements were found to be within limits of detection, and of the 38 elements within limits of detection only 20 relevant elements were selected for discussion in this report to reduce the bulk of data. The elements were selected either because of being essential elements or elements of toxicological concern. The elements discussed in this study are cadmium (Cd), cobalt (Co), tin (Sn), vanadium (V), mercury (Hg), lead (Pb), chromium (Cr), selenium (Se), barium (Ba), manganese (Mn), copper (Cu), strontium (Sr), zinc (Zn), iron (Fe), aluminum (Al), silicon (Si), sodium (Na), calcium (Ca), potassium (K) and magnesium (Mg). The hypothesis was that the coal power plant in Longyearbyen was the main source of local metal pollution and that there was a pollution gradient from the coal power plant towards mine 6 mines in Adventdalen. The old cable line from Longyearbyen town to mine 6 was used as a line transect during sampling of snow bunting nestlings from nests along the old cable line. Besides the main hypothesis, other expectations were that at some points along the cable way the concentrations of elements would tend to be high due to other pollution sources like human settlement and coal drop offs during coal transportation but these were considered to be minor sources of elements compared to the coal power plant which in this study was considered to be the main source of pollution.

This study was part of an ongoing project “Vinterspurv”, whose objectives are to find out which routes and where the snow buntings of Longyearbyen spend their winter, implications of climate change on timing of migration and food availability, exposure to pollutants in their winter destination and implications of the pollutants on their breeding success. Therefore the results of this study will provide baseline information local bioavailable metal pollution that will be compared with metal pollutant levels in feathers of the adult birds accumulated from the wintering areas. Since there is already information about the hatching success from previous studies done in the project, with these results it will be possible to assess effects of metal pollution on the reproduction success of snow bunting.

2.0 Materials and Methods

2.1 Study Area

Fig 1: Sampling locations in Spitsbergen, Svalbard. The feathers of snow bunting nestlings were collected from Longyearbyen area and in Adventdalen.

Longyearbyen is the biggest settlement and administrative center of Svalbard a Norwegian archipelago in the Arctic Ocean and is about midway between continental Norway and the North Pole. The islands of the group range from 74° to 81° north latitude, and from 10º to 35º east longitude. These islands cover an area of 61,022 km², of which about 60% is covered by glaciers. The average summer temperature is around 5°C, and in winter -12°C. Longyearbyen has a long history of coal mining although today a few mines still remain in operation. In addition, it has recently undergone increase in urban development with a population of about 2075 people as of 2013 (https://en.wikipedia.org/wiki/Longyearbyen). It also has an abundant population of snow buntings, Svalbard's only songbirds which give a special character to the arctic landscape in spring and serve as a welcome fixture for locals and tourists. The study area mainly comprised the area surroundings the cableway earlier used for coal transportation from the coal mines in Adventdalen to Longyearbyen, a distance of about 8 km.

2.2 Sampling

Nestling feathers were collected from 31 nests in the neighboring area around Longyearbyen and along the old cable line between Longyearbyen town and coal mine 6 between May and June 2014. The old cable line served as a line transect during the sampling of individuals (Fig 2). Nests used for sampling were located on land, powerline, buildings and the cable line.

Feathers were collected from 5-6 weeks old nestlings and stored immediately in small labelled paper envelopes at room temperature until the time of chemical analysis. In total 147 nestlings from 31 nests were sampled. The number of nestlings sampled per nest ranged from 2-7 with an average of 4.7 nestlings per nest. Four out of the 31 nests had 3 individuals per nest and only one nest had 2 individuals. Feathers from all nestlings in one nest were pooled together thus concentration of metals is per nest. This was done to reduce the bulkiness of the data and also because few feathers were plucked from the nestlings and their weight was less than the 1 mg which is the minimum required sample weight for chemical analysis by high resolution inductively coupled Plasma mass spectrometer (HR-ICP-MS) in this present study.

2.2.1 Sampling locations in Longyearbyen and Adventdalen

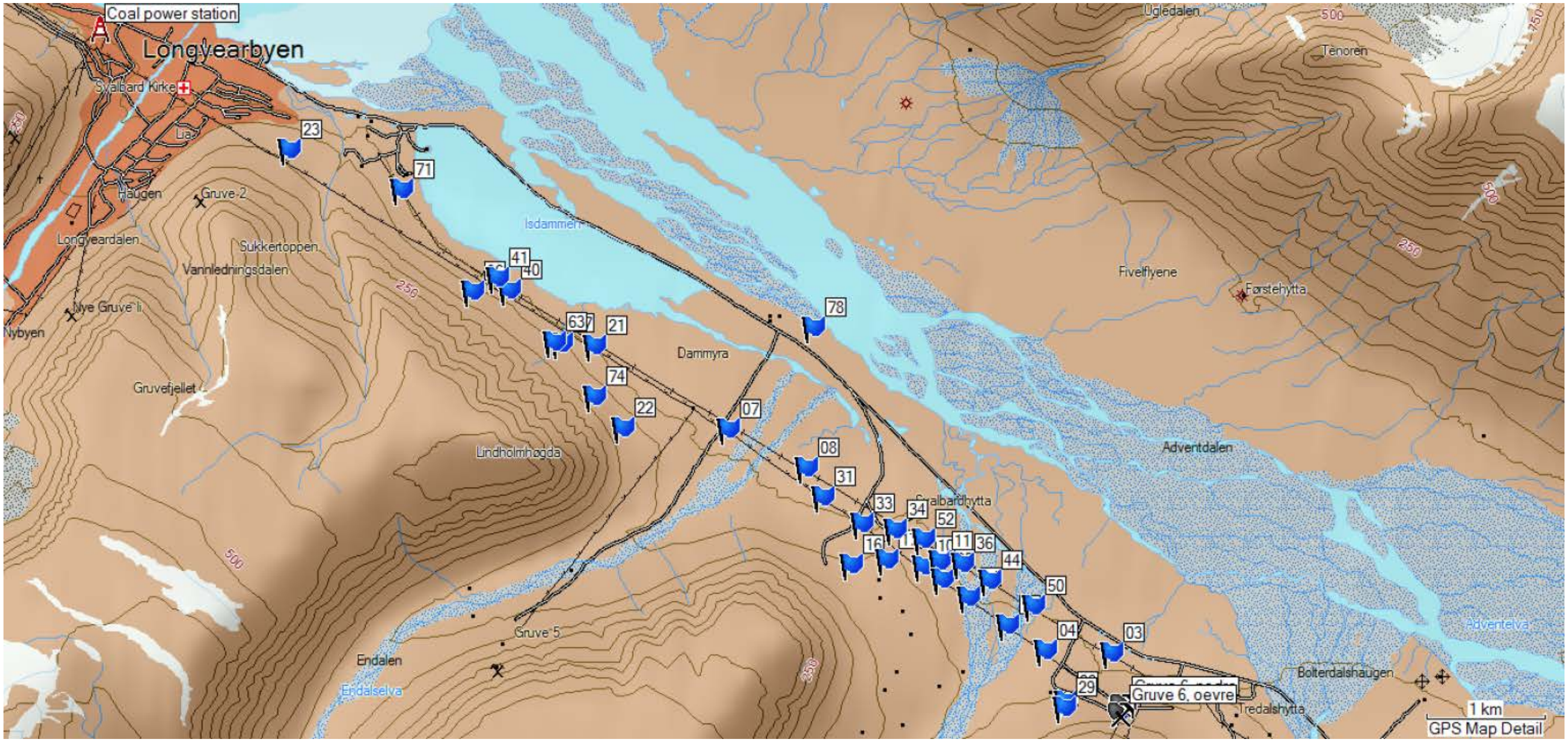


Fig 2. Locations of snow bunting nests where nestlings were sampled. The blue flags with numbers on the map represent nest locations.

2.3 Chemical analysis

A total of 74 elements were analyzed in Trondheim at NTNU Department of Chemistry and only 38 were above limits of detection (Appendix B). For this study 20 relevant elements that is Cd, Co, Sn, V, Hg, Pb, Cr, Se, Ba, Mn, Cu, Sr, Zn, Fe, Al, Si, Na, Ca, K, Mg of the 38 elements above limits of detection are presented and discussed in this report. The elements with concentrations below limit of detection were not included in this report.

2.3.1 Preparation of Feathers

Prior to chemical analysis, feathers were washed in acetone followed by milli-Q water, then acetone again and rinsed in milli-Q water. The washed feathers were then placed in clean vinyl petri dishes and covered with clean filter paper and left to dry overnight under a hood. The dry feathers were then covered with clean vinyl petri dish covers and stored safely in a box at room temperature awaiting the next procedures.

2.3.2 Ultraclave Digestion

Before ultraclave digestion the feathers were carefully transferred into PTFE-Teflon vials (18 mL), weighed and then 2.3 g ultrapure water (Q-option, Elga Labwater, Veolia Water Systems LTD, UK) and 4.2 g concentrated nitric acid, HNO3 (Scanpure, equal to ultrapure grade, Chemscan, Elverum, Norway) were subsequently added to the vials. Digestion of these portions was carried out in a high-pressure microwave system (Milestone UltraClave, EMLS, Leutkirch, Germany) according to a temperature profile which increases gradually from room temperature up to 250 within 1 h. In addition there was a cooling step which allowed temperature to return back to the initial value within ca. 1 h. After cooling to room temperature, the digested samples were diluted with ultrapure water to 60 mL in polypropylene vials to achieve a final HNO3 concentration of 0.6 M.

