Concentrations of polycyclic aromatic hydrocarbons and trace elements in Arctic soils: A case-study in Svalbard

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ABSTRACT

A combined assessment on the levels and distribution profiles of polycyclic aromatic hydrocarbons (PAHs) and trace elements in soils from Pyramiden (Central Spitsbergen, Svalbard Archipelago) is here reported. As previously stated, long-range atmospheric transport, coal deposits and previous mining extractions, as well as the stack emissions of two operative power plants at this settlement are considered as potential sources of pollution. Eight top-layer soil samples were collected and analysed for the 16 US EPA priority PAHs and for 15 trace elements (As, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sn, Tl, V and Zn) during late summer of 2014. The highest levels of PAHs and trace elements were found in sampling sites located near two power plants, and at downwind from these sites. The current PAH concentrations were even higher than typical threshold values. The determination of the pyrogenic molecular diagnostic ratios (MDRs) in most samples revealed that fossil fuel burning might be heavily contributing to the PAHs levels. Two different indices, the Pollution Load Index (PLI) and the Geoaccumulation Index (Igeo), were determined for assessing soil samples with respect to trace elements pollution. Samples collected close to the power plants were found to be slightly and moderately polluted with zinc (Zn) and mercury (Hg), respectively. Spearman correlation showed significant correlations between the concentrations of 16 PAHs and some trace elements (Pb, V, Hg, Cu, Zn, Sn, Be) with the organic matter content, indicating that soil properties play a key role for pollutant retention in the Arctic soils. Furthermore, the correlations between ∑16 PAHs and some trace elements (e.g., Hg, Pb, Zn and Cu) suggest that the main source of contamination is probably pyrogenic, although the biogenic formation and the petrogenic origin of PAHs should not be disregarded according to the local geology.

Keywords:
Svalbard (Arctic)
Soil
Environmental Pollution
Polycyclic aromatic hydrocarbons (PAHs)
Trace elements

1. Introduction

Studies on fate and distribution of environmental pollutants in remote areas are not only contributing to the elucidation of transportation pathways and transformation profiles of pollutants, but they are also providing information to scientific sound regional environmental risk assessment (Bazzano et al., 2015). For many long range transported pollutants, the Polar regions (including Arctic and Antarctic), are considered as deposition and accumulation regions (Kallenborn et al., 2012a,b; Ma et al., 2011). Organic compounds and trace elements, are both found in various compartments of polar ecosystems (Bargagli, 2016; Ge et al., 2016; Nadal et al., 2015; Turetta et al., 2016). Although the Arctic environment is still considered as marginally affected by anthropogenic influences, a combination of local pollution sources and long-range transport is contributing to environmental pollution. Historically, the human presence on the Svalbard archipelago was due to hunting, as well as industrial activities such as coal mining (Abramova et al., 2014). According to Russian estimates, the total resources of the archipelago, including adjacent sea areas, exceeds 6 billion tons of oil equivalents (Dahle et al., 2006). Currently, three coal mines are still active on Svalbard (Svea, Longyearbyen and Barentsburg). In addition to these still active mines, several locations with abandoned mine facilities exist on the main island (Spitsbergen). Thus, coal mining has been widely identified as a major local source for pollution.

The abandoned mining town Pyramiden is located in the northern part of Isfjorden (Billefjorden, Svalbard, 78°39′22″N 16°19′30″E). Pyramiden was founded by Sweden in 1910, and sold to the Soviet Union in 1927. In 1983, agricultural soil was imported as supplement to the thin layer of local soils, which were characterized by a poor content of nutrients. This allowed to grow imported grass and crop types as food source for the local animal husbandry cultivated for food provision of the workers and their families. Despite of the unknown exact origin of these soils, they were classified as chernozem sourced from southern European Russia or Ukraine (Coulson et al., 2015). In 1998, Pyramiden was abandoned, although the infrastructure is still in place. Nowadays, the human impact is related to the coal and diesel combustion driven power plants, as well as tourist and research related traffic, shipping and a local heliport.

Polycyclic aromatic hydrocarbons (PAHs) and trace elements such as mercury, are relevant local pollutants identified as indicator chemicals for human activities and coal mining. PAHs have been widely found in the Svalbard atmosphere (Cecinato et al., 2000;

Kallenborn et al., 2011; Weinbruch et al., 2015), water (Polkowska et al., 2011; Ruman et al., 2014), biota (Carrasco-Navarro et al., 2015; Nahrgang et al., 2013; Szczybelski et al., 2016; Wang et al., 2009), sediments (Konovalov et al., 2010; Sapota et al., 2009; van den Heuvel-Greve et al., 2016), snow (Abramova et al., 2016), and soils (Gulińska et al., 2003; Wang et al., 2009). In addition, there are recent findings of trace elements in air particulate matter (Bazzano et al., 2015; Bazzano et al., 2016), sea water (Bazzano et al., 2014), biota (Fenstad et al., 2016; Węgrzyn et al., 2016), marine particulate and sediments (Ardini et al., 2016; Frankowski and Zioła-Frankowska, 2014), ice (Lehmann et al., 2016; Łokas et al., 2016), and soils (Gulińska et al., 2003; Krajcarová et al., 2016; Wojtuń et al., 2013).

Only few reports exist on PAH levels in Svalbard soil (Gulińska et al., 2003; Thomas, 1986; Wang et al., 2009). Depending on their physicochemical properties, contaminants can be deposited on snow surfaces, being accumulated in the snow and subsequently transferred into soil during ice-snow melting (Perrette et al., 2013), and also volatilized from those matrices (Cabrerizo et al., 2014). The purpose of the present study was to examine the fate of 16 US EPA priority PAHs and selected trace elements in surface soil samples from Pyramiden (Svalbard).

2. Materials and methods

2.1. Sampling and sample treatment

Surface soil samples were collected in the vicinity of Pyramiden (Spitsbergen, Svalbard) in the period September 2-4, 2014. Seven soils (P1-P7) were sampled in the center of the town. One reference soil sample (P8) was collected in a background area, approx. 2 km away from potential local emission sources (Fig. 1). All soil samples were collected from the surface layer (0-5 cm depth) and kept in polyethylene bags (immediately covered with aluminum foil). All samples were carefully dried at 30ºC in a closed heating cabinet (Thermo, Finland) to eliminate the influence of soil moisture on the PAH extraction efficiency while preventing the loss of the most volatile PAHs during the process (Berset et al., 1999; Lau et al., 2010). Once their weights were stable (±0.001 g), all soil samples were sieved through a 2-mm mesh screen to standardize particle size. Finally, samples were stored in polyethylene bags and placed in the freezer (-20ºC) prior to the extraction. Qualitative data and physicochemical properties of collected soils are summarized in Table 1.

