



Short Communication

A screening of select toxic and essential elements and persistent organic pollutants in the fur of Svalbard reindeer



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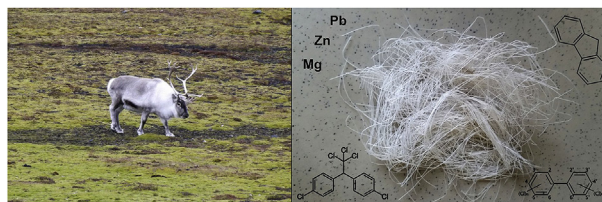
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HIGHLIGHTS

- A first indication of Ca, K, Mg, Mn, Se, Sr in Svalbard reindeer fur.
- Semi-volatile PAHs detected at low levels.
- PCB28 and DDT metabolites found in most samples.

GRAPHICAL ABSTRACT



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ABSTRACT

Reindeers play an important role in the polar ecosystem, being long-lived sole vegetarians feeding on local vegetation. They can be used as a valuable bioindicator, helping us to understand contaminants' impact on the polar terrestrial ecosystem. Still, scarce data exist from research in which polar herbivores (especially those from the European parts of the Arctic) were a major study subject for trace elements and persistent organic pollutant determination. Here, Svalbard reindeer fur has been used to determine metals, non-metals and metalloids using ICP-MS, and several persistent organic pollutants including polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) using gas chromatography coupled to a tandem mass spectrometer (GC-MS/MS). Samples were collected from reindeer populations living in the area near Ny-Ålesund and Longyearbyen. Essential elements like Fe, Mg, Zn, K, Ca, Cu predominated in the trace elements profile. Median values of As, Cd, Co, Li, Ni, Se and V were all below 0.5 µg/g dw. Mercury was below detection limit in all samples, while the Pb median varied from 0.35 to 0.74 µg/g dw. Except acenaphthylene and fluorene, PAHs were detectable only in samples collected in the vicinity of Longyearbyen. Of 15 studied pesticides, only DDT and its metabolites were above the detection limit, and, of PCBs, only PCB28.

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1. Introduction

Arctic herbivores, though they have a crucial impact on polar ecosystems, are rarely included in ecotoxicological studies, especially those from the European part of the Arctic. Due to the

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prevalent climate conditions, with cold, dense air and darkness in winter time, the possibility of compound deposition and accumulation in Arctic is increased, which may lead to the accumulation of those compounds in higher trophic level species (Halbach et al., 2017). Svalbard (74–81°N), is part of the European Arctic, and subject to the long-range transport of contaminants. Due to its unique geographical location, it has become a significant recipient of contaminants emitted at mid and low latitudes and transported by air and sea currents into Arctic areas (Braune et al., 2005; de Wit et al., 2004; AMAP, 2005; Halbach et al., 2017). While contaminants are to some extent introduced into the Arctic environment from local natural sources, it is assumed that emission transported long-range from Europe and Asia is majorly responsible for the non-essential metals and persistent organic pollutants levels observed in the polar region (AMAP, 2005, 2011; Reimann and de Caritat, 2005; Eckhardt et al., 2007; Halbach et al., 2017; Zaborska et al., 2017). Contaminants may also be transported from the marine environment to land by biovectors such as seabirds (Choy et al., 2010) and by volcanic activity, as well as being redeposited from glaciers and soil (Samecka-Cymerman et al., 2011; Zaborska et al., 2017; Koziol et al., 2017). Additionally, increasing research and tourist activities, and runoffs from coal mines, may add to the local contamination (Granberg et al., 2017; Aslam et al., 2019; Wojtuń et al., 2019).

Feeding ecology and preferences have a major effect on the intake of contaminants (Bocharova et al., 2013). In terrestrial ecosystems, the bioaccumulation process would be affected by different physiological and ecological factors than in marine ecosystems (van den Brink et al., 2015). Trace elements can be divided into groups, as some of them are essential for proper functioning (e.g. Zn, Se, Cu), while others are toxic without any known beneficial role in the organism (e.g. Hg or Pb) (Eisler, 1987; Burger and Gochfeld, 2000a,b; Peakall and Burger, 2003). Essential elements may also be toxic in excessive quantities (Burger and Gochfeld, 2000b; Peakall and Burger, 2003). Persistent organic pollutants are a group of contaminants with properties that provide them a high bioaccumulation potential (lipophilicity, persistence in the environment, volatility). They are usually produced in processes associated with anthropogenic activities, and transported long distances to the Arctic. Several studies confirmed the presence of polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs) in the polar biota (see references in Letcher et al., 2010 and Marquès et al., 2017). PCBs and OCPs have potential negative biological effects and thus are frequently studied compounds in polar research (Jones and Voogt, 1999; Jaspers et al., 2010; Letcher et al., 2010). PAHs may have natural or anthropogenic origin, since, for example, pyrogenic PAHs can be emitted during incomplete combustion of fossil fuels and organic matter (Balmer et al., 2019). The PAHs found in terrestrial compartments (including soil and sediments) mostly originate from atmospheric and combustion-derived sources (Balmer et al., 2019).

