Soil Contamination in High Arctic Areas of Human Impact, Central Spitsbergen, Svalbard

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Abstract

Thirty-one metals and fifteen PAHs were examined in soils of central Spitsbergen, high Arctic. One of the world's northernmost human settlements and natural tundra were sampled to estimate the local human impact and its range. The contamination caused by local sources is significant only in the closest vicinity, and is usually at least an order of magnitude lower than European limits. The metal concentrations are closely related to bedrock geology and they are at similar levels as elsewhere in Svalbard. The long-distance transport of contaminants was not found at a significant level.

Keywords: heavy metals, PAH, contamination, soils, Svalbard

Introduction

Ecosystems in the Arctic belong to the most sensitive to human impacts. A relatively simple food web causes even a minor amount of contaminants to influence a major part of the ecosystem. Although several reports on human impact exist [e.g. 1-3], there is currently no environmental assessment criteria specifically aimed at Svalbard [4]. While local sources of contamination can be identified and remedied, the Arctic is also subject to continuous long-distance transport of contaminants [1, 2, 5-7]. Among the most harmful pollutants are heavy metals and polycyclic aromatic hydrocarbons (PAH). The presence of heavy metals were studied

The aims of this paper are threefold:

- to present data on heavy metals and PAH concentrations in soils from a range of different settings in order to contribute to the growing body of reference material on pollution in the Arctic;
- to examine the relationship of their concentrations to the distance from local and remote sources of human impact; and

in different components of the environment: water [8], soils [9-11], plants [12, 13] and animals [3,14]. However, the studies were limited in both space and number of analyzed elements. The presence of PAHs were investigated in the Svalbard area, in marine biota and sediments only and their concentrations were found to be up to 30 times higher than assumed background levels [3, 15].

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3. to compare the data with existing information on local basement geology and soils in other parts of Svalbard.

Study Area and Sampling Sites

The investigated area is located in central Spitsbergen - the largest island of the Svalbard archipelago (Fig.1). Sampling was done at the northern reaches of Billefjorden (Fig 1.) - the innermost branch of Isfjorden. The geology of the study area is dominated by N-S trending Billefjorden Fault Zone [16], which divide main geological units along the fjord axis [17, 18].

Dotted areas-shallow water and tidal flats; isobath -5m is also marked. Svalbard in the Arctic is shown on the inset map (summer and winter sea ice extents are included).

The eastern side of Petuniabukta, where sampling sites D1, D2, S3 and S4 are located is dominated by the Middle and Upper Carboniferous carbonates, anhydrites and sandstones [18], and the western shore of Mimerbukta (sites P1-P4) is composed of conglomerates, sandstones, mudstones and coals of the Devonian and the Lower Carboniferous age [17]. The sampling sites are situated on the Holocene marine terraces, which were formed during glacioisostatic uplift. The lowest locations (Skottehytta and Pyramiden harbour are about 5m a.s.l.) emerged at least 3,000 years B.P.[19] - it is also the maximum time span for soil evolution at those points. The soils belong to initial loose soils and poorly developed soils, which are typical for rare vegetation and dry tundra ecosystems [20]. The plant cover is diversified and in the town of Pyramiden and close to a wooden house Skottehytta, anthropogenic influence on their composition is observed (Tab.1).

Most of the investigated sites were in direct influence of a Russian mining town - Pyramiden (sites P1-P3), where coal fields had been explored by the Soviet Trust Arktikugol since the World War II. The town was settled

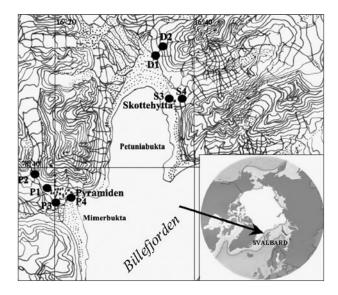


Fig.1 Location of the study area. Points D1-2, S3-4 and P1-4 represent sampling sites.

by 600-1200 persons and at that time it was one the world's largest northernmost human settlements. In 1994 most of the population was removed, and in March 1998 the mines were closed. In the period of the most intensive mining the exploitation reached even 250,000 tons of coal per year. The Pyramiden was supported with the whole infrastructure of harbour, heliport, farm, school, pool, greenhouses, roads, etc. In recent years some new drilling was done in search for oil and gas, one of the sampling sites was located in near vicinity of such a place (D1). Another site chosen for the study is the Skottehytta (S3). It was built in 1910 (or in 1920s) and since that time it serves as a temporal base for scientific and tourist expeditions. Samples were also collected from sites with no visible human impact to obtain background levels of concentrations (Tab.1).