2.2. *Sample preparation and analytical procedures*

2.2.1. *PAHs*

Briefly, 10 g of soil were extracted with dichloromethane:*n*-hexane (1:1, v:v) (Scharlau Chemie S. A., Barcelona, Spain) by performing three 10-min subsequent extractions with ultrasonic bath (Selecta ULTRASONS-HD 5L, Abrera, Spain). The resulting extracts were filtered and further concentrated using a rotary evaporator VV2000 with water bath type WB2000, coupled to a manual vacuum controller (Heidolph Instruments GmbH, Germany).

Concentrated extracts were further purified with solid phase extraction (SPE). The method developed by Khan et al. (2015) and Lundstedt et al. (2014) was modified for PAH analysis in Pyramiden soil. Discovery DSC-18® cartridges containing 500 mg of C^{18} modified (Supelco®, Bellefonte, PA, USA) were conditioned with 10 mL of *n*-hexane. The sample extract was then added, followed by elution with 9 mL of dichloromethane:*n*-hexane (1:9, v:v), and with 8 mL of 100 % dichloromethane. Finally, samples were concentrated with a gentle stream of N_2 (6,0 quality, Air products, Allentown, PA, USA). The final extracts were quantitatively analysed with a 7890A Series gas chromatograph coupled to a 7000 QqQ (Agilent Technologies, Santa Clara, CA, USA), equipped with a J&W Scientific DB-XLB chromatographic column (30 m x 0.25 mm i.d., 0.25 µm film, Agilent Technologies). A volume of 1 µL of sample was automatically injected into a split/splitless inlet operated in splitless mode at 280ºC. Helium (5.0 quality, Air products) was used as carrier gas, at a flow rate of 1.2 mL min^{-1} in constant flow mode. The oven program was set at an initial temperature of 80°C, being immediately ramped to 320°C with 10°C min^{-1}, and held at 320°C for 22 min isothermal. The total separation time was 46 min. Ionization performed was electron ionization mode (EI), with an electron energy of 70 eV and a source temperature of 230ºC. Mass spectra data were recorded after a solvent delay of 3 min. The triple quadrupole (QqQ) mass selective analyzer was operated in multiple reaction mode (MRM) under conditions shown in Table S1 (Supporting Information).

2.2.2. *Trace elements*

The contents of arsenic (As), beryllium (Be), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), thallium (Tl), tin (Sn), vanadium (V) and zinc (Zn) were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) (Perkin Elmer Elan 6000, Waltham, MA, USA), using rhodium (Rh) as internal standard. One-half gram of soil was digested with 5 mL of nitric acid (65% Suprapur, E. Merck, Darmstadt, Germany) in hermetic Teflon vessels. Samples were pre-digested for 8 h at room temperature, being subsequently heated at 80ºC for 8 h. Once cooled down, solutions were filtered and the volume was adjusted to 25 mL with ultrapure water. Finally, the extracts were kept at -20°C until the quantitative analysis of trace elements. Additional details of analytes determination were reported (Nadal et al., 2011; Rovira et al., 2010; Vilavert et al., 2015).

2.2.3. *Quality assurance and quality control (QA/QC)*

Triplicates of soil samples were spiked with known amounts of the target PAHs for assessing the average PAH recoveries and the method reproducibility (standard deviations). The standard mixture (Supelco, Bellfonte, PA, USA) contained the following 16 US EPA priority PAHs: naphthalene (99.7% of purity), acenaphthylene (99.4% of purity), acenaphthene (99.3% of purity), fluorene (98.7% of purity), phenanthrene (98.0% of purity), anthracene (99.0% of purity), fluoranthene (99.5 % of purity), pyrene (99.2% of purity), benzo(*a*)anthracene (98.5% of purity), chrysene (97.4% of purity), benzo(*b*)fluoranthene (97.3% of purity), benzo(*k*)fluoranthene (99.5% of purity), benzo(*a*)pyrene (96.7% of purity), dibenzo(*a,h*)anthracene (98.3% of purity), benzo(*g,h,i*)perylene (99.4% of purity) and indeno(*1,2,3-c,d*)pyrene (99.0% of purity). Due to coelution on the chosen capillary column, benzo(*b*)fluoranthene and benzo(*k*)fluoranthene were quantified together as benzo(*b+k*)fluoranthene. In order to determine any potential laboratory contamination, extraction blanks were included following the entire sample preparation procedure. PAH recoveries were determined between 43% and 123%. The recovery for the surrogate standards were 46±14%, 63±10%, 85±21% and 64±14%, for d_{10}-acenaphthene, d_{10}-phenanthrene, d_{12}-chrysene and d_{12}-perylene, respectively (Supelco). Two compounds, d_{10}-fluorene and d_{12}-benzo(*a*)pyrene (Supelco) were used as internal standards, being added prior to the chemical analysis. Target substances satisfying the recovery and calibration criteria of the method are summarized in Table S2 (Supporting Information). The calibration curve for determining the linear range of the instrument for PAH quantitation covered the range from 0.5 to 100 µg mL^{-1}. The limits of quantification (LOQs) of the individual PAHs in soil were in the range 2-70 pg g^{-1} of dry weight.

For the quantitative determination of trace elements, background levels were also determined in blank samples and standards, which were added for every batch analysed. Loamy clay 1 CRM052-050 (National Institute of Standards and Technology, Gaithersburg, MD, USA) was used as certified reference material to check the accuracy of the method. Metal recoveries were ranged between 86% and 106% (Zn and Co, respectively). The limits of detection (LODs) of trace elements were in the range 0.03-0.50 mg kg^{-1} of dry weight.

2.3.Statistical analysis

Spearman correlations were calculated by using XLSTAT 2016 (Addinsoft SARL™, Paris, France), with a significance value set at $p<0.05$ for the determination of correlations among the variables.

3. Results and discussion

3.1. Soils characterization

Qualitative information and results of the soil characterization are shown in Table 1. All soil samples collected in Pyramiden and surrounding areas were non-saline, alkaline (pH between 7.2 and 8.01), and calcareous. Most of them (P1, P2, P4, P5, P6 and P7) were coarse-textured, while P3 and P8 were fine-textured, with a notable content of silt and clay, respectively. A relatively higher content of organic matter was found in three locations (2.25%, 4.68% and 4.08% in P3, P6 and P7, respectively) in comparison with the remaining sampling sites. In turn, nitrate content of these soils was low, ranging between 4.2 and 29.6 mg kg^{-1}.