Contaminant upload and redistribution is an essential factor that may affect a species' ability to survive changes connected with climate warming. Non-lethally and non-invasively collected samples have been gaining much attention recently, including keratinised tissues such as mammal fur or the feathers of bird species (D'Havé et al., 2005; Duffy et al., 2005; Jaspers et al., 2006; Pacyna et al., 2018; Pacyna et al., 2019a). Fur collection does not imply any harm to the animal, storage is relatively easy, compounds do not metabolise and tissue levels correspond to long-term exposure (Duffy et al., 2005; Jaspers et al., 2010). Hair samples have been proven to be a useful matrix for biomonitoring of trace elements and several POPs (Duffy et al., 2005; Jaspers et al., 2010; Pacyna

et al., 2018). However, due to the low lipid content of hair, POP levels in them can be low, comparing to internal tissue (D'Havé et al., 2005; Jaspers et al., 2010), and thus, depending on contaminant concentration, hair mass should be appropriately high for reliable quantification (Covaci et al., 2002; Jaspers et al., 2006).

Here, we intend to add new data related to the only large grazing mammal in the European High Arctic – the Svalbard reindeer (*Rangifer tarandus platyrhynchus*). This endemic, widespread resident of Svalbard is exposed to contaminants mostly through its diet, which is composed of different types of locally grown vegetation, lichen and moss (Robillard et al., 2002; Węgrzyn et al., 2018, 2019). The present study describes the concentrations of 18 elements, 16 polycyclic aromatic hydrocarbons (PAHs), 10 polychlorinated biphenyls (PCBs), and 15 organochlorine pesticides (OCPs) in the moulted fur of Svalbard reindeer. Moulted fur (shed by the reindeer during the natural process of renewing their coats) was used, as it does not require direct contact with an individual, eliminating the stress factor for an animal. The main goal of this study was to investigate the distribution pattern of contaminants, and to depict their possible co-exposure and/or similar bioaccumulation and excretion patterns. It also serves to provide background data on the levels of POPs and six elements not studied before in reindeer fur. Moreover, comparison analysis between elemental contents in reindeer fur collected in 2015 in a previous study (Pacyna et al., 2018) and here was performed to investigate differences in element concentration in time. To the best of our knowledge, the present study is the first to examine organic compounds and Ca, K, Mg, Mn, Se and Sr in Svalbard reindeer fur and the second for the other elements analysed.

2. Materials and methods

2.1. Study site and sampling

Sampling was conducted in the 2017 summer season in Spitsbergen in two locations, in the vicinity of Longyearbyen (15°35'/15°39'E, 78°02'/78°13'N) and in the vicinity of Ny-Ålesund (11°48'/12°04'E, 78°54'/78°55'N) (Fig. 1). Spitsbergen is the largest island in the Svalbard archipelago, and Longyearbyen, being the administrative centre of Svalbard, represents the largest settlement on the island. The Longyearbyen area can be affected by local contamination sources, including exhausts from power plants, industrial waste dumps, and coal mines (Wojtuń et al., 2019). The northernmost settlement of Ny-Ålesund has visitors only for research purposes.

Reindeer fur grows at a specific time and the coat is replaced seasonally. Contaminants deposited in hair tissue reflect blood concentrations at the time of hair growth (Jaspers et al., 2010). Freshly moulted fur was collected manually from the ground into separate string bags. All reindeer fur samples (n = 8 in total) were collected at a given location within one day. Samples were collected in places where reindeers wiped their winter fur on the ground. The sampling localities were about 1 km apart. Individual reindeers were identified by observation from a distance so as to avoid having the same animal's fur collected on repeat occasions. Samples were stored at ambient temperature.

2.2. Chemical analysis

To prevent possible interferences caused by different melanin contents, only white hairs were analysed. Hair strands were separated manually from the collected sample with clean tweezers to separate them from any moss debris or soil collected with the fur ball. To remove adherent external contamination such as dust