Analytical Procedure and Materials

Samples were collected in July 2001 from the uppermost 20cm of the soil. The sampled range is the maximum depth for root systems of vascular plants.

For heavy and trace metals the samples were subjected to the following analytical procedure: (1) drying in air (room temperature); (2) extraction by 6 ml nitric acid and 5 ml hydrogen peroxide, for 1g of soil sample. Then, elemental analyses were performed (Tab.2) by the ICP MS method. The measurements were performed on an Elan 6100 DRC spectrometer (Perkin-Elmer) equipped with a concentric quartz nebulizer. The experimental parameters (plasma power, gas flow rate, integration time) for simultaneous determination of elements of interest were chosen to ensure the optimum signal-to-noise ratio. In most cases the precision of determination was bellow 0.5%. For comparison purposes, heavy metals concentrations were corrected for grain size effect according to the method of Ackermann [21], using rubidium as a grain-size proxy, measured as a part of the same analysis. Two certifield reference soil samples, namely SRM 2711 Montana Soil, NIST (for Al 6.53 ± 0.009 ; Ca 2.88 ± 0.08 ; Fe 2.69 ± 0.06 ; Mg 1.05 ± 0.03 ; P. 0.086 ± 0.007 ; K 2.45 ± 0.08 ; Si 30.44 \pm 0.19; Na 1.14 \pm 0.03; S 0.042 \pm 0.001; Ti 0.306 \pm 0.023; Sb 19.4 ± 1.8 ; As 105 ± 8 ; Ba 726 ± 38 ; Cd 41.70 ± 0.25 ; Cu 114 ± 2 ; Pb 1162 ± 31 ; Mn 638 ± 28 ; Hg 6.25 ± 0.19 ; Ni 20.6 \pm 1.1; Se 1.52 \pm 0.14; Ag 4.63 \pm 0.39; Sr 245.3 \pm 0.7; V 81.6 \pm 2.9; Zn 350.4 \pm 4.8 ppm) and RM SOIL S-1, Laboratory of Radiometric Analysis, Kraków (for As 3.4 ± 0.54 ; Co 3.90 ± 0.30 ; Mn 266 ± 18 ; Rb 52.0 ± 2.2 ; Zn 35 ± 3.3 ; Zr 620 ± 102 ; Cd 0.30 ± 0.08 ; Ce 44 ± 3.5 ; Cr 38 ± 9 ; Pb 15.0 ± 3.6 ; Sb 0.50 ± 0.09 ; Sc 4.00 ± 0.16 ppm) were analyzed to demonstrate the accuracy and precision of the method. The values of accuracy and precision were not only within the range of confidence but in agreement with the certifield values, which confirms that the method proposed can be successfully used.

Analytical procedure for PAHs was as follows:

- 1. drying in air (room temperature) in the dark;
- 2. fractionating sifting through a 2 mm sieve;
- 3. extraction (HPLC) by petroleum ether in portions of

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Table 1.	Summarized	data o	n investi	gated sam	piing sites.

Sample	D1	D2	S3	S4	P1	P2	Р3	P4	
Latitude	78°43.12'	78°43.30'	78°41.99'	78°42.02'	78°39.39'	78°39.59'	78°39.19'	78°39.25'	
Longitude	16°34.58'	16°34.64'	16°36.71'	16°36.90'	16°18.50'	16°17.25'	16°20.70'	16°21.45'	
Location	Drilling site	100m from D1	Skottehytta	50m from S3	Centrum of Pyramiden town	400m from P1	Fuel station in Pyramiden	Harbour in Pyramiden	
Dominating rock types	Limesto	nes covered wi	th local marine	gravels		Sandstones. shales and coal			
Soil type	Initial loose soils (regosols)		Poorly developed soils		Poorly developed soils	Poorly developed soils	Initial loose soils (regosols)	Initial loose soils (regosols)	
Plant cover	No dense tundra formation; in clumps occur: Papaver dahlianum. Draba alpina. Dryas octopetala. Polygonum viviparum. Saxifraga cespitosa. Salix polaris. Saxifraga oppositifolia Heath vegetation with: Salix polaris. Saxifraga oppositifolia. Polygonum viviparum and Cassiope tetragona. In S3 Saxifraga cernua was also observed, which may be related to human impact.		The human related species: Festuca rubra. Cerastium arcticum. Draba norvegica. Saxifraga cernua. Barbarea vulgaris. Oxyria digyna. Cochlearia groenlandica	Natural vegetation: Papaver dahlianum. Cassiope tetragona. Salix polaris. Silene uralensis		regetation			
Human impact	Drilling infrastructure; soil surface covered with spots of oil; vehicle tracks	Not visible	Wooden house from 1910; soil is destroyed; dump site of litter: ash, metal equipment, glass etc.	Not visible	Intensively changed soils; swimming pool and roads and pavements next to sampling site	Not visible	Fuel station, totally destroyed natural vegetation; a lot of coal dust; dump site for metal equipment	Dump site for mining and building parts	