3.2. PAHs

The concentrations of the individual 16 US EPA priority PAHs, the sum of these 16 PAHs and 7 carcinogenic PAHs, as well as the levels expressed as benzo(*a*)pyrene equivalents (BaP_{eq}), are shown in Table 2, together with the limit of quantification (LoQ) for all PAHs. The arithmetic mean ± standard deviation of PAHs analysis is shown in Table S3 (Supporting Information).

The levels of all compounds were above the detection limits, excepting acenaphthylene, acenaphthene and anthracene in the blank soil (P8). P3 was, by far, the most contaminated site, showing a Σ16 PAH concentration of 11600 µg kg^{-1} dry weight (dw). The P1 and P3 sampling sites were nearly located to each other close to the power plants (coal- and diesel- fired). However, the PAH values registered in P3 were considerably higher. As P3 was located downwind, it would indicate that prevailing winds blowing from ENE and N (Fig. 1) have a critical impact on the deposition of PAHs near the power plants. Furthermore, this sampling site could be a lawn, grass-plot of already polluted soil imported in the past. P6 and P7 sampling sites also presented high concentrations of PAHs (6370 and 2350 µg kg^{-1} dw, respectively). P6 is located 500 m upwind from the power plants, being close to the harbor, which was an operating port of coal loading in the past. P7 is in a zone with no visible source contribution, but it is located downwind the 2 power plants (distance of 600 m). In addition, there is a seasonal river running melted water from mountains and a glacier in spring, leading to a potential source of pollution input in this area. The lowest value of PAHs in soil corresponded the background point (P8), with 52.8 µg kg^{-1} dw. The Σ16 PAHs levels near the power plants were about 220-times higher than those in the background area.

Since there is a lack of threshold levels for PAHs in Svalbard soil, target and intervention values for soil remediation from the Netherlands were used for comparison purposes (ESdat, 2000). According to the Dutch legislation, the sum of 10 PAHs (naphthalene, anthracene, phenanthrene, fluoranthene, benzo(*a*)anthracene, chrysene, benzo(*a*)pyrene, benzo(*g,h,i*)perylene, benzo(*k*)fluoranthene and indeno(*1,2,3-c,d*)pyrene) should not exceed 1 mg kg^{-1} dw for soils with an organic matter content below 10%. Three sampling sites (P3, P6, and P7) showed levels above this target value (8.33, 5.63 and 2.07 mg kg^{-1}, respectively). However, PAH levels did not exceed the intervention values, set at 40 mg kg^{-1} (Table 2).

To the best of our knowledge, there are only two scientific articles reporting soil concentrations of PAHs in Svalbard (Gulińska et al., 2003; Wang et al., 2009), as well as a Technical Report (No. 5, 2011) from the Arctic Monitoring and Assessment Programme (AMAP, 2011). The current concentrations of ∑16 PAHs in soils were clearly higher than those previously reported. Gulińska et al. (2003) found that the total level of ∑16 PAHs in a sample of soil collected in Pyramiden was 158 µg kg^{-1} dw. On the other hand, Wang et al. (2009) collected in July and August 2007 samples of surface soil, moss and reindeer from 12 sites at Ny-Ålesund, Svalbard. The mean concentration of PAHs in soil was 157 µg kg^{-1} of dw, with levels ranging from 37 to 324 µg kg^{-1} dw. The AMAP Technical Report No. 5 (AMAP, 2011) provides PAH levels in soils from Kinnvika Station. The mean Σ16 PAHs in Pyramiden soils here reported is in the same range as the upper limit found in Kinnvika soils (Σ16 PAHs range 17-6380 µg kg^{-1} dw). The relatively high background level at Kinnvika, which is significantly above the natural local background, was probably a combination of both, natural (local geology) and anthropogenic sources (AMAP, 2011).

PAH levels in soil samples collected in Svalbard were also compared with data from zones surrounding other power plants. Our results were of the same order of magnitude than those found in the vicinity of the coal-fired power station in Plomin, Croatia (Medunić et al., 2016). In addition, they were in the upper part of the range in comparison to PAH levels found in soils surrounding coal-fired power plants in Xuzhou, China (165-3495 µg kg^{-1} of dry soil) (Kumar et al., 2014), the Yangtze River Delta region, China (285-504 µg kg^{-1} of dry soil) (Ma et al., 2016), or Korba, India (7-2100 µg kg^{-1} of dry soil) (Wang et al., 2017).

The contribution of each individual PAH to the sum of 16 PAHs is depicted in Fig. 2. Naphthalene and phenanthrene were the most abundant, showing an average contribution of 33% and 25%, respectively. Therefore, similar sources might be responsible for PAH contamination in the study area, being the potential biogenic formation of these compounds not disregarded (Wilcke 2007; Cabrerizo et al., 2014; 2016). In fact, the contribution of naphthalene increased with the distance to the power plants. This compound was identified as the most abundant hydrocarbon in the sampling site (P8). Furthermore, low molecular weight PAHs may be present at large distances to the potential emission sources, while high molecular weight PAHs, which are more associated to the particulate matter, tend to be deposited close to the emission sources (Nadal et al., 2009). However, measurements of air-soil diffusive exchange and dry/wet deposition should be carried out to confirm its potential transport from combustion sources to further areas in front of its biogenic formation. PAH profile was different in

P3, the most polluted site, where fluoranthene and pyrene were the most important contributors to the total concentration (20% and 17%, respectively).

According to the International Agency for Research on Cancer (IARC), benzo(*a*)pyrene is a carcinogenic substance to humans, being classified as Group 1 carcinogen. Due to this, it is a good indicator for the assessment of the health risks associated to the PAH exposure (Domingo and Nadal, 2015; Domínguez-Morueco et al., 2015). Since the 16 US EPA priority PAHs show different degrees of toxicity, the levels of PAH mixtures are sometimes normalized as BaP_{eq} concentrations (Albuquerque et al., 2016). These values are calculated by adding all quantities obtained after multiplying the concentration of each individual PAH with the corresponding toxicity equivalency factor (TEF), according to the following equation:

$$\mathrm{BaP_{eq}} = \sum_{i=1}^{n} \mathrm{PAH_i} \times \mathrm{TEF_i}$$

TEFs used by Nadal et al. (2004), which are adapted from Nisbet and LaGoy (1992) and Larsen and Larsen (1998), were here applied. The BaP_{eq} concentrations of PAHs in each sampling site are summarized in Table 2. As expected, P3 showed the highest value (1255 µg BaP_{eq} kg^{-1}), being almost 700-times higher than that at the background site (1.80 µg BaP_{eq} kg^{-1}). Considering the 7 sampling points in Pyramiden, the mean PAH concentration in soils was 252±452 µg BaP_{eq} kg^{-1}. This is a surprisingly high value compared to previously reported data from other impacted middle latitude locations, such as a chemical/petrochemical zone in Tarragona, Spain (Nadal et al., 2004), the industrial city of Changzhi, China (Liu et al., 2017) or several residential areas in Sahibabad-Ghaziabad, India (Kumar et al., 2016) among other. Although naphthalene and phenanthrene were the most abundant PAHs in absolute concentration, their contribution to the ΣBaP_{eq} was low (6.4% in average). However, even if benzo(*a*)pyrene and dibenzo(*a*,*h*)anthracene had a small contribution to the Σ16 PAHs total concentration (mean: 4.8%), these compounds showed the greatest impact on the ΣBaP_{eq} concentration, up to 77%. The abundance of heavy PAHs (4-, 5- and 6- ringed PAHs) in the total concentration of Σ16 PAHs is an important indicator that local pollution at this location is contributing significantly to the overall pollutant profile.