2.3.3 High resolution inductively coupled plasma mass spectrometry

High resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) analyses were performed using a Thermo Finnigan model Element 2 instrument (Bremen, Germany) according to (Sørmo et al. 2011). The radio frequency power was set to 1400 W. The samples were introduced using a SC-FAST flow injection analysis system (ESI, Elemental Scientific, Inc. Omaha, NE) with a peristaltic pump (1 mL/min). The instrument was equipped with a PFA-ST nebulizer, spray chamber (PFA Barrel 35 mm), demountable torch, quarts standard injector as well as Al sample skimmer and X-skimmer cones. The nebulizer argon gas flow rate was adjusted to give a stable signal with maximum intensity for the nuclides lithium (7Li), indium (115In) and uranium (238U). Methane gas was used in the analysis to minimize interferences from carbon and to provide enhanced sensitivity, especially for Se and As. The instrument was calibrated using 0.6 HNO3 solutions of matrix-matched multielement standards. A calibration curve consisting of five different concentrations was made from these standards. To check for the instrument drift, one of these multielement standards was analyzed every 10 samples. The accuracy of the method was verified by analyzing the certified reference material Oyster Tissue NIST 1566b (National Institute of Standards and Technology, Gaithersburg, MD). The concentrations found were within 90-115% of the certified values for all trace elements. To assess possible contamination during sample preparation, blank samples of HNO3 and ultrapure water were prepared using the same procedure as for the samples. Method detection limits (MDL) ranged from 0.01 µg/kg to 0.02 mg/kg for Au and Zn respectively. MDLs were calculated based on 3 times the standard deviation of the blanks, or on the instrument detection limits (IDL). The IDLs were estimated from the subsequent analysis of solutions, containing decreasing, low concentrations of the element. Finally, the concentration resulting in a relative standard deviation of approximately 25% (n = 3 scans) were selected as IDL with baseline corrections applied for these values.

2.3.4 Quality assurance

All handling of samples was done under the hood in a very clean and non-contaminated environment. Furthermore, water, acetone, petri dishes, spatula and gloves were changed between each sample handling procedure to avoid sample contamination during sample preparation. Also blanks of HNO3 and ultrapure water were used to assess possible contamination during sample preparation.

2.4 Statistical Analysis

All data sorting and validation was done in Microsoft Excel. Statistical analyses: that is basic descriptive statistic, correlation analysis and principal component analysis (PCA) were performed using IBM SPSS 2.1 statistics. Correlation between metals was tested by Spearman correlation matrix because the metal concentrations varied greatly from different nests and were not normally distributed after log transformation. To further understand the metal pollution patterns in Longyearbyen, the nests were categorized into four groups according to their location physical terrain and distance from the coal power plant in Longyearbyen; that is “Town” representing nests in the range of 1.6-2.7 km from the coal power plant, “Hillside” representing nests in the range of 3.3-4.8 km from the coal power plant, “Valley” representing nests in the range of 6.0-7.2 km from the coal power plant, “River” representing nests in the range of 7.0-8.2 km from the coal power plant and “Mine 6” representing nests in the range of 8.3-8.6 km from the coal power plant. The differences in mean metal concentration among the mentioned nest locations were tested by one way ANOVA (with Scheffe post hoc tests). In the analysis a significant difference was considered when $p \leq 0.05$ and p- values between 0.05 and 0.1 were regarded as near to significance trends in the correlation analysis. Also overall mean metal concentration of all elements above limits of detection was calculated to facilitate comparison of results of this study with other studies easy.

3.0 Results

A total of 38 metals were detected during the chemical analysis (Appendix B) but due to the large bulk of data and because the aim of the study mainly focused on essential and toxic elements a detailed presentation and discussion is given on 20 elements (Table 1). Essential elements discussed include Mg, K, Na, Ca, Fe, Zn, Se, Mn, Co and Cu, also toxic elements like Hg, Cd, Pb, Cr, Al, Ba and other elements such as Sn, Sr, Si, V, are discussed in this report. All these metals with their overall mean ±SD are presented in (Table 1).

3.1 Mean concentration of elements

Table 1. Mean ± SD concentrations (µg/g dry weight) of metals in feathers of snow bunting nestlings along the cable way in Adventdalen, Svalbard.

Element	Mean	Minimum	Maximum	Range
Cd	0.01±0.02	0.00	0.12	0.12
Co	0.03±0.03	0.01	0.17	0.17
Sn	0.08±0.22	0.01	1.27	1.26
V	0.21±0.18	0.02	0.80	0.78
Hg	0.23±0.13	0.06	0.57	0.51
Pb	0.27±0.59	0.01	3.31	3.30
Cr	0.33±0.23	0.05	0.78	0.73
Se	1.1±0.6	0.4	3.1	2.7
Ba	1.2±0.9	0.2	4.2	4.0
Mn	1.6±1.5	0.1	6.2	6.1
Cu	2.1±1.7	0.7	9.4	8.8
Sr	2.5±1.2	0.9	5.4	4.5
Zn	66±28	32	145	113
Fe	76±59	11	260	249
Al	86±68	10	266	256
Si	168±127	23	515	492
Na	243±174	18	709	691
Ca	574±236	229	1219	990
K	580±390	37	1648	1611
Mg	606±350	63	1618	1556

Generally, the essential major elements Mg, K, Ca, and Na were the most abundant elements measured and Cd, Co, Sn and V were the least abundant elements measured in this study. Thus the order of the concentrations in the feathers were Mg > K > Ca > Na > S I > Al > Fe > Zn > Sr > Cu > Mn > Ba > Ba > Se > Cr > Pb > Hg > V > Sn > Co > Cd (Table 1).

3.2 Pollution gradient

3.2.1 Correlation of metals with distance

There was no significant association between the concentrations of most elements in the feathers and the distance of the nests from the power plant. This was especially the case for the major elements Na, Ca, K and Mg. However the metals Cd (p=0.012), Mn (p=0.022) and Cr (p=0.028) had a significant positive correlation with distance from the Power plant in Longyearbyen to Mine 6 in Adventdalen.

Table 2: Spearman correlation of metals with distance (km) from the power plant to mine 6 in Adventdalen.

	r	p
Cd	0.406	0.012*
Co	0.255	0.083[a]
Sn	0.243	0.094[a]
V	0.236	0.1[a]
Hg	0.177	0.17
Pb	0.172	0.177
Cr	0.346	0.028*
Se	-0.198	0.142
Ba	0.243	0.094[a]
Mn	0.365	0.022*
Cu	0.179	0.168
Sr	0.069	0.355
Zn	0.089	0.318
Fe	0.265	0.075[a]
Al	0.264	0.076[a]
Si	0.292	0.056[a]
Na	0.111	0.276
Ca	0.037	0.422
K	0.02	0.457
Mg	-0.067	0.361

* Significant correlation $p \leq 0.05$ and [a] near to significance trend $p \geq 0.05$ but $P \leq 0.1$

Also some elements like Si (p=0.056), Fe (p=0.075), Al (p=0.076), Co (p=0.083), Sn (p=0.094) and Ba (p=0.094) had a borderline correlation trend with distance from the power plant in Longyearbyen to mine 6 in Adventdalen. The near to significance trend in this case means that the p value was between 0.05 and 0.1. This gives relevant useful information on the analysis. Graphs further describing the pollution gradient expressed by elements Mn, Cd and Cr are presented in Fig 2.

Correlation between distance from the coal power plant and element concentration for the three elements positively correlated with distance Mn, Cr, and Cd (Table 2).