100 and 50 ml, consecutively over 45 and 15 min, for 50 g of the sample in an ultrasound scrubber;

- 4. compacting on a centrifugal vacuum evaporator to a volume of 1 ml (purification by BACKERBOND SPE PAH columns with silica gel and a cyano phase previously conditioned with 3 portions of petroleum ether followed by 4 ml with the next elution and 3 portions of 3 ml acetonitrile and toluens mixture (HPLC);
- quantitative and qualitative analysis 20 μl of analyte. Shimadzu chromatograph with a Supelcosil column (150 mm length and a diameter of 4 mm - PAHs C₁₈) was used to separate the determined PAHs by the HPLC method. The mobile phase employed an acetonitrile - water system administered in gradient of concentrations from 45 to 95% of acetonitrile over 35 minutes at a through flow rate;
- 6. extraction (TLC) by 50 ml of methanol for 25 min, 5 g sample in an ultrasound scrubber and compacting until dry on vacum evaporator;

- 7. exchange of solvent dissolution of the dry remains in 10 ml of petroleum ether;
- 8. quantitative and qualitative analysis 2 ml of analyte.

In order to determine and separate PAHs using the TLC method, a bi-directional chromatographic technique was employed [26] and the plates covered with a mixture of aluminium oxide and acetylated cellulose. A quantitative assessment was conducted by comparing the intensity of spot fluorescence for individual compounds in UV light. A Shimadzu chromatograph with a Supelcosil column (150 mm lengh and a diameter of 4 mm - PAHs C₁₈) was used to separate the determined PAHs using the HPLC method. The mobile phase employed an acetonitrile-water system administered in a gradient of concentrations from 45 to 95% of acetonitrile over 35 minutes at a through flow rate of 1.3 to 1.5 ml/minute. Identification of peaks of particular PAHs was conduted by means of a UV diode-array detector (SPD - M10AV) using wavelengths of 254 and 300nm, respectively.

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Table 2. Results (in ppm) obtained with ICP MS technique for element concentrations in the studied samples. The legal limits for soils according to Polish norm (PN) [22] are included for comparison.

	Sample D1	Sample D2	Sample S3	Sample S4	Sample P1	Sample P2	Sample P3	Sample P4	PN
Al	257.52	34.56	177.91	151.98	277.25	47.35	229.53	38.77	-
As	0.0952	0.0038	0.0821	0.0601	0.182	0.0526	0.163	0.0319	20
Sb	0.00006	0.00002	0.0021	0.00053	0.0027	0.00011	0.00056	0.0001	-
Se	0.0252	0.0086	0.0262	0.0242	0.0388	0.0056	0.02651	0.0036	-
T1	0.0107	0.0023	0.0039	0.0036	0.0042	0.0007	0.0049	0.0006	-
Ba	1.18	2.29	3.51	2.42	23.17	0.973	11.16	0.566	200
Co	0.172	0.0598	0.233	0.239	0.326	0.071	0.35	0.0654	20
Cu	0.301	0.122	0.608	0.369	1.19	0.15	0.83	0.324	30
Ni	0.961	0.411	0.582	0.478	0.728	0.154	0.799	0.296	35
Pb	0.455	0.144	0.972	0.787	9.33	0.235	0.641	0.154	50
Cr	0.781	0.133	0.549	0.471	0.724	0.105	0.745	0.167	50
Mn	4.7	2.3	8.5	8.82	7.32	3.01	78.07	2.12	-
Fe	282.03	29.38	389.8	292.81	305.02	112.75	373.44	250.25	-
Ве	0.0255	0.0068	0.0244	0.0191	0.0441	0.0119	0.033	0.0095	-
Cd	0.0228	0.0075	0.0154	0.0085	0.0099	0.0016	0.0076	0.0013	1
Mg	1158.31	284.58	633.69	624.12	118.29	23.52	173.66	25.12	-
Ti	0.261	0.052	3.2	3.86	5.2	0.0348	2.79	0.0572	-
Zr	0.0752	0.0013	0.0897	0.0728	0.412	0.0106	0.237	0.0125	-
Zn	0.848	0.582	2.28	12.77	6.33	0.4859	2.9	0.5051	100
Mo	0.0602	0.00005	0.0415	0.029	0.0328	0.003	0.0173	0.0118	10
Те	0.00019	0.00002	0.00031	0.00026	0.0016	0.00016	0.00052	0.00015	-
Sn	0.0043	0.00004	0.418	0.0537	0.0805	0.00092	0.0527	0.005	20
Li	3.18	0.663	0.646	0.535	1.04	0.255	0.819	0.234	-
В	0.441	0.109	0.462	0.257	0.493	0.0194	0.3	0.0268	-
V	0.751	0.036	0.716	0.662	0.604	0.0816	0.699	0.0652	-
Sr	5.23	9.29	5.61	2.63	19.72	0.0853	2.24	0.219	-
Rb	0.384	0.0773	0.282	0.416	0.374	0.0779	0.429	0.0483	-
Ce	0.281	0.11	1.06	0.937	1.57	0.117	0.993	0.103	-
U	0.104	0.0765	0.0498	0.0397	0.0268	0.0082	0.0261	0.0032	-
Sc	0.0873	0.0237	0.0977	0.0894	0.138	0.0202	0.118	0.01456	-
La	0.166	0.0769	0.397	0.345	0.95	0.04	0.353	0.0391	-

