Hydrophobic and hydrophilic properties of pollutants as a factor influencing their redistribution during snowpack melt

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HIGHLIGHTS

- We collected field data on organic pollutant redistribution in snowpack during melt, in two locations on an Arctic glacier.
- The experiment occurred where atmosphere (snowfall), hydrosphere (glacier, meltwater) and anthroposphere (pollution) meet.
- Organic chemicals in the initial snow were mainly hydrophilic, while the later snow and ice stored more hydrophobic ones.
- The hydrophilic organic levels change faster than hydrophobe levels, leading to an overrepresentation of the latter in ice.
- Fluorene and pyrene concentrated near the water table, forming local maxima in water-saturated snow and superimposed ice.

GRAPHICAL ABSTRACT
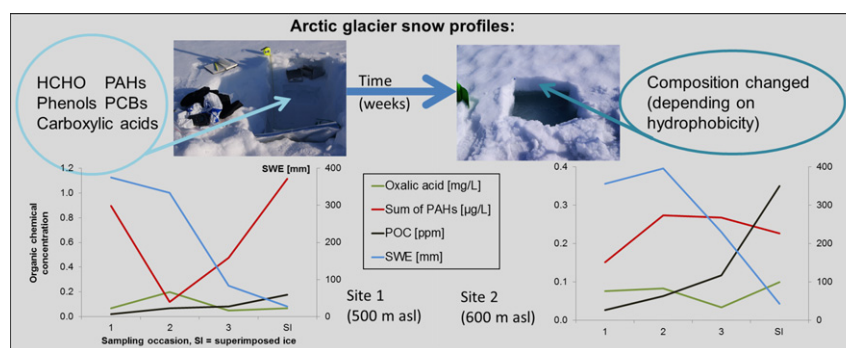
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ABSTRACT

Glaciers accumulate organic pollutants delivered by snow. However, our understanding of the exact dynamics of organic pollutants in the snowpack relies primarily on laboratory experiments and mathematical models. To fill the gap related to the detailed field data, we have conducted observations of melting snow profiles in two locations and three different stages of melting on one High Arctic glacier, as well as in superimposed ice. We monitored the chemical concentrations of formaldehyde, phenols, short-chain carboxylic acids, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) and snow water equivalents to derive chemical loads. The obtained organic contaminant redistribution patterns are compared to the meltwater removal model by Meyer and Wania (2011), in order to link the behaviour of chemicals to their hydrophilic or hydrophobic properties. Both the later snowpits and the superimposed ice layer were generally more abundant in particulate organics and hydrophobic compounds, despite the initial prevalence of hydrophilic organic chemicals. The chemical species with high water solubility also showed less predictable elution patterns, due to their chemical reactivity and possible photochemical reactions in the snowpack. Finally, ice layers in the snowpack showed very different chemical characteristics to the underlying superimposed ice, so one cannot be used as a chemical proxy for another. In order to interpret the ice core records correctly, the temporal changes in concentration of different pollutant types should be considered, as glaciers may preferentially accumulate hydrophobic organics that tarry in the snow cover.

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1. Introduction

Glaciers have been recognised as global reservoirs of organic matter (Hood et al., 2015) and secondary sources of pollutants to downstream environments (Bogdal et al., 2010, 2009; Stubbins et al., 2012). However, the short- and long-term dynamics of the organic compound release depends on the glacial snow cover; the most dynamic part of this hydrological system. The snow cover of the Arctic changes significantly according to shifts in temperature trends (Comiso and Hall, 2014; Hollesen et al., 2015; Liston and Hiemstra, 2011; Zdanowicz et al., 2012). The consequences of these changes include the occurrence of more frequent melt events in the winter, altered snow cover structure, and the modification of pollutant release dynamics from snow. To date, the knowledge about pollutant redistribution in snow is limited, and more insight is needed into the role of chemical properties of the released substances and their environmental dynamics. Modelling based on laboratory experiments of pollutant behaviour (e.g. Meyer and Wania, 2011) provide an important basis for real-life studies of elution behaviours for different pollutant types. Here, we test these idealised patterns in an environmental setting of a High Arctic glacier, focusing on the processes inside the snow cover. As a result, potential effects of these processes on high latitude glaciers are recognised, an important step forward for recognising the role of glaciers as secondary sources of pollutants and the chemical composition of their future snow cover.

In early studies of snowpack chemical composition, elution patterns of inorganic ions were revealed (Brimblecombe et al., 1987; Hodgkins and Tranter, 1998). Furthermore, the nature of the elution process was attributed to snowpack metamorphosis, rather than to the chromatographic properties of snow (Cragin et al., 1996, 1993). A logical consequence of this consideration (at least for the inorganic ions so far considered) is that changes in the snowpack temperatures in winter, particularly facilitating different modes of snowpack metamorphosis, can alter the elution sequence. Pioneers in organic pollutant behaviour in snow (Meyer et al., 2009a, 2009b; Meyer and Wania, 2011) show that the behaviour of these chemicals is more complex and depends partly on their affinity to particles or air and on their water solubility. The latter property points towards the importance of liquid water abundance in the snowpack for the distribution of different organic pollutant types. In this article, we test this hypothesis in field conditions, by looking at two pollutant types of different water solubilities, exemplified by short-chain organic acids and polycyclic aromatic hydrocarbons (PAHs), as well as the less abundant polychlorinated biphenyls (PCBs).