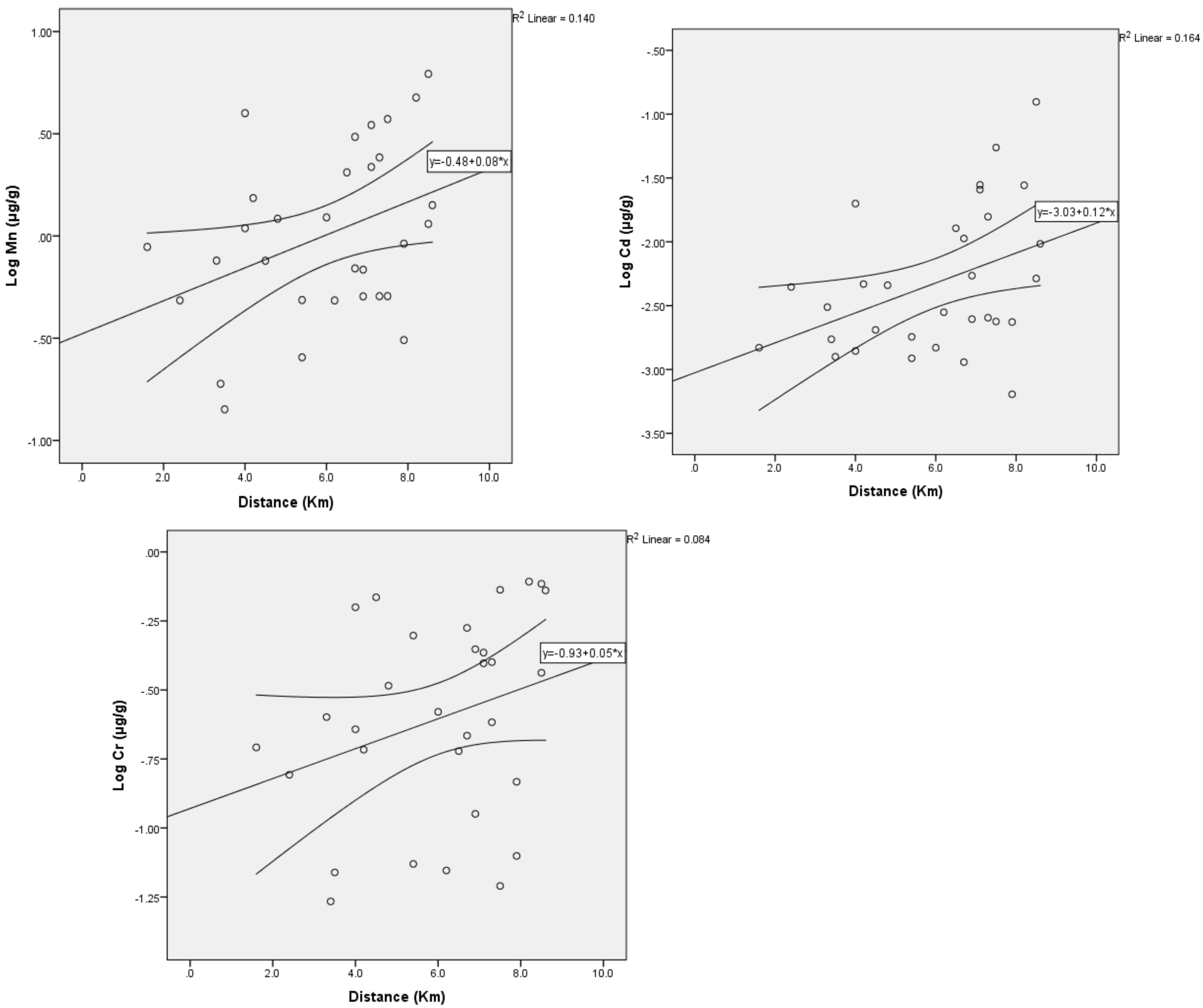


Fig 3: Scatter graph plots illustrating distribution of Mn, Cd and Cr along the cable way from Longyearbyen to Mine 6 in Adventdalen. See table 2 for information on significance of levels

3.2.2 Concentration of metals according to location groups

There was no significant difference in metal concentrations between the groups (town, hillside, valley, river and mine 6) expect for Na that was significantly different between groups and K that showed borderline difference (Table 3). The nests in the area of Mine 6 generally had the highest concentration for most metals that is Co, Cu, Fe, Mn, Si, Cd, Cr, Al, Ba, V and Sn (Table 3). Then Pb and Hg were highest in the area of the valley that is 6-7.2km from the coal power plant in Longyearbyen. In addition Ca, Mg, and Zn were highest close to Longyearbyen town (that is at 1.6-2.7km), whereas Na and K were highest close in the river area (7.3-8.2km from Longyearbyen).

Table 3: Mean concentrations (µg/g) dry weight measured in snow bunting nestlings at four different location categorized according to terrain and distances along the cable way.

Metals	Town(n=2) 1.6-2.7km	Hillside(n=8) 3.3-4.8 km	Valley(n=10) 6-7.2 km	River(n=6) 7.3-8.2km	Mine 6(n=3) 8.3-8.6km	diff. between groups (P=0.05)
Ca	731±54	534.5 ± 272.4	585.3±274	644±210.5	486.07±218.9	0.587
Na	207±175	215.5±206.2	267.6±205.9	318.9±107.1	113.9±134.4	0.035[a]
K	534±465	537.9±463.9	635.6±450.0	708.7±268.1	264.9±327.7	0.074[b]
Mg	835±59	543.9±413.9	656.0±420.7	701.6±208.3	278.2±258.6	0.106
Co	0.022±0.01	0.032±0.021	0.025±0.015	0.036±0.025	0.083±0.078	0.355
Cu	1.59±1.46	1.748±1.147	2.116±1.059	1.848±0.946	4.207±4.259	0.576
Fe	58.9±45	75.72±52.17	58.94±39.87	85.38±65.08	161.88±85.75	0.4
Mn	0.68±0.28	1.209±1.221	1.487±1.131	2.107±1.842	2.922±2.847	0.497
Se	1.304±0.01	1.322±0.805	1.073±0.548	1.181±0.446	0.874±0.218	0.753
Zn	72±4.8	65.44±36.96	70.72±31.44	67.78±25.70	62.22±19.73	0.965
Si	124±96	170.49±119.96	127.76±87.06	204.92±151.37	332.65±162.41	0.449
Sr	2.5±0.2	2.902±1.617	2.311±1.193	2.859±1.168	2.479±0.753	0.839
Cd	0.003±0.002	0.005±0.006	0.009±0.010	0.017±0.021	0.047±0.068	0.303
Cr	0.176±0.028	0.305±0.236	0.289±0.153	0.366±0.325	0.619±0.221	0.448
Hg	0.16±0.001	0.190±0.165	0.271±0.121	0.258±0.144	0.169±0.098	0.35
Pb	0.103±0.104	0.158±0.152	0.527±0.999	0.162±0.147	0.164±0.088	0.843
Al	67.59±54.99	89.19±64.18	62.15±46.86	105.92±81.01	170.42±84.25	0.463
Ba	0.919±0.462	1.489±1.265	0.907±0.625	1.234±0.871	2.163±0.705	0.49
V	0.176±0.148	0.216±0.155	0.152±0.112	0.236±0.186	0.471±0.284	0.421
Sn	0.018±0.009	0.052±0.045	0.035±0.024	0.234±0.506	0.068±0.027	0.673

'a' significantly different when P≤0.05. Highlighted in blue indicates highest concentrations of metals in each group [b] near significance difference between groups when P≥0.05 but ≤0.1

3.3 Correlations among different elements in the feathers of snow bunting nestlings

Most elements were significantly correlated with each other but only Zn and Cu were positively correlated with all elements. Other elements were significantly correlated with several elements but not all (Table 4). Cobalt was positively correlated with all elements but not K and Mg. Vanadium was positively correlated with all elements but not Hg and Mg. Strontium was positively correlated with all elements but not Na and K. Selenium was positively correlated with all elements but not Sn and Cr. Manganese was positively correlated with all elements but not Hg, K and Mg.

Silicon was positively correlated with all elements but Hg, K and Mg. Cadmium was positively correlated with all elements but not Na, K and Mg. Iron was positively correlated with all elements but not Hg, Na, K and Mg. Barium was positively correlated with all elements but not Na, Ca, K, Mg. Chromium was positively correlated with all elements but Se, Na, Ca, K and Mg. Lead was positively correlated with all elements but not Hg, Na, Ca, K and Mg. Aluminum was positively correlated with all elements but not Hg, Na, Ca, K and Mg. Tin was positively correlated with all elements but Hg, Se , Na, Ca, K and Mg.

Mercury was positively correlated with all elements but not Pb, Cr, Mn, Fe, Al, and Si. Calcium was positively correlated with all elements but not Sn, Pb, Cr, Ba, and Al. Sodium was positively correlated with all elements but not Cd, Sn, Pb, Ba, Sr, Fe and Al. Potassium was positively correlated with only V, Hg, Se, Cu, Zn, Na, Ca and Mg. Magnesium was only positively correlated with Hg, Se, Cu, Sr, Zn, Na, Ca and K.