To assess potential emission sources of PAHs, Molecular Diagnostic Ratios (MDRs) are applied for a variety of relevant environmental matrices, including soils (Tobiszewski and Namieśnik, 2012). MDR calculations (Ant/Ant+Phe, Flt/Flt+Pyr, BaA/BaA+Chry, and IP/IP+BghiP) for the 8 soils collected in Svalbard, including typically reported values for some specific processes, are shown in Table 3. Most of these ratios pointed towards combustion sources as the main contributor of PAHs in the area under study. Specifically, Flt/Flt+Pyr, BaA/BaA+Chry and IP/IP+BghiP showed a PAH pyrogenic origin, linking pollution to incomplete combustion of organic material. In contrast, BaA/BaA+Chry in P4, P6, P7 and P8 presented a mixed source profile (pyrogenic and petrogenic). Moreover, Ant/Ant+Phe pointed out a petrogenic source in 5 of 7 sampling locations (P2, P4, P5, P6 and P7). These ratios have been satisfactorily used to identify emission sources (Agarwal et al., 2009; Plachá et al., 2009), although degradation (e.g., photodegradation, biodegradation) and biogenic processes may change PAH profile (Enell et al., 2005; Sabaté et al., 2006; Brändli et al., 2008; Cabrerizo et al., 2011; Tobiszewski and Namieśnik, 2012; Marquès et al., 2017), being their applicability widely discussed (Katsoyiannis and Breivik, 2014). Nonetheless, the occurrence of these processes in permafrost soils, and the resulting impact on diagnostic ratios, needs further attention. Due to the proximity to power plants (P2, P4 and P5) and heliport (P4), as well as the direction of prevailing winds (P7), combustion sources are probably more plausible than petrogenic ones. However, the petrogenic origin related to the local geology, and its associated mining extraction carried out in Billefjord in the past (Vorren et al., 1990), should not be disregarded and should be extensively evaluated.

3.3. Trace elements

The concentrations of trace elements in samples of soils collected in Svalbard are shown in Table 4. All the elements showed levels above their respective LODs. In general terms, the average content of trace elements was lower than the World Soil Average (WSA) (Kabata-Pendias, 2011). In addition, all average concentrations were also below the Target Values reported as regulatory action threshold for the Netherlands (TVN) (ESdat, 2000) (Fig. 3). However, there were some exceptions. Beryllium was found at higher amounts than the threshold value in P6 and P7 sites (1.25 and 1.61 mg kg^{-1}, respectively, being >1.1 mg kg^{-1}). Moreover, Hg, Mn, Ni and Zn punctually exceeded the WSA. The levels of Hg were 0.28, 0.17 and 0.10 in P3, P6 and P7, respectively, higher than 0.07 mg kg^{-1}, which is the WSA. Manganese showed the highest values in P1 and P8 (494 and 513 mg kg^{-1}, respectively), while Ni exceeded WSA in P3 and P7 (32.9 and

30.5 mg kg^{-1}, respectively). Finally, Zn in P3 and P6 (100.1 and 120 mg kg^{-1}, respectively), and Co in P3 and P7 (10.2 and 10.6 mg kg^{-1}, respectively), were also above the TVN. The remaining trace elements (As, Cd, Cr, Cu, Mo, Sn, Tl and V) showed levels below WSA and TVN in all the sampling points. The potential source of trace elements can be due to anthropogenic activities (combustion from power plants, heliport), being probably due to the local geology of the area.

As for PAHs, the number of studies addressing the occurrence of trace elements in polar soils is limited. However, most of them have been conducted in Svalbard soils. Wojtuń et al. (2013) investigated the concentrations of trace elements in 35 topsoil samples (depth of 0-3 cm) from the SW of Svalbard, while Krajcarová et al. (2016) analyzed the top soil (>5 cm) and deeper soil (5-10 cm) in 13 sites surrounding Pyramiden. Previously, Gulińska et al. (2003) determined the levels of trace elements in the uppermost 20 cm of soils collected in Pyramiden. Although the analytical methods of this study were slightly different compared to those of the present survey, very similar results were obtained. The current concentrations of trace elements in Svalbard soils were, in fact, of the same order of magnitude as those reported by Wojtuń et al. (2013), and comparable to those from Krajcarová et al. (2016), with only a few exceptions (e.g., Zn, Cd and Mo). However, our results are not in agreement with those reported by Gulińska et al. (2003), who observed metal contents much lower than the rest of studies, being even lower than world average values. AMAP (2005) provides few data regarding trace elements in Arctic regions. The current Hg and Cd levels were of the same order of magnitude, and in the upper limit, respectively, than those found in Greenland. In contrast, the concentration of Pb was one magnitude higher than that found in the Arctic Circle, according to the AMAP (2005) report. Santos et al. (2005) reported similar concentrations to those recently found in Svalbard when studying trace elements in the Antarctica, with the only exceptions of Ni and Mo.

Because of the presence of power plants as important emission sources of chemical pollution, the current results were also compared with data from the scientific literature regarding areas impacted by power stations. Our results were very similar to those reported by Minkina et al. (2017) and by Noli and Tsamos (2016) in the surroundings of facilities in Russia and Greece, respectively. In turn, As, Cr and Ni concentrations from soils collected around a power plant from Turkey were one order of magnitude higher than those found in Svalbard (Özkul, 2016). Finally, Hg concentrations reported were much lower than soil levels found recently in a wide Spanish investigation to assess the impact of several coal-fired power plants (Rodríguez Martín and Nanos, 2016).