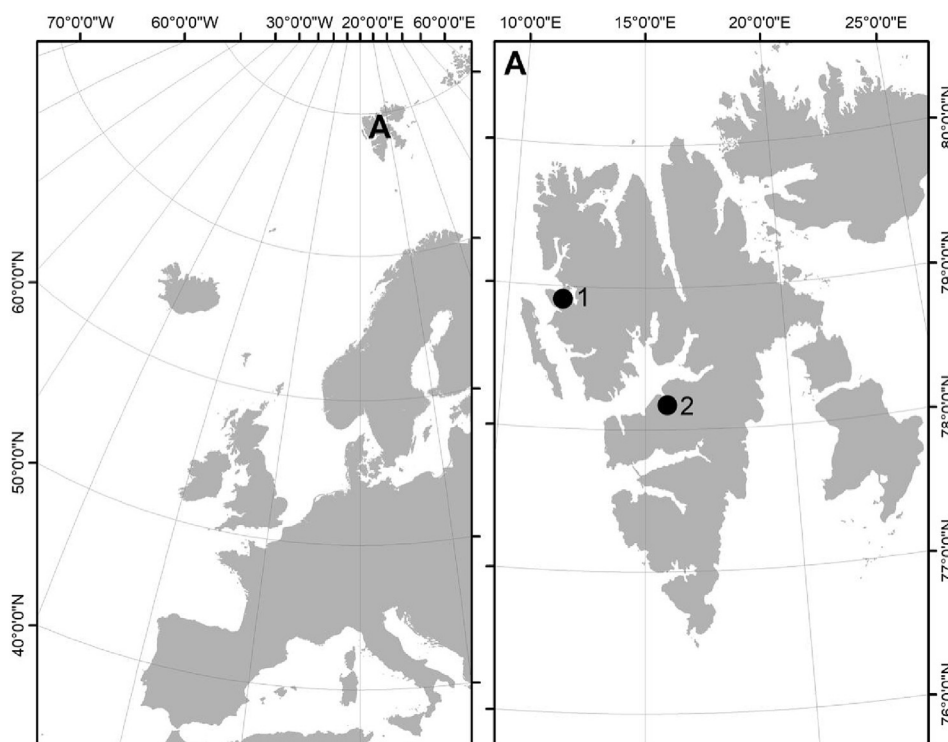


Fig. 1. Study site showing area where Svalbard reindeer fur was collected: A – Svalbard Archipelago, 1 – Ny-Ålesund, 2 – Longyearbyen, map source: Norwegian Polar Institute, www.npolar.no.

particles and loosely bound particulate matter, each pooled sample from one individual was cleaned at least 3 times in double-deionised water (Milipore Mili-Q, France) and then air-dried for 24 h. Organic solvents were not used for cleaning purposes, as they may wash out elements of interest from the hair's internal structure (Jaspers et al., 2010). Then, an appropriate sample amount from each individual (sample mass is given below for each group) was taken for separate analysis. Analysis was performed for: 18 elements (As, Ba, Ca, Cd, Co, Cu, Fe, Hg, K, Li, Mg, Mn, Ni, Pb, Se, Sr, Zn, V); 16 PAHs (naphthalene; acenaphthylene; 2-bromo-naphthalene; acenaphthene; fluorene; phenanthrene; anthracene; fluoranthene; pyrene; benz[a]anthracene; chrysene; benzo[b]fluoranthene; benzo[a]pyrene; indeno[1,2,3-cd]pyrene; dibenz[a,h]anthracene; benzo[ghi]perylene); 10 PCBs (28, 52, 77, 101, 118, 126, 138, 153, 169, 180); and 15 OCPs (alfa-, beta-, delta-hch, hexachlorobenzene, heptachlor, mirex, aldrin, dieldrin, endrin, op-DDT, pp-DDT, op-DDE, pp-DDE, op-DDD, pp-DDD).

2.2.1. Metals, non-metals and metalloids

Dried samples were cut with clean stainless-steel scissors. About 150–170 mg of sample was then weighed, and 10 ml of 65% HNO₃ was added. Samples were digested using a high-pressure microwave emitter (Microwave Digestion System, Anton Paar). The temperature was increased from room temperature to 90 °C and such conditions were maintained for 25 min. After that, the temperature was gradually lowered. Subsequently, mineralised samples were diluted with double-deionised water to 25 ml in clean plastic flasks. To check accuracy, 3 randomly chosen samples were prepared in duplicates. Every batch contained blank samples, to ensure quality control and check for background contamination. Certificate reference material (CRM, Human hair ERM-DB001, Sigma-Aldrich) was used in triplicate to check the accuracy of obtained results. Analysis was performed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS 2030, Shimadzu, Japan).

Measurement conditions and parameters are reported in a previous study (Pacyna et al., 2019a).

2.2.2. Polycyclic aromatic hydrocarbons

Dried samples were cut with clean, acetone-rinsed stainless-steel scissors. Samples (mean 273 mg) were incubated overnight with 20 ml hexane:acetone (2:1), 7 ml 15% HCl and 10 µl internal standards (naphthalene-d8, benzo(a)anthracene-d12; c = 0.1 µg/ml). Next day, samples were vortexed and the organic layer was collected. A fresh solvent layer (5 ml of hexane:acetone 2:1 v:v) was added, the sample was vortexed again, and the organic layer was collected and combined with the previously collected layer into the same tube. Samples were evaporated until approx. 3 ml.

Clean-up was performed on SPE columns filled from the bottom with activated silica gel, and anhydrous Na₂SO₄. Columns were conditioned with 2 vol of hexane (2*2 ml), sample extract was added, and eluted using 2 vol of DCM: hexane (3:7 v:v) (2*3 ml). The volume was evaporated in a nitrogen stream until dry, and reconstituted in 300 µl of hexane. Determination was performed on a gas chromatography instrument coupled to a tandem mass spectrometer (Shimadzu GC-MS-TQ 8050) operating in Multiple Reaction Monitoring (MRM) mode. Measurement conditions and parameters are given in [Supplementary Table 1](#).

