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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. The 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 Σ16 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 and petrogenic origin of PAHs should not be disregarded according to the local geology.

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, 2012b; 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, 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 from 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, 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 (AMAP, 2011; 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). PAHs may also evaporate from those matrices during favourable weather conditions (Cabrerizo et al., 2014). The purpose of the present study was to examine the levels and fate for the 16 US EPA priority PAHs as well as for 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 30 °C 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 dry 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 (-20 °C) 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 5 L, 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 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 soils. 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 × 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 280 °C. 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 230 °C. 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 analysed 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 80 °C 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 already 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