The pollution load index (PLI) and the geoaccumulation index (Igeo), are widely used for classification of local pollution profiles (Adama et al., 2016; Akoto et al., 2016; Krajcarová et al., 2016; Tian et al., 2017; Zarei et al., 2014). These indices are calculated according to the following equations:

$$\mathrm{CF} = {}^{\mathrm{C_m}}\!/_{\mathrm{B_m}}$$

$$\mathrm{PLI} = \sqrt[n]{\mathrm{CF1} \cdot \mathrm{CF2} \cdot \ldots \cdot \mathrm{CFn}}$$

$$\mathrm{I_{geo}} = \log_2 \left(\mathrm{C_m}/1.5 \cdot \mathrm{B_m}\right)$$

where CF is the Concentration Factor, C_m is the measured concentration of the trace element m, B_m is the geochemical background of the trace element *m* taken from the Word Soil Average (Kabata-Pendias, 2011), and *n* is the number of trace elements under study.

The results of both PLI and I_{geo} indexes are presented in Table 5, which also gives in detail the categories of classification for each one. Soil values above the unity (PLI>1) are considered as polluted, while PLI<1 is linked to non-polluted soils. Regarding to the I_{geo} parameter, Müller (1969) provided an identification and classification of soil pollution levels into seven grades (Table 5). The specific value resulting from I_{geo} calculations for each element and sampling site, is included in Table S4 (Supporting Information). According to I_{geo} values, P6 was slightly polluted by Zn and Hg (0.19 and 0.66 I_{geo} grades, respectively), while soil from P3 was moderately polluted by Hg (1.41 I_{geo} grade). These two sampling sites, as well as P7, were identified as the locations showing the highest PLI values (0.63, 0.52 and 0.55 in P3, P6 and P7, respectively). However, all were lower than 1, being all sites classified as "unpolluted", according to the PLI. Finally, as expected, P8 presented the lowest PLI, with a value of 0.17.

3.4. Correlation between PAHs and trace elements

Spearman correlations were performed between the levels of PAHs and those of trace elements, as well as with the organic matter content (Table S5; Supporting Information). The results showed strong correlations between all single PAHs and some metals, such as Pb, Hg, Cu, Zn, Sn and Be. The ∑16 PAHs correlated well with: Hg (0.94; $p<0.01$), Pb (0.88; $p<0.05$), Zn (0.95; $p<0.01$) and Cu (0.88; $p<0.05$), indicating a common source. Although power plants operating in Pyramiden may be the main and more plausible pollution source in Pyramiden, the local geology with coal deposits, as well as previous extraction activities could contribute to the concentrations of PAHs and trace elements. However, further analysis should be carried out for a better assessment of each sources contribution to the occurrence of PAHs and trace elements. Notable differences between sampling sites were also found. They cannot be explained only by the distance to anthropogenic activities: power plants, harbor and heliport transport. Thus, the organic content of soils would probably play a key role, as it showed a strong, significant correlation with each single PAH, the ∑16 PAHs, and also some trace elements (i.e., Pb, V, Hg, Cu, Zn, Sn and Be). Although the distance from the facilities to P1, P2, P3 and P5 sites was similar, the P3 contamination pattern is characterized by the highest concentrations of PAHs in combination with the highest content of organic matter (2.25%) among these sites (P1, P2, P3 and P5). In addition, it should be noted that this soil probably belongs to that previously imported. Therefore, there is the possibility that it was already polluted in the source. Although P6 and P7 were located quite far from the identified combustion processes, PAHs also occurred at relatively high concentrations. It could be partly due to the biogenic formation of some PAHs (i.e., naphthalene and phenanthrene), and also the high capacity of soils with a high content of organic matter (4.68 and 4.08% in P6 and P7, respectively) to accumulate PAHs, regardless of the potential origin (biogenic and/or pyrogenic). Soil organic matter clearly plays a key role in the adsorption/retention of pollutants by soils. The petrogenic source of both PAHs and trace elements, due to coal deposits on that area, as well as coal mining extraction in the past, should be further considered and assessed.

4. Conclusions

The results of the present investigation revealed that Pyramiden (Svalbard) soils are affected by environmental pollution, by PAHs and trace elements. Concentrations of ∑16 PAHs reached up to 11 600 µg kg^{-1}, being more than 200-times higher than the levels from a soil sample collected in a background site (52.8 µg kg^{-1}). When expressed in terms of BaP_{eq}, the difference was even higher, being the levels 700-fold higher in the surroundings of the power stations. Furthermore, according to Dutch Target Values, the concentrations of Hg in soils from the vicinity of the power plant were very close to threshold levels (0.28 vs. 0.3 mg kg^{-1}). The application of the Igeo index pointed out that those soils were moderately polluted by Hg, with levels 4-times higher than the World Soil Average. Despite differences in the total amount of Σ16 PAHs in soils, all samples showed a similar profile, being associated to a common source, which was most probably pyrogenic according to MDRs. However, the potential petrogenic contribution to soil pollution should not be disregarded and will be further assessed.

The current results strongly suggest the importance of environmental monitoring in remote areas of the planet. This kind of actions should be a priority for regulators in areas where local emission sources are located. The extremely low temperatures, the lack of light and the snow cover during a wide part of the year may hinder the degradation of PAHs, through photochemical and microbial reactions in soils. The complementarity of using other environmental matrices, such as air, ice/snow and biota, should be also considered. After the dark season, PAH levels may lead to the formation of oxy- and nitro-PAHs, whose toxic/carcinogenic potential can be even higher than the parental compounds. Therefore, the assessment of emerging PAH derivatives is also extremely important.

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Appendix A. Supporting Information

Supplementary data associated with this article can be found in the online version.