Table 4: Elements correlations

	Cd	Co	Sn	V	Hg	Pb	Cr	Se	Ba	Mn	Cu	Sr	Zn	Fe	Al	Si	Na	Ca	K	Mg
Cd	1																			
Co	0.000[b]	1																		
Sn	0.000[b]	0.000[b]	1																	
V	0.000[b]	0.000[b]	0.000[b]	1																
Hg	0.035[a]	0.03[a]	0.497	0.188	1															
Pb	0.004[b]	0.004[b]	0.006[b]	0.002[b]	0.103	1														
Cr	0.000[b]	0.000[b]	0.000[b]	0.000[b]	0.4	0.04[a]	1													
Se	0.005[b]	0.002[b]	0.17	0.016[b]	0.004[b]	0.033[a]	0.313	1												
Ba	0.000[b]	0.000[b]	0.000[b]	0.000[b]	0.318	0.003[b]	0.000[b]	0.023[a]	1											
Mn	0.000[b]	0.000[b]	0.000[b]	0.000[b]	0.05	0.000[b]	0.000[b]	0.005[b]	0.000[b]	1										
Cu	0.000[b]	0.000[b]	0.000[b]	0.000[b]	0.000[b]	0.005[b]	0.002[b]	0.000[b]	0.000[b]	0.000[b]	1									
Sr	0.000[b]	0.000[b]	0.001[b]	0.000[b]	0.011[a]	0.001[b]	0.016[a]	0.000[b]	0.000[b]	0.000[b]	0.000[b]	1								
Zn	0.000[b]	0.000[b]	0.014[a]	0.002[b]	0.000[b]	0.017[a]	0.039[a]	0.000[b]	0.003[b]	0.000[b]	0.000[b]	0.000[b]	1							
Fe	0.000[b]	0.000[b]	0.000[b]	0.000[b]	0.173	0.002	0.000[b]	0.016[a]	0.000[b]	0.000[b]	0.000[b]	0.000[b]	0.001[b]	1						
Al	0.000[b]	0.000[b]	0.000[b]	0.000[b]	0.21	0.002[b]	0.000[b]	0.02[b]	0.000[b]	0.000[b]	0.001[b]	0.000[b]	0.003[b]	0.000[b]	1					
Si	0.000[b]	0.000[b]	0.000[b]	0.000[b]	0.176	0.002[b]	0.000[b]	0.017[a]	0.000[b]	0.000[b]	0.001[b]	0.000[b]	0.002[b]	0.000[b]	0.000[b]	1				
Na	0.27	0.149	0.135	0.496	0.000[b]	0.331	0.307	0.001[b]	0.328	0.285	0.046[a]	0.084	0.000[b]	0.499	0.486	0.493	1			
Ca	0.005[b]	0.007[b]	0.137	0.04[a]	0.000[b]	0.084	0.33	0.000[b]	0.057	0.009[b]	0.000[b]	0.000[b]	0.000[b]	0.038[a]	0.053	0.048[b]	0.000[b]	1		
K	0.465	0.19	0.133	0.403	0.000[b]	0.395	0.239	0.001[b]	0.263	0.393	0.05[a]	0.097	0.000[b]	0.415	0.392	0.411	0.000[b]	0.000[b]	1	
Mg	0.405	0.452	0.085	0.139	0.001[b]	0.455	0.059	0.000[b]	0.114	0.362	0.021[a]	0.023[a]	0.000[b]	0.139	0.122	0.13	0.000[b]	0.000[b]	0.000[b]	1

Where [a] is correlation when $P \leq 0.05$ and [b] is correlation when $P \leq 0.01$. Highlighted in blue shows no significant correlation

3.4 PCA for the elements

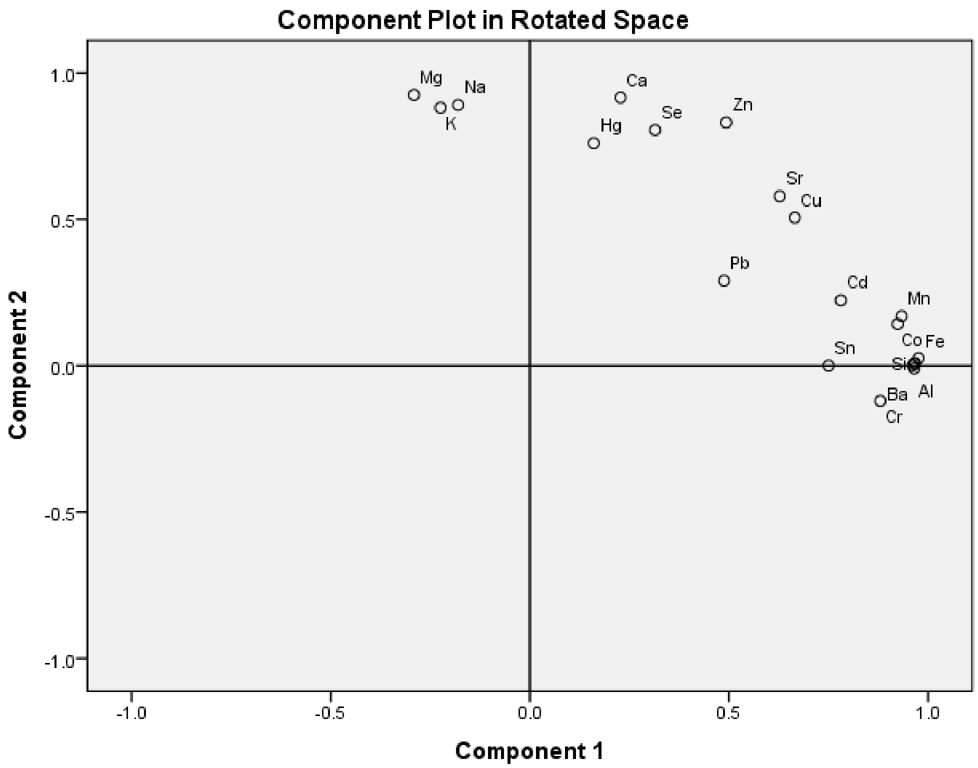
Principle component one (PC1) and two (PC2) explained 79.9% of the variation in data (Fig 4). The PCA showed that the concentrations of elements Mg, Na and K are positively closely correlated, also the elements Mn and Co were very closely correlated, and also that Fe, Si, Ba and Al are closely correlated. This means that closely correlated elements have may similar patterns of accumulation in feathers of snow bunting nestlings and may have a similar source of origin. In contrast, for elements that do not cluster with other elements in the PCA loading plot their accumulation pattern differs from the elements that appear close to each other in the PCA loading plot.

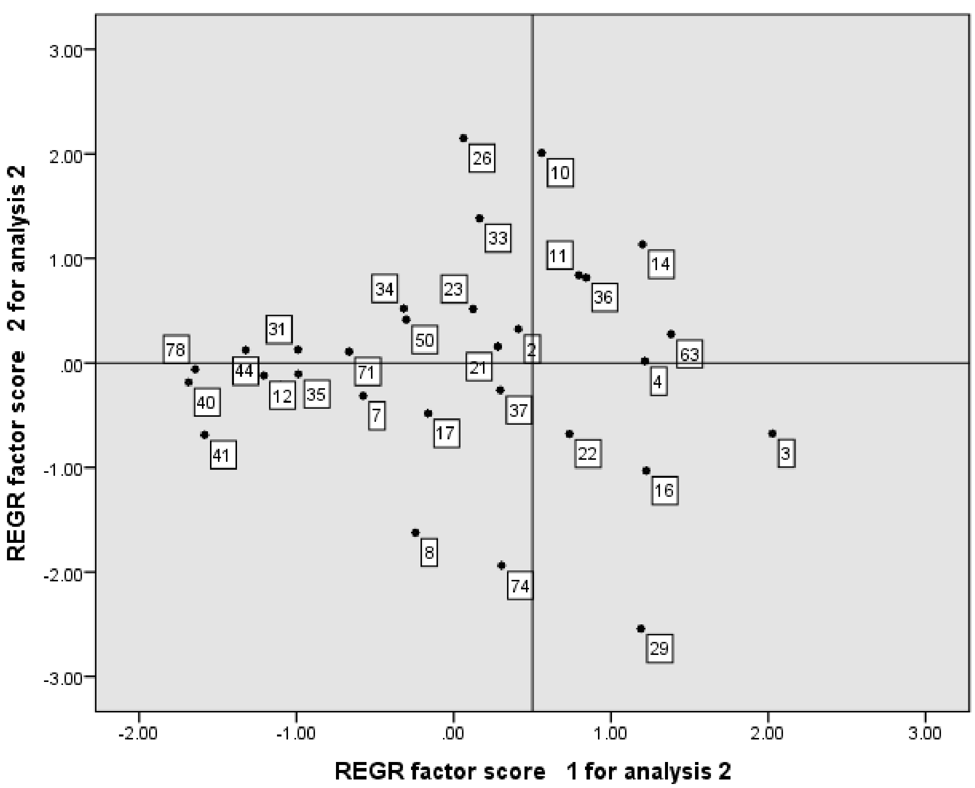
Nests 78, 40, 44, 31, 22, 35 and 71 (Fig 5) had lower concentrations of elements Cd, Mn, Sn, Co, Fe, Si, Ba, Al, and Cr (from Fig 4) and nests 26 and 10 had high levels of Mg, Na and K. Also nests 4, 63 and 3 probably had high levels of elements Cd, Mn, Sn, Co, Fe, Si, Ba, Al, and Cr. Furthermore nests 74 and 8 also had high levels of Mg, Na, and K. It can also be seen from the score plot that nest 29 had low concentrations of Ca, Hg, Se and Zn.

Fig 4 (below): PCA output plot for the metals measured in feathers of snow bunting nestlings of Longyearbyen. PC1 explained 52.8% and PC2 explained 27.1%

Fig 5 (below): Factor score plots for all snow bunting nests where snow bunting nestling feathers were sampled.