•**Results** Heavy Metals

The results of the determination of the concentrations of several investigated elements are presented in Tab.2. In most cases in-between sample variations is very low only in the case of Mg, Cd, Sr, Zr, Al. The samples can be grouped in two - from western Petunia-

bukta (D1, D2, S3, S4) and from Mimerbukta region (P1-P4). This could be related to a bedrock geology on an element's concentrations. An example is shown in Fig.2, where a discrimination diagram between clastic (sandstone, mudstone) rocks and carbonate (limestone, dolomite) rocks support the relationship. However, for samples taken from the same geological setting the difference in concentrations can be related to human

impact (e.g. Mg and Cd in Pyramiden). The most commonly reported heavy metals are shown in Fig.3. Pb, Zn and Cr show concentrations which are relatively elevated in the samples from sites of human impact. Nethertheless, the values are far below European legal norms [e.g. 22].

A comparison of results obtained from samples of the same location but which differ in human impact shows that in all the cases the anthropogenically influenced places have higher values of most of the analyzed elements. At the drilling site all the elements are elevated in comparison to the site (D2) 100m further. Only Ba and Sr are more common in the D2 site, The increase in D1 is especially visible in As, Zr, Mo, and Sn. In the vicinity of Skottehytta values at the both sites (S3 and S4) are similar to that at D1. They are slightly higher Pb values near Skottehytta. In the direct vicinity of the house only Sb, Cd and Sn are more common than at S4, on the other hand S4 has higher values of Zn. In Pyramiden sites P1 and P3 have the highest values of the most elements, and P4 concentrations are close to the ones of the P2 (used as background). The values of impacted sites (D1, S3, S4) lie in between them. Evidently the highest values are in sample P1 - it is especially expressed in the amount of Pb. Unexpectedly very low contaminations are in P4, which is in fact almost at background level.

PAHs

PAHs were analyzed with the help of two techniques: with HPLC (Tab.3) and TLC (Tab.4). Evidently, elevated concentrations are observed in samples D1, S3, P3 and P4 although their concentrations in most cases do not reach $100\mu g/kg$. In the impacted soils the common PAHs varied between 42 and $48\mu g/kg$ for naphtalene, 8 and $14\mu g/kg$ for anthracene, and 10 to 12 for fluorene. The highest concentrations are found in sample S3 (dump-site) and P3 (fuel station), and the lowest in reference sites D2 and S4.

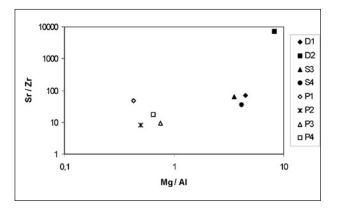


Fig.2. Discrimination diagram to divide carbonate rock (usually with higher Sr and Mg content) and clastic rock related soils (often with elevated Zr and Al.). Note the logarithmic scale.