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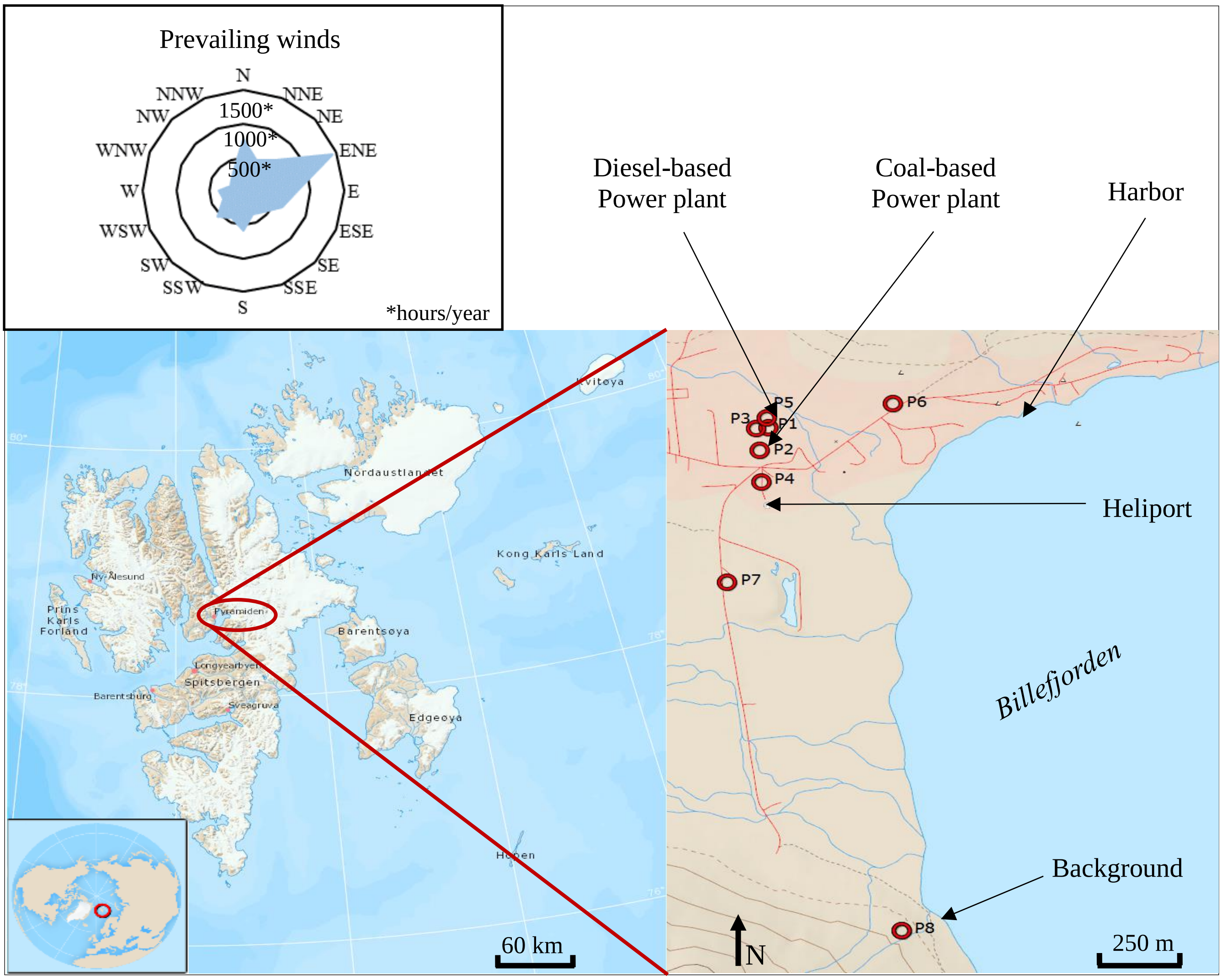

Fig. 1. Location of the study area. Points P1-8 represent sampling sites.

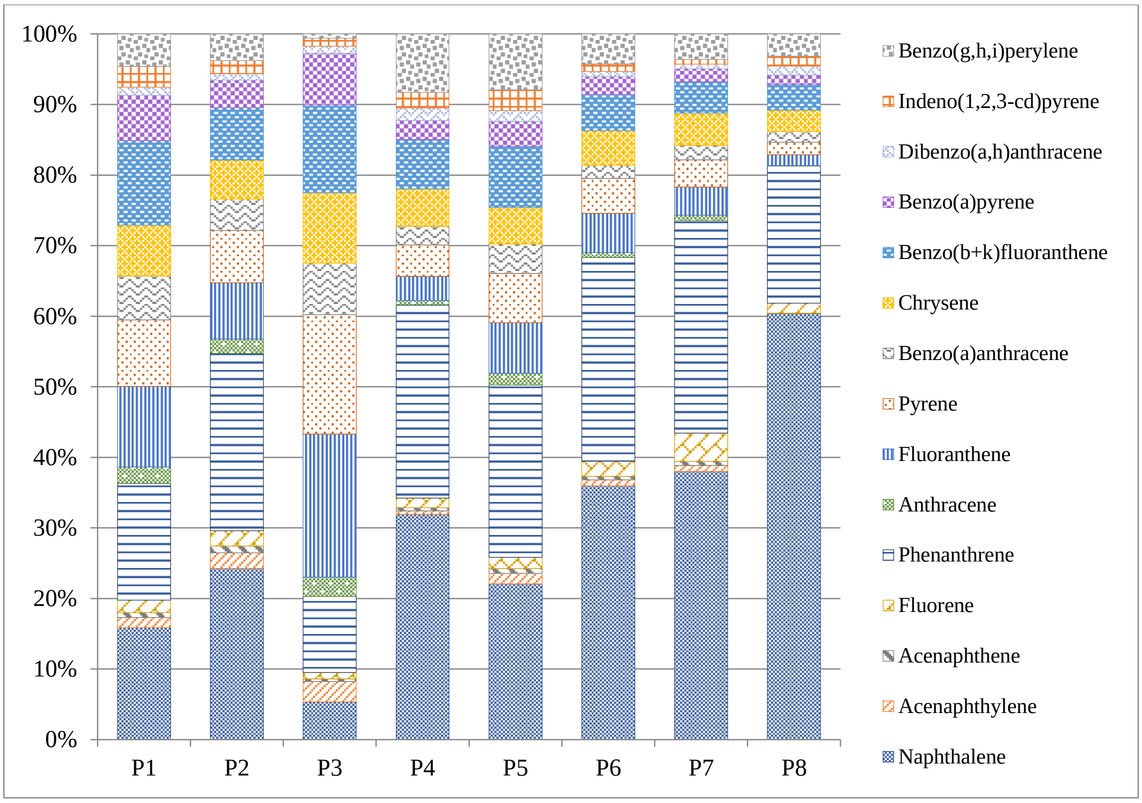

Fig. 2. Contribution (%) of each individual PAH to the total concentration of Σ16 PAHs.