PCA for metals and Factor score plots for the nest locations





4.0 Discussions

The aim of this study was to assess local metal pollution due to the coal mining activities and urban settlement in Longyearbyen using snow bunting nestlings as biomonitors. This was done by measuring the levels of elements in feathers of snow bunting nestlings using high resolution inductively coupled mass spectrometry. Originally I probed the concentration of 74 elements in feathers but only 38 elements (Appendix B) were found to be within limits of detection, and of the 38 elements within limits of detection only 20 relevant elements were selected for discussion in this report. These elements were selected either because of being essential elements or elements of toxicological concern. The elements discussed in this study are Cd, Co, Sn, V, Hg, Pb, Cr, Se, Ba, Mn, Cu, Sr, Zn, Fe, Al, Si, Na, Ca, K, and Mg. The hypothesis was that the coal power plant in Longyearbyen was the main source of local metal pollution and that there was a pollution gradient from the coal power plant towards mine 6 mines in Adventdalen. The old cable line from Longyearbyen town to mine 6 was used as a line transect during sampling of snow bunting nestlings from nests along the old cable line. Other expectations were that at some points along the cable way the concentrations of elements would tend to be high due to other pollution sources like human settlement and coal drop offs during coal transportation but these were considered to be minor sources of elements compared to the coal power plant which in this study was considered to be the main source of pollution.

4.1 Pollution gradient

There were no significant correlations between the distance from the power plant and the feather concentrations for most of the metals except for Cd (Spearman's correlation, p=0.012), Mn (p=0.022) and Cr (p=0.028) which showed a positive significant correlation with distance from the coal power plant to mine 6 in Adventdalen. This means that the concentrations of these elements in the feathers increased with the distance from the coal power plant. There were also some metals that showed tendencies of near significance positive correlation with distance from the power plant to mine 6 such as Si (p=0.056), Fe (p=0.075), Al (p=0.076), Co (p=0.083), Sn (p= 0.094, and Ba (p=0.094). Near significance correlation is where p= ≥0.05 but ≤0.01 (Table 2). Thus the concentration in feathers of these elements that showed near significance positive correlation with distance also showed a tendency to increase with distance from the power plant to mine 6. The results therefore challenged the hypothesis that the elements concentration would be higher closer to the coal power plant meaning that the main source of pollution was close to mine 6 in Adventdalen and not the coal power plant in Longyearbyen.

Also further analysis based on terrain categories and distance (Table 3) indicated that the concentrations for most elements were highest near mine 6, thus proving otherwise the expectation that metal concentration would be high close the coal power plant. The tendency for the increase in element concentrations from Longyearbyen to mine 6 may be due to a dumping site of incineration wastes from the coal power plant and other wastes from Longyearbyen town which is just a few kilometers further into Adventdalen from mine 6. Winds blowing from this waste site may spread and deposit elements to the nearby areas. Therefore since mine 6 has not been active for some time, it's most likely that the high levels of metals close to mine 6 were from coal incineration wastes that were disposed off at the damping site. It should also be noted that concentrations of elements were high at some points along the cable line (Fig 3) for example nest s number 63, 33 and 16 in case of Mn (Appendix B, Table B1) fulfilling the expectations that there would be other minor sources of pollution like coal drop offs during transportation

4.2 Correlation of metals and PCA

Most correlations of metals from PCA and the Spearman's correlation matrix were probably indicative of their sources and could also indicate similar patterns of accumulation in feathers for the elements that are very closely related. Therefore the high association between major essential elements Mg, Na, and K could probably indicate that they are of natural origin given their necessity for proper functioning of biological processes in animals. Also the high correlation between Mn and Co then Fe, Si, Ba and Al may be indicative of their origin from coal mining activities (Finkelman 1993, Mishra et al. 2008) which may explain their positive correlation with distance from Longyearbyen to mine 6 in Adventdalen (Table2) where Mn had a significant positive correlation and metals Co, Fe, Si, Ba, and Al had borderline correlation with distance from the power plant in Longyearbyen and mine 6.

4.3 Metal concentrations and comparison with other previous studies

The concentrations of elements in this present study were compared to the concentrations of elements measured in feathers from some previous studies in birds listed in (Table 5 below) to find out if high levels could be due to pollution from the coal power plant in Longyearbyen and if the levels of elements measured were of toxicological significance in snow buntings (later in the discussion).

The essential metals Mg (606±350 µg/g dw), K (580±390 µg/g dw), Na (243±174 µg/g dw) and Ca (574±236 µg/g dw) respectively had the highest concentration, most likely from natural sources given their demand in relatively large quantities for normal body physiological functions. In comparison to a previous study done in cattle egret (*Bubulcus ibis)* feathers of 4-6 day old chicks in Pakistan (Malik and Zeb 2009) that measured much higher levels of essential metals Mg (1304 µg/g), Ca (21577 µg/g dw), Zn (142.5 µg/g dw), and Fe (135.4 µg/g dw) than those measured in this current study.

The levels of trace essential metals Zn (66±28 µg/g), Fe (76±59 µg/g), Se (1.1±0.6 µg/g dw), Mn (1.6±1.5 µg/g dw), Cu (2.1±1.7 µg/g dw) and Co (0.03±0.03 µg/g dw) also required for normal physiological functions of the body but in in small amounts were also measured in high levels in the current study than other elements in the current study. Very high levels of these trace essential metals than normal can be as a result of release from anthropogenic activities like coal mining (Sabbioni et al. 1984, Mishra et al. 2008). However in comparison to previous studies of metals in feathers of fledging great egrets (*Ardea alba)* and cattle egrets (Burger 2013 and Malik and Zeb 2009) respectively the levels of the trace essential elements Zn, Fe, Se, Cu, and Co were lower, except for Mn whose level in this current study was greater than that found in fledging great egrets (Burger 2013). Also compared to previous studies in other adult passerine birds such as the blue tit *(Cyanistes caeruleus)* and the great tit (*Parus major*) in Belgium (Dauwe et al. 2002), the levels of Zn and Cu were much higher than in the current study, and only the levels of Se were lower in great tit (Janssens et al. 2001) than levels of Se in this current study. Other trace essential element levels like Mn, Zn, Cu and Co measured by Janssens et al. 2001also in Belgium were higher than in this current study.

Table 5: Comparison of mean metal concentrations of the current study with mean metal concentrations (µg/g dw) in bird feathers from some previous studies. Concentrations from some studies were converted to µg/g dry weight for easy comparison with the current study.

Authors	**Area**	**Bird species**	**Cd**	**Co**	**Hg**	**Pb**	**Cr**	**Se**	**Mn**	**Cu**	**Al**	**Zn**	**Fe**	**Ca**	**Mg**
Current study	Longyearbyen Svalbard	Snow bunting nestlings (n=147)	0.01	0.03	0.23	0.27	0.33	1.1	1.6	2.1	86	66	76	574	606
Burger 2013	New jersey	Fledging great egrets (n=14)	0.031		2.61	0.054	0.102	1.124	0.329						
Frantz et al. 2012	Paris	Adult urban pigeons (n=92)	0.8			13.82			13.15			204.8			
Pon et al. 2011	Patagonian Shelf	Adult Black-browed Albatross (n=27)	0.33			5.71				4.86		102.76	101.73		
Tsipoura et al. 2011	Harrier Meadow-New Jersey	Adult Canada geese (n=13)	0.0693		0.2	1.65	0.801								
Malik and Zeb 2009	Pakistan(over all mean)	Cattle egret chicks (n=30)	2.73	6.57		58.2	6.36		19.7	3.9		142.5	135.4	21577	1304
Burger and Gochfeld 2009	Aleutians - Alaska	Adult common eiders (n=26)	0.798		0.84	0.992	0.172	0.878	1.87						
Burger and Gochfeld 2009	Aleutians-Alaska	Adult tufted puffins (n=39)	0.08		2.54	1.26	1.82	6.6	0.622						
Burger et al. 2008	Shoup Bay Alaska	Adult Black-legged Kittiwakes (n=61)	0.035		2.91	0.707	0.954	2.42	0.751						
Burger et al. 2007	Prince William Sound Alaska	Adult pigeon guillemots (n=40)	0.099		2.81	1.02	1.33	2.61	1.75						

Authors	Area	Bird species	Cd	Co	Hg	Pb	Cr	Se	Mn	Cu	Al	Zn	Fe	Ca	Mg
Current study	Longyearbyen Svalbard	Snow bunting nestlings (n=147)	0.01	0.03	0.23	0.27	0.33	1.1	1.6	2.1	86	66	76	574	606
Burger et al. 2007	Amchitka Alaska	Adult pigeon guillemots (n=21)	0.0331		7.72	0.903	0.804	2.91	0.897						
Burger et al. 2007	Kiska Alaska	Adult pigeon guillemots(n=17)	0.0284		6.36	0.903	2.69	3.9	1.24						
Dauwe et al. 2003	Bird sanctuaries in Flanders - Belgium	Adult Sparrow hawks inner primary feathers (n=7)	0.09	0.06	1.10	2.61	1.97		5.52	3.16	17.1	23.8	118		
Dauwe et al. 2003	Bird sanctuaries in Flanders - Belgium	Adult little owls inner primary feathers(7)	0.05	0.22	0.32	3.99	0.50		12.1	8.98	39.0	35.7	252		
Dauwe et al. 2002	Polluted site Antwerp - Belgium	Adult great tits (n=32)	7.1			250				88		240			
Dauwe et al. 2002	‘’	Adult Blue tits (n=8)	8			271				69		244			
Janssens et al. 2001	Union Minie`re in Flanders Belgium	Adult great tits (n=40)	9.3	0.66	3.13	230.5	1.89	22.4	17.4	54.89	27.7	264	76.7		
Janssens et al. 2001	Brasschaat - Flanders Belgium	Adult great tits (*n* =10)	0.56	0.04	0.84	8.07	2.17	0.83	43.8	6.47	58.34	119.5	83.1		

In the present study elements Si and Al were also detected in high concentrations and this could be due to their wide spread occurrence in nature, especially for Si where SiO_2 is the most abundant compound in the earth's crust commonly taking the form of ordinary sand and existing in rock crystals which further explains its correlation with all the metals except for Hg. Although Al is a very abundant element in the earth's crust, the high levels of Al that were found in this study compared to other previous studies in adult passerine birds; great tits and blue tits (Janssens et al. 2001, Dauwe et al. 2003) could be as a result of coal mining activities in Longyearbyen since Al compounds are found in coal and released into the environment during coal mining and in coal ash after coal burning (Finkelman 1993).