2.2.3. Pesticides and polychlorinated biphenyls

Dried samples were cut with clean, acetone-rinsed stainless-steel scissors. A modified procedure used by Jaspers et al. (2010) was applied. About 300 mg of the samples was incubated overnight with 25 ml hexane:DCM (4:1), 7 ml 4 M HCl and 10 µl internal standards (DDT-D8, PCB-28 C13 and PCB-180 C13, c = 0.1 µg/ml). Next day, samples were put in ultrasounds for 1 min, vortexed, and the organic layer was collected into a tube. A fresh solvent layer (2*10 ml of hexane:DCM (4:1v:v) was added, and the organic layer was collected again and combined into the same tube. Samples

were evaporated until approx. 3 ml. Clean-up was performed on SPE columns filled from the bottom with acidified silica gel and anhydrous Na₂SO₄. Columns were conditioned with 4 ml of hexane/DCM mixture (4:1, v/v), then sample extract was added and eluted using 2 vol of hexane/DCM (4:1 v:v) (2*4 ml). The volume was evaporated in a nitrogen stream until almost dry, and reconstituted in 200 µl of isoctane. Determination was performed by a gas chromatograph (Agilent 7890B) coupled to a tandem mass spectrometer (Agilent 7000D) (GC-MS/MS) operating in MRM mode. Measurement conditions and parameters are given in [Supplementary Table 1](#).

2.3. Quality QA/QC

The limit of detection (LOD) for trace elements, OCs and PCBs was calculated as the concentrations corresponding to a signal equal to three times the standard deviation of blank solution signal. For PAHs and compounds not detected in blank sample, LODs were calculated based on the standard deviation of the response (s), and the slope of the calibration curve (b) according to the formula: LOD 3.3(s/b). LOD was 0.004–0.92 ng/g dw for all elements, 0.013–0.38 ng/g dw for PAH, and 0.011–1.38 ng/g dw for OC and PCBs. Details for trace element quality control are reported in a previous study ([Pacyna et al., 2019a](#)). Mean recovery for internal standards was 133% for benzo[a]anthracene, 83% for DDT, 89% for PCB28 and 92% for PCB180. All studied compounds were blank corrected by a mean procedural blank value. Parameters used in MRM analysis are given in [Supplementary Tables 2a and b](#).

2.4. Data analyses

The U Mann–Whitney test was used to assess differences in elemental contents in reindeer fur collected in Longyearbyen in 2015 (previous study by [Pacyna et al., 2018](#); excluding three outliers with Fe level higher than 5000 µg/g dw) and 2017. Levene's test was performed to assess the equality of variances, while the Shapiro–Wilk test helped determine the normality of the data set. The statistical analyses were carried out using STATISTICA 13 (Statsoft, Tulsa, OK, USA).

3. Results

Mean ± SD and median for all elements are listed in [Table 1](#) and in [Table 2](#) for organic pollutants. The highest concentration based

Table 1
Results for 18 analysed elements, mean ± SD (median) µg/g dw.

Element	Longyearbyen (n = 5)	Ny-Alesund (n = 3)
As	0.102 ± 0.067 (0.072)	0.196 ± 0.167 (0.118)
Ba	1.42 ± 0.68 (1.01)	1.46 ± 0.38 (1.40)
Ca	42.00 ± 10.03 (42.0)	109.4 ± 128.4 (44.8)
Cd	0.026 ± 0.008 (0.023)	0.309 ± 0.469 (0.044)
Co	0.424 ± 0.558 (0.178)	0.768 ± 0.823 (0.402)
Cu	5.23 ± 0.52 (5.37)	6.57 ± 0.47 (6.43)
Fe	180.3 ± 238.2 (92.9)	379.9 ± 406.4 (190.3)
Hg	<LOD	<LOD
K	55.0 ± 22.0 (59.9)	31.1 ± 32.2 (18.2)
Li	0.191 ± 0.250 (0.089)	0.251 ± 0.181 (0.214)
Mg	86.0 ± 90.8 (45.6)	1275.5 ± 2088.4 (85.3)
Mn	2.85 ± 3.00 (1.48)	4.50 ± 4.30 (3.05)
Ni	0.134 ± 0.173 (0.047)	0.519 ± 0.496 (0.244)
Pb	0.471 ± 0.327 (0.354)	0.796 ± 0.444 (0.743)
Se	0.167 ± 0.022 (0.163)	0.182 ± 0.029 (0.187)
Sr	2.04 ± 1.26 (1.79)	8.24 ± 13.3 (0.642)
V	0.198 ± 0.302 (0.098)	0.440 ± 0.581 (0.147)
Zn	52.7 ± 7.25 (49.6)	73.1 ± 22.2 (73.7)

on median value was found for the essential elements Fe, Mg, Zn, K, Ca, Cu. The median values of As, Cd, Co, Li, Ni, Se and V were all below 0.5 µg/g dw. A Pb level above 0.5 µg/g dw was found only in Ny-Ålesund samples (median 0.743 µg/g dw). This is the first report on Se in Svalbard reindeer fur, which was at a similar level in all samples (median 0.163–0.187 µg/g dw). Sr, Mn and Ba were all below 2 µg/g, with the exception of Mn from Ny-Ålesund. Mercury was <LOD in all samples.