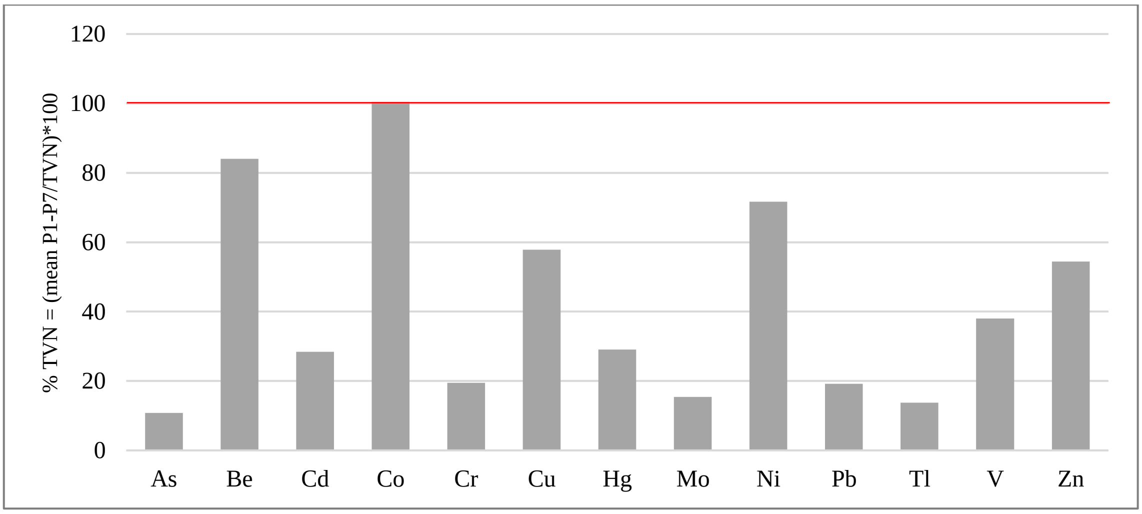

Fig. 3. Comparison between the mean concentration of trace elements in Svalbard soils with the Target Values of the Netherlands (TVNs). No data are given for Mn and Sn, as TVNs have not been established for these elements.

Table 1

Characterization of soils collected in Pyramiden (Svalbard).

	P1	P2	P3	P4	P5	P6	P7	P8
GPS coordinates	78.655ºN 16.337ºE	78.654ºN 16.336ºE	78.655ºN 16.336ºE	78.653ºN 16.336ºE	78.655ºN 16.337ºE	78.655ºN 16.355ºE	78.650ºN 16.331ºE	78.639ºN 16.354ºE
Soil cover	Bare soil, spreading of coal pieces close to the sampling site	Few grass, lichens	Few grass, less lichens than in P2	Bare soil	Few grass, mostly bare soil	Grass, lichens, stones	Bare soil	Bare soil, stones
Human activity	Power plants	Power plants In front coal combustion	Power plants	Power plant Traffic Heliport	Power plants In front diesel combustion	Harbor	No visible	No visible
Level above the sea (m)	9	7	9	7	9	20	10	43
pH[a]	8.01	7.74	7.85	7.44	7.60	7.63	7.17	7.61
Electrical conductivity at 25ºC (µS cm^{-1})[a]	1105	189	308	1145	170	1506	719	102
Oxidizable C (%) [b]	0.86	0.39	1.30	0.52	0.25	2.71	2.36	0.25
Organic Matter (%) [b]	1.48	0.67	2.25	0.90	0.42	4.68	4.08	0.42
Texture: sand/silt/clay (%)[c]	85/9/6	88/7/5	62/26/12	83/8/9	73/21/6	72/21/7	84/11/5	67/14/19

$CaCO_3$ [d]	c^{++}	c^{++}	c^{++}	c^{++}	c^{++}	c^{+}	c^{+}	c^{+}
NO_3^- (mg kg^{-1}) [e]	6.8	6.6	5.5	4.2	5.2	6.8	29.6	6.1

[a] Aqueous extracts 1:2.5; [b] Organic Carbon by Walkley-Black method (Page et al., 1985); [c] sedimentation method; [d] qualitative method: $0 < c^{+} < 10\%$ and $10 \leq c^{++} < 20\%$; [e] Extracted in soil to water ratio 1:10 elutriates and quantified by ion chromatography (Dionex D-300; Chromeleon software v6.80).

Table 2. Concentration of PAHs in soils (µg kg^{-1} of dry soil) collected in Pyramiden (Svalbard), and reference values.

	Naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo(*a*)anthracene	Chrysene	Benzo(*b+k*)fluoranthene	Benzo(*a*)pyrene	Dibenzo(*ah*)anthracene	Indeno(*123-cd*)pyrene	Benzo(*ghi*)perylene	∑16 PAHs	∑7 carcinogenic PAHs	∑ 10 PAHs	$\sum BaP_{eq}$
P1	133	12.1	5.88	14.5	139	19.2	95.5	79.0	52.2	60.2	100	53.6	9.43	24.8	38.6	837	349	666	82.0
P2	66.9	6.10	2.64	6.07	69.2	5.68	22.0	20.4	12.3	15.2	20.6	10.7	2.47	5.12	10.5	276	79.6	228	14.4
P3	622	333	43.4	108	1250	315.5	2360	1960	849	1160	1450	846	114	132	72.7	11600	5312	8330	1255
P4	182	2.79	2.59	7.79	156	3.50	19.7	25.2	15.2	30.3	39.9	15.3	10.1	12.7	47.2	571	156	502	33.8
P5	40.9	2.83	1.23	2.97	45.3	3.11	13.2	13.0	7.79	9.54	16.11	6.55	2.89	5.45	14.7	186	63.5	155	12.8
P6	2290	57.1	31.6	134	1840	44.3	356	314	118	311	328	162	45.9	67.4	271	6370	1261	5620	281
P7	893	19.7	14.0	93.5	707	18.7	93.3	91.0	47.3	108	104	44.3	14.6	15.9	84.6	2350	387	2060	81.1
P8 (background)	31.9	<LoQ	<LoQ	0.74	10.3	<LoQ	0.80	0.95	0.80	1.59	1.95	0.69	0.66	0.74	1.68	52.8	6.80	49.4	1.80
Mean± SD[1]	604± 809	62.0± 121	14.5± 16.6	52.32± 56.82	601± 704	58.57± 114	422± 861	358± 716	157± 307	242± 418	294± 520	163± 306	28.5± 40.6	37.6± 46.8	77.0± 89.8	3170± 4320	1087± 1910	2510± 3210	252± 452
LoQ	0.02	0.02	0.05	0.02	0.01	0.06	0.002	0.003	0.01	0.01	0.004	0.07	0.03	0.05	0.07	-	-	-	-
Svalbard[2,4]	42-48	NA	8-14	10-12	24-45	Nd-69	1.8-28	8-109	ND-18	ND-22	ND-19	ND-18	1-12	ND-28	ND-9.8	-	-	-	-
Pyramiden (Svalbard)[3,4]	42	NA	12	12	42	ND	23	8	ND	ND	9	3	1	3	3	158	16	120.5	-
Ny-Ålesund (Svalbard)[5]	12	0.4	3	10	59	5	10	10	7	10	18	7	0.5	3	3	157	38.5	125	13.48
Kinnvika (Svalbard)[6]	0.015 -330	2.02-82.0	4.74-188	0.324-146	0.131-55.3	0.001-221	0.021-120	0.007-20.3	0.003-98.6		0.003-131	4.63-308	0.077-388	2.92-151	2.1-4140	17.0-6380	7.63-1030	9.82-5490	5.06-616