The feather concentration of the heavy metals of most toxicological concern Cd (0.01±0.02 µg/g dw), Pb (0.27±0.59 µg/g dw) and Hg (0.23±0.13 µg/g dw), were relatively low compared to the concentrations reported in some previous studies of adult passerine bids such as great tits and blue tits (Janssens et al. 2001, Dauwe et al. 2002), presented in Table 5. However Pb (0.27±0.59 µg/g dw) levels were somewhat higher than the levels measured in feathers of great egret fledglings of New Jersey U.S.A. (Burger 2013) in (Table 5). Furthermore Cr (0.33±0.23 µg/g dw) levels in the current study were also a bit higher than Cr levels found in great egret fledglings of New Jersey (Burger 2013) and Cr levels found in adult common eiders (*Somateria mollissima)*of Aleutians Alaska (Burger and Gochfeld 2009).

4.4 Toxicological significance of feather concentrations of some toxic and essential elements

Cadmium was found to have a positive significant correlation with distance from the coal power plant in Longyearbyen to mine 6 in Adventdalen, indicating that the pollution source may be the waste site for coal ash from the power plant, which is situated close to mine 6. Cadmium is considered a toxic element and not an essential element but is known to induce deficiencies of the essential element Ca, by competing with Ca for uptake in important biological molecules (Casarett and Doull 2013). At high concentrations Cd may cause kidney damage, testicular damage, hinder egg production, egg shell thinning and altered behavior. Exposure to elevated levels of Cd in feathers was found to correlate with reduced fledging success and reduced growth rates of bones at the population level in little blue heron chicks (*Egretta caerulea)* (Spahn and Sherry 1999). Burger and Gochfeld (2000) considered a Cd concentration of 2,000 ppb (2 µg/g dw) as a threshold concentration in feathers that may have adverse effect in kidneys. Cadmium concentration of 0.01±0.02 µg/g dw measured in snow bunting nestlings in this study was thus far less than the sub lethal thresh hold levels suggested above. Thus these Cd levels may pose no serious health challenges to the snow bunting nestlings.

Manganese also showed a significant positive correlation with distance from the coal power plant to mine 6. This indicates that the waste site may also be a source for Mn in feathers of snow bunting nestlings. Manganese is an essential metal required for many metabolic and cellular functions for example it is a cofactor for a number of enzymatic reactions. However the presence of high Mn concentration in the feathers could be linked to contaminated diet and to a smaller extent inhalation (Hui 2002). Manganese tends to accumulate in bone, liver, pancreas and kidney of avian species and elimination mechanism of Mn in birds is primarily through the fecal matter but can also be excreted through egg laying in female birds (Malik and Zeb 2009). Teratogenic effects (such as micromelia, twisted limbs, hemorrhage, and neck defects), behavior impairments, altered growth rates and reduction of hemoglobin formation have been linked to sub-lethal Mn exposure in animals and avian embryos (Burger and Gochfeld 1995a). Herring gull chicks (*Larus argentatus*) administered manganese acetate 50 mg/kg (50µg/g) expressed reduced growth and behavior effect than the control groups (Burger and Gochfeld 1995b). Thus the levels Mn (1.6±1.5 µg/g dw) measured in this study are much lower than the levels that have been found to cause adverse effects in birds. It is therefore unlikely that snow buntings in this present study experienced any toxic effects due to the Mn levels they were exposed to.

Chromium was also positively and significantly correlated with distance from the coal power plant in Longyearbyen to mine 6 in Adventdalen. Chromium although previously thought to be an essential element scientific studies have continuously failed to produce convincing evidence for this status. Kertész and Fáncsi 2003 found that Cr produced adverse effects on the embryonic development, hatching and viability of the mallard (*Anas platyrhynchos)*. Then according Burger and Gochfeld (2000) Cr concentration of 2,800 ppb (2.8 µg/g dw) in bird feathers might be associated with adverse effects. The Cr concentrations (0.33±0.23 µg/g dw) found in the present study were therefor much lower than chromium levels known to cause adverse effects in birds. Therefore the snow buntings in this current study may not be experiencing any toxic effects due to the Cr levels they were exposed to.

Lead is a highly toxic metal that readily accumulates in bones, hairs, feathers and nails and is known to cause damage to the nervous system, cause deficiences of Ca in birds by interupting the Ca metabolism (Hutton and Goodman 1980), and causing imbalances in animals (Dauwe et al. 2006). Higher incidence of mortality among the Pb exposed nestlings has been reported (Spahn and Sherry 1999). Adverse effects of Pb- in birds like impaired thermoregulation, locomotion, depth perception, feeding behavior, and lowered chick survival in gulls were found to occur at levels of 4 ppm (4 µg/g dw) in feathers (Eisler 1987; Custer and Hohman 1994 ; Gochfeld 2000). The level of Pb of 0.27±0.59 µg/g measured in this study was therefor very low compaared to the level known to cause adverse effects. Therefore its unlikely that snow buntings in this present study experienced any toxic effects due to Pb leveles they were expsed to.

Mercury which also is a very toxic element known to cause behavioral, physiological, and impaired reproductive effects (Burger and Gochfeld 1997) was not correlated with distance from the power plant to mine 6. Levels of 5 ppm (5µg/g dw) in feathers have been associated with adverse reproductive effects in birds (Eisler 1987, Burger and Gochfeld 2000). For Se, an element that provides a protective effect for Hg toxicity has been found to cause mortality in birds at levels of 3.8 ppm to 26 ppm (3.8 - 26 µg/g dw) depending upon species in feathers (Burger 1993). However, the Hg and Se concentrations in this study were 0.23±0.13 µg/g dw and 1.1±0.6 µg/g dw respectively therefore well below levels that have been found to cause adverse effects in birds. Thus it is unlikely that Hg exerted any toxic effects in the snow buntings of the present study.

Zinc also an essential heavy metal showed no correlation with distance in this current study. Zinc is required for proper body functioning as a component of various enzyme systems for example it is involved in catalysis and co-catalysis by the enzymes which control many cell process. These cell processes include DNA synthesis, normal growth, brain development, behavioral response, reproduction, fetal development, membrane stability, bone formation, wound healing and protection from Cd renal toxicity (Park et al. 2004). The mean concentration of 66±28 µg/g dw (0.066 mg/g dw) in this study was far less than the concentration of 200 mg/g dw known to cause kidney damage according to (Hutton and Goodman 1980). Therefor it is not likely that snow buntings in this present study experienced kidney damage due to the levels of Zn they were exposed to.

5.0 Short comings

There were some few weaknesses in the methodology in this study for example during sampling few nests were sampled close to Longyearbyen town and also close to mine 6 which were suspected point sources of pollution in this study. This makes comparisons of levels of metals from other sampled locations with these two locations hard. Also very few feathers were collected from the nestlings at some nest locations and the number of nestlings sampled per nest was not uniform. Although this was accounted for in data processing and analysis, uniform sampling methods for future biomonitoring studies in snow bunting in this area is highly recommended for better results.

6.0 Recommendations

I would highly recommend further biomonitoring studies of metals in snow buntings of Longyearbyen since this is the first study to measure elements in feathers of snow buntings in Longyearbyen. Also biomonitoring of elements in other birds and areas of Svalbard is recommended since levels of elements measured in this current study seemed to be low. Therefore these future studies could either confirm that bioavailable levels of elements in feathers of birds of Longyearbyen are low or that they are high. It would also be interesting for future studies to assess toxicological effects of the elements that were found to correlate positively with distance from

Longyearbyen to mine 6 in Adventdalen in snow buntings which make good biomonitors for this kind of study given their distribution in Svalbard.

7.0 Conclusions

Levels of metals measured in feathers of snow bunting nestlings of Longyearbyen in this study are low compared to most levels found in studies done in feathers of young birds and studies involving feathers of adult birds. Thus the concentration of the potential toxic elements measured in this study are well below the threshold levels in feathers known to cause adverse effects in birds from other studies. Therefore it is probably not likely that metal pollution due to coal mining activities in Longyearbyen is of environmental concern. However additional studies are recommended to confirm this conclusion.