Discussion and Conclusions

The obtained results confirmed that heavy metals and PAHs have locally elevated concentrations at places where human impact was observed. The comparison with the reference sites supports the hypothesis of a very local distribution of pollutants. However, it should be underlined that the heavy metals and PAHs are not remedied in the same way. As an example, we can serve reference site S4, which does not differ significantly from the S3 in the metal concentrations, but is depleted in PAHs. A reverse situation can be observed in the Pyramiden harbour.

In the studied case the influence of the bedrock geology on soil geochemistry is strong (Fig.2), and some of the minor fluctuations can be considered as dependent on local rock type. The drilling site (D1) and nearby sampling point D2 can be influenced by migration of elements and compounds along the tectonic zone [16,23]. This could be indicated by elevated concentrations of uranium and selected PAHs (underlying rocks are prospected for oil and gas). Rachlewicz et al. [unpublished] observed also in the direct vicinity a small stream which was flowing even after several days below zero temperatures, which would also indicate deep circulation patterns in that place.

Comparison of the total values with European legal norms [22] or areas, which are industrially contaminated [24,25] show that the concentrations of pollutants in the studied soils are at least one order of magnitude smaller (Tab.2). The available data on heavy metals in soils from the Svalbard area [9-11] falls in the same range. The elevated concentrations were also found only in some points (small dump sites, etc.). A limited effect on soil and plants was also found in vicinity of polar stations [13]. An exception was only found in the case of organic soils, which are composed mainly of guano [10] - a concentration of elements occurs in web chain and it results in higher heavy metal concentrations. PAHs were not studied in Svalbard soils, a comparison of our results with data from industrialised areas reveals differences in both qualitative and quantitative compositions and reaches even a few orders of magnitude. The results

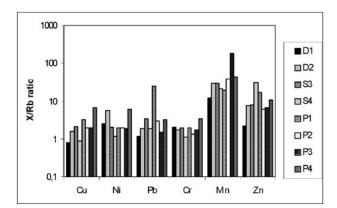


Fig.3. Main heavy metals corrected for grain size effect using rubidium as a grain-size proxy [21]. X-certain metal concentration; note a logarithmic scale.

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Table 3. The results of PAH determinations in the soil samples by HPLC. Values are given in µg/kg.

Sample symbol	D1	S3	Р3	
Naphtalene	42	48	42	
Acenaphtalene	8	14	12	
Fluorene	11	10	12	
Phenanthrene	24	45	42	
Anthracene	-	69	-	
Fluoranthene (Fl)	10	24	23	
Pyrene	11	109	8	
Benzo(a)anthracene	2	18	-	
Chrysene	17	22	-	
Benzo(b)fluoranthene (B(b)F	3	19	5	
Benzo(k)fluoranthene (B(k)F	2.5	16	4	
Benzo(a)pyrene (B(a)P)	3	18	3	
Dibenzo(ah)anthracene	7	12	1	
Benzo(ghi)perylene (B(ghi)P)	1	-	3	
Indeno(1,2,3-c,d) pyrene (IP)	-	28	3	

Table 4. The results of PAH determinations in the soil samples by TLC. Values are given in μg/kg; ND - not detected.

	D1	D2	S3	S4	P1	P2	P3	P4
Fl	7	ND	21	ND	4.2	1.8	28	8
BaP	1	ND	16	ND	ND	ND	3.2	1.6
BbF	1.5	ND	17	ND	ND	ND	4	0.8
BkF	1.5	2.1	14	5	2.3	2.3	4.8	2.8
IP	ND	ND	22	ND	ND	ND	3.4	17
BghiP	ND	ND	9.8	ND	ND	ND	1.8	1.8

of PAH determinations of soil samples originating from the Poznań city center, shown that volatile aromatic hydrocarbons are dominant among the 15 determined compounds. Their concentration is within several or several thousand μg/kg [24]. A similar study conducted in Great Britan [25] stated that the highest concentrations were fluoranthene (55.3 mg/kg), phenanthrene (50.7 mg/kg), pyrene (20 mg/kg), benzo(a)antthracene (39 mg/kg) and benzo(a)piren (13.8 mg/kg). A different proportion of perpendicular PAHs points to difference in potential sources of contamination, although it is difficult to recognise them yet. It is also possible, as mentioned above, that some geogenic PAHs are included along the tectonic zones.

Long-distance transport of contaminants, although found in other environmental components [2,5,7] is not detectable in the studied soils. The reference (background) samples reveal very low concentrations of po-

tentially contaminating substances, and the local sources' influence seems to be limited to a few tens or hundreds of meters.

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