For long-term impacts, the same physical properties of pollutants are important, because of their impact on the biota. The water soluble compounds are more easily degradable in the environment; the degradation also increases with the abundance of metabolising organisms, and in the case of PAHs, also in a neutral or slightly alkali solution (Haritash and Kaushik, 2009; Yuan et al., 2000). Since the snow cover of Svalbard is generally an acidic environment (e.g. Hodgkins and Tranter, 1998; Joranger and Semb, 1989), with low temperature and relatively poor microbial life, e.g. less abundant than in sea ice (Amato et al., 2007) or soils (Kastovská et al., 2005), it is particularly prone to conservation of pollutants and their transfer into ice as a long-term storage. On the other hand, upon release from snowpacks, hydrophobic pollutants have the highest potential to harm organisms on higher levels of the trophic chain, due to their bioaccumulation tendencies (by binding to fatty tissues; see review in Kozak et al., 2013).

The aim of this paper is to explore the potential of modeled and known properties of organic chemicals in snow cover in the explanation of their actual distribution in melting snowpack in the field. This will help recognise other processes that may also be important in shaping the snowpack and meltwater chemical signature, thus placing the elution process in a wider context. It can also be a starting point for recognition of the way in which a certain chemical's properties lead to its behaviour in melting snowpack, since the mechanism of interaction between the elution type and snow properties has yet to be fully established.

2. Methods

2.1. Fieldwork and sampling

All fieldwork was undertaken within the summer season of 2014, on the small Arctic glacier Foxfonna in Nordenskiöld Land, Svalbard, in two sampling sites differing by altitude and slope (Fig. 1). The main focus was the analysis of snow and ice layers in temporal development during the melt season. In order to establish the order of chemical events in the melting snowpack, sequential snowpits were dug, in two locations on the glacier at three different times of the melt season: prior to major melt events, while melting was already advanced, and in the final stages of melting. Following that, superimposed ice (SI) was also cored (immediately after this layer was exposed from under the melted snow), as was the underlying shallow glacial ice. This action aimed at showing the leftover pollutants on the glacier surface after snowpack melting (superimposed ice, which is refrozen meltwater), as compared to the background inside the glacier (glacial ice). Additionally, for each period between the snowpit samplings, atmospheric deposition was also estimated from the increase in concentration of a given chemical in snow stored in glass container on the glacier surface (with a round opening with a surface area of 0.053 m^2).

Snow samples were taken from snowpit layers with a stainless steel wedge 1 L density cutter, with the opening to one side; from these, also the density of each layer was estimated in duplicate, using electronic scales with a precision of $\pm$ 10 g (with a repeatability between duplicates below 10%). From the product of density and layer thickness, snow water equivalent (SWE) was established, and totals for snowpits (also for chemical loads) were calculated through the summation of the characterised layers. In order to avoid external and cross-contamination, the sampling was preceded by cleansing the cutter by dipping it in the sampled snow layer. The distinct snow layers were determined based on their hardness (measured by hand test) and visual characteristics, and a representative sample was taken from each stratigraphical layer, in amount between 2 and 8 per snowpit. Superimposed ice samples were taken with a Kovacs corer. The superimposed ice was cored in the full layer thickness (8 cm in the upper site, 5 cm in the lower site). The obtained samples were placed in plastic, pre-cleaned zip-lock bags (prepared with a triple deionised water wash), transported and stored frozen in dark conditions. In the laboratory at the University Centre in Svalbard (UNIS), samples were melted in + 4 °C in the dark. Aliquots of the melted, agitated samples were poured into 1 L non-transparent HDPE bottles, and kept in the same temperature and light conditions as during the melting, with no headspace. A separate small aliquot was then poured into a 50 mL vial for organic carbon analyses, and stored frozen (− 18 °C). Another 12 mL sample was preserved with formaldehyde solution (2% final concentration) for cell counting, and stored in an airtight vial, at + 4 °C in the dark. At the earliest opportunity, the 1 L samples were sent for analysis to Gdańsk University of Technology (GUT), Poland, by "Horyzont II", a research vessel of the Gdynia Maritime University (within 1–3 months following collection), while the smaller aliquots were transported as airplane luggage to the University of Sheffield (UoS).

2.2. Laboratory analysis

The analytical procedure of PAHs and PCBs followed an internal standard method, where a known volume of sample is spiked with a ^{13}C–marked standard in the beginning of the extraction procedure, to account for any losses that may have occurred during sample processing. PCBs and PAHs were extracted from the water matrix using liquid-liquid extraction method with 60 mL dichloromethane (purity 99.9%, Merck, Germany) in total, in two extraction steps. The final volume of the extract was reduced to 300 μL by evaporation under laminar flow of nitrogen (99.8% purity; AGA, Poland). 2 μL of the extract was then injected in a GC–MS system, composed of an automatic injector