[1] calculated without considering P8 (blank soil); [2] Range of all sampling sites; [3] Soil collected in Pyramiden; [4] Gulińska et al. (2003); [5] Wang et al. (2009); [6] AMAP (2011); SD= Standard Deviation LoQ= Limit of Quantification; NA= No Analysed; ND= non-detected; 7 carcinogenic PAHs= chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno(*123-cd*)pyrene, dibenzo(*ah*)anthracene; 10 PAHs= naphthalene, anthracene, phenanthrene, fluoranthene, benzo(*a*)anthracene, chrysene, benzo(*a*)pyrene, benzo(*ghi*)perylene, benzo(*k*)fluoranthene, indeno(*123-cd*)pyrene

Table 3
Diagnostic ratios of soils collected soils in Pyramiden (Svalbard) and typical reported values for particular processes.

	P1	P2	P3	P4	P5	P6	P7	P8	Petrogenic[2]	Pyrogenic[2]
Ant/Ant+Phe	0.12	0.08	0.20	0.02	0.06	0.02	0.03	0.03[1]	<0.1	>0.1
Flt/(Flt + Pyr)	0.55	0.52	0.55	0.44	0.50	0.53	0.51	0.46	<0.4	>0.4
BaA/(BaA + Chry)	0.46	0.45	0.42	0.33	0.45	0.28	0.30	0.33	<0.2	>0.35
IP/(IP + BghiP)	0.39	0.33	0.64	0.21	0.27	0.20	0.16	0.31	<0.2	>0.2

[1] Anthracene concentration was assumed to be LoQ/2; [2] Katsoyiannis et al. (2011); Ant=anthracene, Phe=phenanthrene, Flt=fluoranthene, Pyr=pyrene, BaA=benzo(*a*)anthracene, Chry=chrysene, IP=Indeno(*123-cd*)pyrene; BghiP=benzo(*ghi*)perylene.

Table 4

Levels of trace elements in soils (mg kg^{-1}) collected in Pyramiden (Svalbard), and comparison with guidelines and data from the scientific literature.

	As	**Be**	**Cd**	**Co**	**Cr**	**Cu**	**Hg**	**Mn**	**Mo**	**Ni**	**Pb**	**Sn**	**Tl**	**V**	**Zn**
P1	3.50	0.72	0.23	8.43	15.9	14.8	0.03	494	0.48	21.4	13.4	0.10	0.08	13.1	62.7
P2	2.71	0.66	0.21	8.75	16.5	14.2	0.01	350	0.42	22.5	11.9	0.05	0.09	13.6	55.5
P3	4.81	0.77	0.26	10.2	24.9	30.4	0.28	307	0.76	32.9	23.3	0.40	0.13	16.6	101
P4	3.12	0.70	0.16	8.42	13.8	18.0	0.01	347	0.35	22.2	10.6	0.05	0.12	14.2	59.7
P5	2.96	0.75	0.24	8.91	17.6	14.5	0.01	353	0.42	23.7	12.2	0.10	0.09	14.2	57.3
P6	2.58	1.25	0.27	7.90	15.6	22.6	0.17	202	0.35	22.3	25.8	0.20	0.28	17.9	120
P7	2.22	1.61	0.22	10.6	32.0	31.4	0.10	95.5	0.46	30.5	16.9	0.79	0.18	22.1	77.6
P8 (background)	1.22	0.45	0.05	3.88	8.99	10.8	0.01	513	0.12	10.5	4.84	0.01	0.16	8.19	15.9
Mean[1]	3.13	0.92	0.23	9.04	19.5	20.8	0.09	307	0.46	25.1	16.3	0.24	0.14	15.9	76.2
SD[1]	0.85	0.36	0.04	1.01	6.57	7.46	0.10	127	0.14	4.65	6.02	0.27	0.07	3.21	25.0
LOD	0.10	0.05	0.03	0.05	0.25	0.05	0.10	0.05	0.05	0.05	0.03	0.05	0.05	0.10	0.50
WSA[2]	6.83	1.34	0.41	11.3	59.5	38.9	0.07	490	1.1	29	27	2.5	0.5	129	70
TVN[3]	29	1.1	0.8	9	100	36	0.3	-	3	35	85	-	1	42	140
Pyramiden (Svalbard)[4]	0.03-0.2	0.0068-0.044	0.001-0.02	0.06-0.3	0.11-0.78	0.12-1.19	NA	20-80	0.00005-0.06	0.2-1	0.1-9	0.00004-0.42	0.0006-0.011	0.04-0.75	1.0-13
SW Spitsbergen (Svalbard)[5]	NA	NA	0.05-0.4	13-60	16-47	17-92	0.01-0.25	240-1450	NA	12.0-78	9.0-38	NA	NA	NA	70-300
Pyramiden (Svalbard)[6]	4.46	NA	6.04	13.8	40.4	37.3	0.025	600	17.7	36.4	-	NA	NA	NA	0.08
Greenland[7]	-	-	0.04-0.10	-	-	-	<0.01-0.03	-	-	-	-	-	-	-	-
Arctic circle[7]	-	-	0.17	-	-	-	-	-	-	-	8	-	-	-	-

SD= Standard Deviation; NA= No Analyzed.

[1] Mean concentration of P1-P7, excluding the background site (P8); [2] World Soil Average, according to Kabata-Pendias (2011); [3] Target Value in the Netherlands (ESdat (2000); [4] Gulinska et al., 2003; [5] Wojtuń et al., 2013; [6] Krajcarová et al., 2016; [7] AMAP, 2005.

Table 5

Geoaccumulation index (Igeo) and pollution load index (PLI) in 8 soils collected in Pyramiden (Svalbard).

Sampling point / metal	Zn	Cd	Hg	As	V	Cr	Pb	Ni	Mn	Co	Sn	Tl	Be	Mo	PLI
P1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.38
P2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.31
P3	1	1	3	1	1	1	1	1	1	1	1	1	1	1	0.63
P4	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.32
P5	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.35
P6	2	1	2	1	1	1	1	1	1	1	1	1	1	1	0.52
P7	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.55
P8	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.17

Grade Igeo	Pollution status
1	Unpolluted
2	Slightly polluted
3	Moderately polluted
4	Moderatedly to strongly polluted
5	Strongly polluted
6	Strongly to extremely polluted
7	Extremely polluted

Grade PLI	Pollution status
<1	Unpolluted
>1	Polluted