Comparison of metal contents in reindeer fur was performed for samples collected in the vicinity of Longyearbyen in 2015 (study by [Pacyna et al., 2018](#)) and 2017. The majority of studied elements significantly differed between 2015 and 2017 ([Fig. 2](#); [Supplementary Table 3](#)). Among eleven analysed elements (As, Ba, Cd, Co, Cu, Fe, Li, Ni, Pb, V, Zn) only Co, Li and Zn did not reveal significant differences in their contents between the compared years ([Fig. 2](#); [Supplementary Table 3](#)).

Of the 15 studied pesticides, only DDT and its metabolites were above detection limit, with the highest values found for p,p-DDD, in a single sample from Longyearbyen (57.5 ng/g dw). However, with the exception of this one outlier, p,p-DDD level was much lower in the rest of the samples (median value 1.44 ng/g dw). PAHs and PCBs were mostly below LOD in samples collected in Ny-Ålesund, and the only exceptions were fluorene (0.152 ± 0.166 ng/g dw) and PCB28 (1.39 ± 0.40 ng/g dw). Fifty percent of studied PAHs were detected in at least one fur sample from Longyearbyen, but for acenaphthylene, naphthalene, 2-bromo- and fluorene only, more than 65% of the samples were above LOD ([Table 2](#)). Of 10 PCB congeners, only PCB28 was found (1.38 ± 1.17 ng/g dw).

4. Discussion

The Svalbard reindeer is highly stationary, and reluctant to migrate beyond its territory, which is mostly established by natural barriers such as glaciers and steep mountains ([Hansen et al., 2010](#)). It eats locally growing vegetation including vascular plants, bryophytes and lichens, all determined to accumulate high levels of essential and non-essential elements (e.g. [Samecka-Cymerman et al., 2011](#); [Wojtuń et al., 2019](#)). Thus it can be a valuable indicator of local contamination.

Svalbard plants have high levels of Zn, Fe and Mn, resulting in high availability of those elements for herbivores ([Hanaka et al., 2019](#); [Aslam et al., 2019](#)). Previously significant differences between the concentrations of several elements were found between foraging sites and seasons, based on reindeer droppings ([Pacyna et al., 2019b](#)). The elemental profile in soil and vegetation from Svalbard was shown to be similar, but with differences in elemental concentrations occurring between the sample types ([Aslam et al., 2019](#)). Here, seven elements had concentrations above 5 µg/g dw, with more than 40 µg/g dw found for Fe, Mg, Ca, K and Zn ([Tables 1 and 3](#)). The level of Mn in fur was also relatively high, with mean values of 2.85–4.50 µg/g dw. The elemental profile in plants growing in the High Arctic (Fe > Zn ≥ Mn > Ni ≥ Pb > Cu ≥ Cd; [Hanaka et al., 2019](#)) is mostly in agreement with our findings on element profiles in reindeer fur ([Table 3](#)). This suggests that reindeers can deposit excess amounts of elements accumulated from their diet, and that fur can be used to track their exposure.

In a previous study by [Pacyna et al. \(2018\)](#) the concentrations of 18 elements were analysed in Svalbard reindeer fur samples collected from two separate subpopulations (living in proximity to Longyearbyen and the Polish Polar Station in Hornsund). Of those, 12 (As, Ba, Co, Cd, Cu, Fe, Hg, Li, Ni, Pb, V and Zn) were also studied here, thus comparison between them is possible. Cu, Fe and Zn were found in all samples in high concentrations, with Fe having been at a much higher level in a previous study (median value

Table 2

Results for the found persistent organic pollutants, mean \pm SD, and minimum/maximum value, results in ng/g dw. Mean is calculated only when 65% of the samples were above LOD.

Compound	Longyearbyen (n = 5)	min-max	Ny-Ålesund (n = 3)	min-max
Naphthalene	<LOD	<LOD-0.068	<LOD	<LOD
Acenaphthylene	0.034 \pm 0.022	<LOD-0.058	<LOD	<LOD-0.040
Naphthalene, 2-bromo-	0.035 \pm 0.019	<LOD-0.053	<LOD	<LOD
Fluorene	0.385 \pm 0.236	0.020–0.595	0.152 \pm 0.166	<LOD-0.334
Phenanthrene	<LOD	<LOD-0.034	<LOD	<LOD
Anthracene	<LOD	<LOD-0.093	<LOD	<LOD
Fluoranthene	<LOD	<LOD-0.257	<LOD	<LOD
Indeno[1,2,3-cd]pyrene	<LOD	<LOD-0.025	<LOD	<LOD
Benzo[ghi]perylene	<LOD	<LOD-0.022	<LOD	<LOD
PCB28	1.38 \pm 1.17	<LOD-2.65	1.39 \pm 0.40	0.84–1.79
p,p-DDE	<LOD	<LOD-1.54	<LOD	<LOD-1.29
p,p-DDT	<LOD	<LOD-4.24	<LOD	<LOD
o,p-DDT	<LOD	<LOD-4.21	<LOD	<LOD-0.51
p,p-DDD	2.66 \pm 2.85 ^a	0.84–57.5	<LOD	<LOD-3.61

^a One outlier removed from the mean, but is shown as the maximum value.