This study is one of the first studies to the best of my knowledge to biomonitor levels of metals in terrestrial arctic birds of Svalbard using bird feathers. Therefore results of this study will provide useful baseline information on which future metal biomonitoring studies in birds in other parts of Svalbard can make reference

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Appendix A: Nest biographic information

Table A1: Information about nests from which snow bunting nestlings were sampled in Longyearbyen and Adventdalen – Svalbard.

Nest ID	Area	Date of first egg	No eggs	Date of hatching	No hatchlings	No fledglings	Clutch body mass	Day of weighing	Mean nestling growth rate
2	3	41	6	56	6	6	156	8	3.25
3	3	36	6	52		5	153	8	3.82
6	3	42	6	58	6	6	152.5	8	3.18
7	3	42	3	58	3	3	83.5	8	3.48
8	3	42	6	57	6	6	143.5	8	2.99
10	3	43	4	58	4	3	89	8	3.71
11	3	43	6	59	6	6	170.5	8	3.55
12	3	43	3	59	3	3	83	8	3.46
14	3	43	7	59	7	5	131.5	8	3.29
16	3	42	6	58	5	5	129.5	8	3.24
17	3	40	5	56	5	5			
21	3	38	6	54	6	6	193.5	9	3.58
22	3	43	6	59	6	4	100	7	3.57
23	2	47	6	63	5	5	119.5	7	3.41
26	3	47	6	63	5	5	152	9	3.38
29	3	39	6	55	6	4	115.5	8	3.61
31	3	44	6	59	6	6	157.5	8	3.28
33	3	44	5	60	4	4	110	8	3.44
34	3	34	5	49	5	4	130	9	3.61
35	3	47	6	63	6	5	116.5	8	2.91
36	3	40	7	56	7	7	180.2	8	3.22
37	3	42	6	58	6	6	154	8	3.21
40	3	48	5	63	5	5			
41	3	45	6	61	6	4	127	7	4.54
44	3	46	8	64	6				
50	3	49	5	64	5	5	141.5	8	3.54
52	3	49	7	65	7	6	153.5	8	3.2
63	3	37	7	52	6	6	150	8	3.13
71	2	50	6	66	6	3	78	9	2.89
74	3	39		55		6	186	8	3.88
78	3	50	6	66	6	4	113.5	8	3.55

Appendix B. Levels of elements at different nest locations in Longyearbyen and Adventdalen

Table B.1: Concentration in µg/g dw of major essential and trace essential elements measured in snow bunting nestlings at different nest locations.

D/km	nests	Ca	K	Na	Mg	Zn	Fe	Si	Al	Sr	Cu	Mn
1.6	23	693	862	331	793	76	91	192	106	2.58	1.69	0.88
2.4	71	770	205	84	877	69	27	56	29	2.33	1.49	0.48
3.3	26	1149	1648	709	1516	145	62	119	65	4.82	4.26	0.76
3.4	41	369	354	139	425	37	14	35	16	1.26	0.94	0.19
3.5	40	412	447	189	528	38	11	23	10	1.53	1.00	0.14
4	63	585	450	188	438	88	168	375	195	5.43	2.34	3.99
4	37	489	566	211	482	56	105	253	135	1.62	1.22	1.09
4.2	21	541	393	148	516	71	65	137	65	3.80	1.91	1.53
4.5	74	229	182	60	127	35	68	161	84	1.83	0.75	0.76
4.8	22	501	263	79	318	55	112	261	143	2.93	1.58	1.21
5.4	7	449	572	202	584	49	34	61	30	1.52	1.22	0.49
5.4	78	432	642	246	581	39	15	29	14	0.90	0.66	0.25
6	8	272	224	75	225	32	46	104	52	1.13	0.75	1.23
6.2	31	493	416	162	628	55	21	42	19	2.22	1.36	0.48
6.5	33	668	1258	605	959	100	60	124	60	4.25	2.79	2.05
6.7	34	564	620	240	697	74	51	108	52	2.10	3.16	0.69
6.7	16	471	130	45	133	58	141	302	167	2.68	1.86	3.05
6.9	52	398	556	257	424	42	21	47	19	1.05	1.20	0.51
6.9	17	423	403	167	470	55	44	97	45	1.28	1.93	0.68
7.1	10	1219	1582	662	1618	132	75	163	71	4.31	3.94	3.49
7.1	11	861	596	219	803	104	110	245	116	2.62	3.05	2.18
7.3	35	486	569	244	602	55	21	45	21	1.47	1.12	0.51
7.3	36	815	1040	436	856	94	144	321	177	3.16	2.34	2.42
7.5	14	987	945	397	960	106	104	242	131	4.91	3.47	3.73
7.5	44	588	443	171	695	51	14	28	12	2.88	1.31	0.51
7.9	12	465	526	210	606	42	21	48	22	1.66	0.99	0.31
7.9	50	520	852	381	732	56	57	178	85	1.82	1.09	0.92
8.2	4	487	445	318	360	58	172	412	209	2.74	1.89	4.75
8.5	2	693	640	267	565	78	103	204	106	2.57	1.62	1.15
8.5	3	507	117	57	207	69	260	515	266	3.18	9.44	6.21
8.6	29	259	37	18	63	40	122	279	139	1.68	1.56	1.42

Table B.2: Concentrations in µg/g dw of toxic elements in snow bunting nestling feathers at different nest locations along the cable way from the coal power plant in Longyearbyen to mine 6 in Adventdalen.

D/km	nests	Se	Hg	Cd	Cr	Pb	Ba	Co	V	Sn
1.6	23	1.30	0.16	0.001	0.20	0.18	1.25	0.031	0.28	0.02
2.4	71	1.31	0.16	0.004	0.16	0.03	0.59	0.011	0.07	0.01
3.3	26	3.12	0.57	0.003	0.25	0.06	1.08	0.060	0.17	0.02
3.4	41	0.94	0.06	0.002	0.05	0.01	0.24	0.006	0.03	0.01
3.5	40	1.05	0.09	0.001	0.07	0.46	0.18	0.005	0.02	0.01
4	63	1.74	0.19	0.020	0.63	0.31	4.19	0.059	0.46	0.09
4	37	1.10	0.15	0.001	0.23	0.09	1.76	0.037	0.31	0.04
4.2	21	1.24	0.23	0.005	0.19	0.10	0.98	0.027	0.15	0.14
4.5	74	0.50	0.08	0.002	0.68	0.07	1.78	0.022	0.21	0.03
4.8	22	0.89	0.13	0.005	0.33	0.17	1.69	0.036	0.36	0.09
5.4	7	0.77	0.14	0.002	0.50	0.04	0.44	0.023	0.07	0.03
5.4	78	0.85	0.30	0.001	0.07	0.03	0.16	0.013	0.04	0.01
6	8	0.38	0.12	0.001	0.26	0.06	0.85	0.017	0.11	0.03
6.2	31	0.61	0.33	0.003	0.07	0.34	0.42	0.008	0.05	0.02
6.5	33	1.53	0.41	0.013	0.19	0.65	0.80	0.033	0.15	0.03
6.7	34	1.05	0.43	0.001	0.22	0.05	0.49	0.023	0.14	0.02
6.7	16	1.31	0.13	0.011	0.53	0.38	2.10	0.051	0.40	0.06
6.9	52	0.80	0.23	0.005	0.11	0.04	0.33	0.010	0.05	0.01
6.9	17	0.60	0.18	0.002	0.44	0.08	0.69	0.017	0.11	0.09
7.1	10	2.07	0.40	0.026	0.43	3.31	1.39	0.028	0.18	0.03
7.1	11	1.65	0.32	0.028	0.40	0.33	1.73	0.047	0.29	0.04
7.3	35	0.72	0.15	0.003	0.24	0.03	0.28	0.013	0.05	0.02
7.3	36	1.49	0.18	0.016	0.40	0.12	1.79	0.059	0.42	0.05
7.5	14	1.90	0.25	0.055	0.73	0.11	2.16	0.045	0.30	1.27
7.5	44	0.84	0.12	0.002	0.06	0.05	0.28	0.006	0.03	0.02
7.9	12	0.77	0.16	0.001	0.08	0.16	0.27	0.013	0.06	0.01
7.9	50	1.22	0.35	0.002	0.15	0.07	0.87	0.026	0.15	0.01
8.2	4	0.87	0.50	0.028	0.78	0.45	2.04	0.068	0.46	0.05
8.5	2	1.07	0.25	0.005	0.37	0.09	1.44	0.035	0.27	0.05
8.5	3	0.92	0.20	0.125	0.77	0.26	2.84	0.174	0.80	0.06
8.6	29	0.64	0.06	0.010	0.73	0.14	2.21	0.041	0.34	0.10

Table B.3: Concentration in µg/g dw of other elements (above detection limits but not discussed in this report) in snow bunting nestling feathers at different nest locations along the cable way from the coal power plant in Longyearbyen and mine 6 Adventdalen.