494–602 $\mu\text{g/g dw}$, Pacyna et al., 2018). In samples collected in 2015 (those reported in Pacyna et al., 2018), Fe levels in samples from around Longyearbyen were almost 6.5 times higher than those reported here, and 3 times higher than the present results in samples from Ny-Ålesund. This huge difference may be partially caused by the difference in sample size, as here only 8 samples in total were analysed. In a previous study 3 outliers with extraordinary levels of Fe were found, indicating that some individuals were feeding on more contaminated food. This difference may also be caused by differences in local geological conditions in Svalbard (Halbach et al., 2017), and the ability of moss to sequester high amounts of trace elements (Wojtuń et al., 2019). In Longyearbyen, mining activities and a power plant may be sources of local contamination, creating hotspots of increased element abundance (Marquès et al., 2017; Wojtuń et al., 2019). The runoffs from mines are characterised by high levels of elements such as Fe, Mn, Ni, Cu and Zn (Sřndergaard et al., 2007; Granberg et al., 2017; Aslam et al., 2019). Thus, depending on sample site, high differences in element concentrations can be found in soil and vegetation, e.g. in moss *Sanionia uncinata* levels varied from 4240 to 13,300 $\mu\text{g/g dw}$ for Fe, from 30 to 261 $\mu\text{g/g dw}$ for Zn, and from 3.4 to 55 $\mu\text{g/g dw}$ for Cu (Marquès et al., 2017; Wojtuń et al., 2019).

Mercury accumulates in the surface soil layer, and is available for vegetation. It was found in concentrations of $0.111 \pm 0.036 \mu\text{g/g}$ in Svalbard surface soils, and mostly originated from atmospheric deposition (Halbach et al., 2017). Hg levels in moss *Sanionia uncinata* and the dwarf-shrub *Salix polaris*, a widely distributed species, were found to be low, at $<0.013\text{--}0.12 \mu\text{g/g}$ (Samecka-Cymerman et al., 2011; Wojtuń et al., 2013, 2019; Krajcarová et al., 2016). Here, mercury was undetectable, and in the previous study was also at a very low level (median $0.06\text{--}0.13 \mu\text{g/g dw}$) (Pacyna et al., 2018). As keratinised tissue is usually a target tissue for mercury (Monteiro and Furness, 1995), it seems that it is not currently a concern for Svalbard reindeer.

Several factors affect atmosphere transport of Cd, with the most significant being aerosol particle size, temperature, height of release, wind speed and precipitation conditions (AMAP, 2005; Aslam et al., 2019). Both here and in the previous study (Pacyna et al., 2018) Cd were at low levels, below $0.5 \mu\text{g/g dw}$. Cobalt, lithium and zinc levels were comparable between studies (Fig. 2, Pacyna et al., 2018). Lead levels were higher in a previous study, with seven individuals having more than $4 \mu\text{g/g dw}$ Pb in fur. Here, Pb level was more equally distributed, with a concentration range of $0.12\text{--}1.26 \mu\text{g/g dw}$.

PAHs are a class of lipophilic semi-volatile organic compounds, originating mainly from incomplete combustion processes such as

burning of fossil fuels and biomass (Wang et al., 2009; Balmer et al., 2019). Soil is one of the major sinks for PAH deposition (Wang et al., 2009; Marquès et al., 2017), but atmospheric PAHs may also be deposited in sediments and surface water by wet and dry deposition, and as a secondary emission re-volatilised from ground surfaces (Balmer et al., 2019). PAHs can also be accumulated in the snow and be transferred into soil during ice-snow melting process (Kozioł et al., 2017).

Moss tissue can also accumulate PAHs. A study from Ny-Ålesund found the concentration of ΣPAH_{16} in moss to vary from 158 to 244 ng/g dw, while levels in reindeer dung were from 49 to 340 ng/g dw (Wang et al., 2009). Soil was characterised by a higher percentage of median and higher molecular weight PAHs, whereas both moss and reindeer dung had a higher percentage of low molecular weight PAHs, such as naphthalene, acenaphthylene, acenaphthene and fluorene (Wang et al., 2009). This difference in distribution between those three components was probably caused by the physicochemical properties of individual PAHs, meteorological conditions, different uptakes, as well as differences in accumulation routes, with soil accumulating PAHs mostly through dry/wet deposition, and moss sequestering PAHs from the vapour phase. The composition profiles of PAHs in reindeer dung and moss varied only insignificantly (Wang et al., 2009).

Although they have lipophilic properties, PAHs are subject to biotransformation processes, and can be readily metabolised in vertebrates and seem not to biomagnify through food chains (Hylland, 2006; Wan et al., 2007). Here, mostly lighter PAHs with 2 and 3 rings were detected, predominantly in samples collected from the area close to Longyearbyen where beside long-range transport, coal mining activities and human settlement may also be sources of parent PAHs. Coal mining has gone on in Svalbard for almost 100 years, but most of the mines are now closed, with the exception of Mine 7 in Longyearbyen (Aslam et al., 2019; Wojtuń et al., 2019). Previous reports from this region revealed high PAH levels in soils collected close to the power plants (coal- and diesel-fired) (Marquès et al., 2017).

As primary emissions of several POPs were significantly reduced, the concern about secondary re-emissions on the atmospheric levels in the High Arctic have arisen (Hung et al., 2005; Eckhardt et al., 2007; Balmer et al., 2019). Biomass-burning emissions are an important source of long-range transported PCBs and other POPs into the High Arctic (Eckhardt et al., 2007). PCB congeners – both lower and higher chlorinated (PCB 52, 66/95, 101, 118, 138, 153, 180) – can be bioaccumulated in reindeers (Kelly and Gobas, 2001), but some, such as PCB 52, can also be eliminated efficiently from the reindeer body (Kelly and Gobas, 2001).

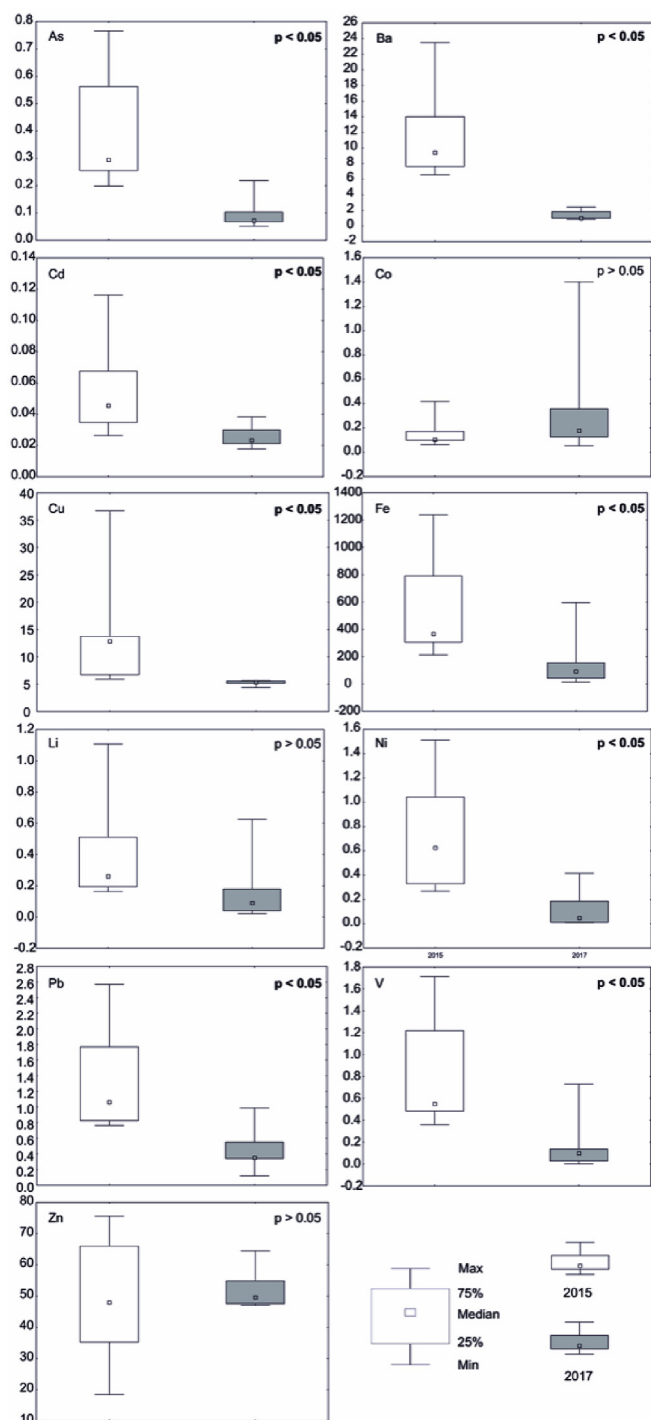


Fig. 2. Comparison between elemental concentration in fur samples collected from Longyearbyen ($n = 5$) with samples from Longyearbyen collected in 2015 in previous study by Pacyna et al. (2018) (excluding three individuals with Fe level higher than $5000 \mu\text{g/g dw}$; $n = 8$), $\mu\text{g/g dw}$.

PCB congeners were found in environmental samples from Ny-Ålesund and in the vicinity of Longyearbyen. The mean concentration of ΣPCBs was $0.57\text{--}10.8 \text{ ng/g dw}$ in soils, $0.30\text{--}56.3 \text{ ng/g dw}$ in vegetation (Zhang et al., 2014; Zhu et al., 2015; Aslam et al., 2019) and $0.56\text{--}39.6 \text{ ng/g dw}$ in reindeer dung (Zhang et al., 2014; Zhu et al., 2015). The PCB concentrations in vegetation from the Canadian high Arctic were lower – ΣPCB_{70} varied from 0.19 to 4.82 ng/g dw (Cabrerizo et al., 2018).