D/km	nests	P	S	Ti	Rb	Ce	Cs	Tl	U	Bi
1.6	23	1096	11140	6.7	0.34	0.12	0.009	0.003	0.003	0.015
2.4	71	515	10615	1.8	0.15	0.04	0.003	0.008	0.001	0.014
3.3	26	2052	20231	4.4	0.79	0.12	0.007	0.022	0.002	0.065
3.4	41	483	5189	0.9	0.29	0.02	0.002	0.005	0.001	0.006
3.5	40	563	5731	0.6	0.24	0.01	0.001	0.005	0.000	0.010
4	63	781	16658	12.2	0.43	0.24	0.016	0.006	0.005	0.256
4	37	663	8838	8.1	0.46	0.16	0.010	0.005	0.004	0.018
4.2	21	626	11867	4.7	0.24	0.08	0.006	0.003	0.003	0.083
4.5	74	248	5900	5.0	0.16	0.10	0.008	0.002	0.002	0.033
4.8	22	346	10076	9.1	0.25	0.18	0.014	0.003	0.004	0.067
5.4	7	730	7263	1.8	0.21	0.04	0.003	0.002	0.001	0.011
5.4	78	665	5366	0.7	0.21	0.02	0.001	0.002	0.000	0.006
6	8	298	5212	2.9	0.12	0.06	0.005	0.001	0.002	0.018
6.2	31	702	8392	1.2	0.15	0.02	0.002	0.001	0.001	0.007
6.5	33	1791	14273	3.2	0.45	0.08	0.006	0.002	0.002	0.017
6.7	34	851	12412	3.1	0.28	0.06	0.004	0.002	0.001	0.029
6.7	16	239	12424	10.7	0.24	0.21	0.013	0.003	0.005	0.017
6.9	52	716	6375	1.2	0.14	0.02	0.002	0.001	0.001	0.008
6.9	17	540	7342	3.4	0.26	0.05	0.005	0.002	0.002	0.029
7.1	10	1956	19814	4.8	0.46	0.08	0.008	0.005	0.003	0.016
7.1	11	894	19015	7.1	0.27	0.12	0.009	0.003	0.003	0.012
7.3	35	750	7761	2.1	0.10	0.02	0.002	0.001	0.001	0.036
7.3	36	1502	14630	10.5	0.46	0.19	0.013	0.003	0.004	0.028
7.5	14	1395	17165	7.4	0.39	0.14	0.011	0.003	0.004	0.036
7.5	44	621	8201	0.9	0.12	0.02	0.001	0.002	0.001	0.009
7.9	12	696	6530	1.3	0.17	0.03	0.003	0.001	0.001	0.004
7.9	50	987	7727	3.7	0.33	0.09	0.006	0.002	0.002	0.008
8.2	4	712	10930	12.2	0.37	0.23	0.018	0.002	0.007	0.016
8.5	2	754	14440	6.7	0.30	0.14	0.009	0.003	0.004	0.020
8.5	3	140	21816	15.7	0.30	0.28	0.017	0.003	0.009	0.144
8.6	29	70	7992	9.4	0.17	0.16	0.011	0.002	0.004	0.107

Table B.3 continued...: concentrations µg/g dw of other elements (above detection limits but not discussed in this report) in snow bunting nestling feathers at different nest locations along the cable way from the coal power plant in Longyearbyen and mine 6 Adventdalen.

D/km	nests	Au	La	Nd	Pr	Th	Y	Sb	Sm	Er
1.6	23	0.001	0.061	0.050	0.014	0.016	0.028	0.016	0.011	0.0027
2.4	71	0.001	0.020	0.017	0.004	0.005	0.031	0.002	0.003	0.0031
3.3	26	0.001	0.058	0.051	0.013	0.014	0.020	0.008	0.008	0.0023
3.4	41	0.000	0.008	0.007	0.002	0.002	0.005	0.002	0.001	0.0006
3.5	40	0.000	0.005	0.003	0.001	0.002	0.002	0.007	0.001	0.0002
4	63	0.022	0.118	0.104	0.025	0.028	0.057	0.025	0.016	0.0053
4	37	0.001	0.074	0.069	0.018	0.019	0.041	0.005	0.011	0.0051
4.2	21	0.005	0.041	0.034	0.009	0.011	0.019	0.006	0.006	0.0031
4.5	74	0.002	0.045	0.042	0.010	0.011	0.024	0.005	0.006	0.0020
4.8	22	0.034	0.077	0.075	0.020	0.023	0.033	0.010	0.014	0.0043
5.4	7	0.002	0.016	0.016	0.004	0.005	0.008	0.004	0.003	0.0011
5.4	78	0.001	0.008	0.012	0.003	0.003	0.004	0.001	0.002	0.0004
6	8	0.002	0.030	0.024	0.006	0.008	0.012	0.002	0.006	0.0011
6.2	31	0.001	0.010	0.008	0.002	0.003	0.004	0.006	0.001	0.0007
6.5	33	0.003	0.036	0.032	0.009	0.008	0.018	0.005	0.005	0.0022
6.7	34	0.003	0.024	0.022	0.006	0.006	0.015	0.009	0.005	0.0018
6.7	16	0.037	0.094	0.090	0.026	0.023	0.053	0.032	0.017	0.0051
6.9	52	0.001	0.007	0.009	0.002	0.003	0.006	0.002	0.002	0.0007
6.9	17	0.008	0.025	0.023	0.005	0.010	0.010	0.006	0.004	0.0014
7.1	10	0.011	0.037	0.034	0.008	0.011	0.025	0.012	0.005	0.0025
7.1	11	0.041	0.054	0.048	0.013	0.016	0.029	0.013	0.010	0.0033
7.3	35	0.001	0.008	0.008	0.002	0.003	0.005	0.005	0.002	0.0007
7.3	36	0.004	0.096	0.081	0.021	0.025	0.045	0.042	0.014	0.0048
7.5	14	0.003	0.065	0.065	0.015	0.017	0.032	0.070	0.012	0.0039
7.5	44	0.001	0.007	0.007	0.001	0.002	0.003	0.005	0.001	0.0005
7.9	12	0.001	0.015	0.013	0.003	0.004	0.005	0.002	0.002	0.0005
7.9	50	0.001	0.042	0.035	0.010	0.009	0.016	0.015	0.006	0.0015
8.2	4	0.033	0.104	0.100	0.026	0.028	0.052	0.012	0.019	0.0055
8.5	2	0.002	0.067	0.060	0.015	0.016	0.031	0.018	0.010	0.0034
8.5	3	0.015	0.130	0.123	0.031	0.034	0.079	0.015	0.024	0.0089
8.6	29	0.004	0.077	0.065	0.016	0.019	0.034	0.018	0.011	0.0043

Appendix C. Limits of detection

Table C.1: Limits of detection (LOD) for the 38 elements above LOD in this study.

Sign	Isotope	Element	Resolution	IDL-25% (µg/l)	DL in original sample (Feather) µg/g
Al	27	Aluminium	Mr	0.2	0.701754
Ba	137	Barium	Mr	0.013	0.045614
Bi	209	Bismuth	Lr	0.001	0.003509
Cd	114	Cadmium	Lr	0.002	0.007018
Ca	44	Calcium	Mr	2	7.017544
Ce	140	Cerium	Lr	0.0002	0.000702
Cs	133	Cesium	Lr	0.0005	0.001754
Co	59	Cobalt	Mr	0.004	0.014035
Cu	63	Cupper	Mr	0.03	
Er	166	Erbium	Lr	0.0003	0.001053
Au	197	Gold	Lr	0.0002	0.000702
Fe	56	Iron	Mr	0.02	0.070175
La	139	Lanthanum	Mr	0.002	0.007018
Pb	208	Lead	Lr	0.002	0.007018
Lu	175	Lutetium	Lr	0.0002	0.000702
Mg	24	Magnesium	Mr	0.1	0.350877
Mn	55	Manganese	Mr	0.006	0.021053
Hg	202	Mercury	Lr	0.001	0.003509
Nd	146	Neodymium	Lr	0.0002	0.000702
P	31	Phosphor	Mr	0.4	1.403509
Pr	141	Praseodymium	Lr	0.0003	0.001053
Rb	85	Rubidium	Mr	0.012	0.042105
Sm	147	Samarium	Lr	0.0005	0.001754
Se	82	Selenium	Lr	0.05	0.175439
Na	23	Sodium	Mr	10	35.08772
Sr	88	Strontium	Mr	0.025	0.087719
S	34	Sulphur	Mr	20	70.17544
Tl	205	Thallium	Lr	0.00025	0.000877
Th	232	Thorium	Lr	0.0005	0.001754
Sn	118	Tin	Lr	0.001	0.003509
U	238	Uranium	Lr	0.00025	0.000877
V	51	Vanadium	Mr	0.003	0.010526
Y	89	Yttrium	Lr	0.0004	0.001404
Zn	66	Zink-66	Mr	0.025	0.087719

Lr, Mr, Hr = Low, Medium and High Resolution
DL, IDL= Detection limits. Instrumental detection limits