Here, levels of most PCB congeners were below quantification level, apart from PCB28. PCB28 presence in Svalbard is affected by emission from Western Russia and partially from Scandinavia and Eastern Europe (Ubl et al., 2012). Its concentration in the Arctic air is generally higher during summer, and correlated with temperature, which could suggest re-volatilisation of PCB28 from the surface deposits into the air when temperatures are high (Wania et al., 1998; Eckhardt et al., 2007). In the future there is a high possibility of increasing concentration of lighter PCB congeners in the Arctic components due to re-emission from the ocean and ice, as well as the microbial degradation of heavier PCBs (Hung et al., 2016; Fagervold et al., 2007; Aslam et al., 2019).

Several organochlorine pesticides have been detected in High Arctic biota (Letcher et al., 2010), but to the best of our knowledge, no OCPs have been analysed before in the fur of Svalbard reindeer. Organochlorine compounds were previously examined in the hairs of polar bears living in East Greenland (Jaspers et al., 2010). As the diet of those carnivores is composed in most part of fat-rich seals, the determined OCP levels in their internal tissue can be high (Gebbinck et al., 2008; Letcher et al., 2010), but a much smaller number of compounds was found in clean hair samples (Jaspers et al., 2010). As a possible reason for that, the authors suggest that the sample amount was too low for reliable determination of analysed pesticides above the limit of quantification ($13\text{--}140 \text{ mg}$), inefficient uptake into the hair of polar bears and the unique capacity of polar bears to metabolise p,p'-DDT and to a lesser extent p,p'-DDE (Letcher et al., 1998; Polischuk et al., 2002; Jaspers et al., 2010). Here, out of 15 studied OCS, only DDT and its metabolites were detected, mostly at low levels. Some studies suggest that reindeers also have the ability to metabolise or eliminate p,p-DDT, but cannot effectively metabolise the persistent metabolite p,p-DDE (Kelly and Gobas, 2001). More research is needed to understand mechanisms enabling this herbivore to eliminate OCS from its body.

5. Conclusion

The Svalbard reindeer is a long-lived herbivore that is part of a relatively simple food chain and can be used for monitoring changes in the terrestrial trophic network. Beside mercury, all studied elements could be quantified in the hair of Svalbard reindeer. In future studies, samples collected from the area close to Longyearbyen should be analysed in higher numbers, as the elemental concentration can be affected by locally created hotspots with elevated levels of contaminants. Here, essential elements like Fe, Mg, Zn, K, Ca, Cu were found in the highest concentrations. Further studies should be performed to examine whether high levels of those elements can be related to adverse health effects. Levels of most elements of ecotoxicological interest, such as As, Cd, Co, Hg and Ni were low, and currently not a threat to studied individuals. Only a few POPs could be determined, including PCB28, p,p-DDD and some of the parent PAHs. Reindeers living close to Longyearbyen had higher levels of POPs than those living close to Ny-Ålesund, where mostly research activities are performed. Thus it seems that local activities close to Svalbard's largest settlement may affect the contaminant levels in the local ecosystem. Further

Table 3

Comparison between element profiles in samples collected from studied populations and previous study from Pacyna et al. (2018), based on median value ($\mu\text{g/g dw}$), L1 – samples from Longyearbyen ($n = 5$), Ny-A – samples from Ny-Ålesund ($n = 3$), L2 – samples from Longyearbyen collected in 2015 ($n = 11$), H – samples from Hornsund, collected in 2016 ($n = 16$).

	>5 $\mu\text{g/g}$	5.0–0.5 $\mu\text{g/g}$	<0.5 $\mu\text{g/g}$
L1	Cu, Ca, K, Mg, Fe, Zn	Ba, Mn, Sr	As, Cd, Co, Hg, Li, Ni, Pb, Se, V
Ny-A	Cu, Ca, K, Mg, Fe, Zn	Ba, Mn, Pb, Sr	As, Cd, Co, Hg, Li, Ni, Se, V
L2	Ba, Cu, Fe, Zn	As, Pb, Ni, V, Cr, Rb	Co, Li, Hg, Cd, Be, Ga, Cs, La
H	Ba, Cu, Fe, Zn	As, Pb, Ni, V, Li, Cr, Ga, Rb, La	Co, Hg, Cd, Be, Cs

research with a larger sample size is recommended to confirm our findings and to draw more definitive conclusions on using Svalbard reindeer fur for biomonitoring of POPs.

Author contributions section

Aneta Dorota Pacyna-Kuchta: Conceptualization, Methodology, Validation, Formal analysis, Experimental, Writing - Original Draft, Writing - Review & Editing, Funding Acquisition, Paulina Wietrzyk-Pelka: Formal analysis, Writing - Original Draft, Writing - Review & Editing, Funding Acquisition, Michał Hubert Węgrzyn: Writing - Original Draft, Writing - Review & Editing, Funding Acquisition, Marcin Frankowski: Methodology, Validation, Writing - Original Draft, Writing - Review & Editing, Żaneta Polkowska: Writing - Original Draft, Writing - Review & Editing

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Appendix A. Supplementary data

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