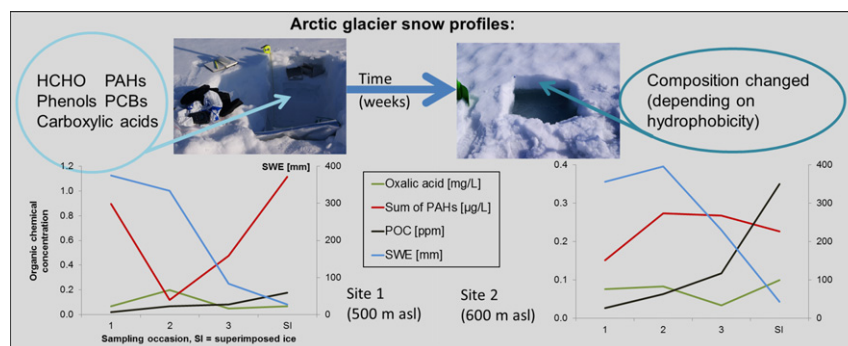


Hydrophobic and hydrophilic properties of pollutants as a factor influencing their redistribution during snowpack melt

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GRAPHICAL ABSTRACT



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.

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.

Keywords: Snow cover, Elution, Persistent organic, pollutants Glacier, High Arctic, Superimposed ice

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 m²).

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 ± 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 ¹³C-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 μ L by evaporation under laminar flow of nitrogen (99.8% purity; AGA, Poland). 2 μ L of the extract was then injected in a GC-MS system, composed of an automatic injector

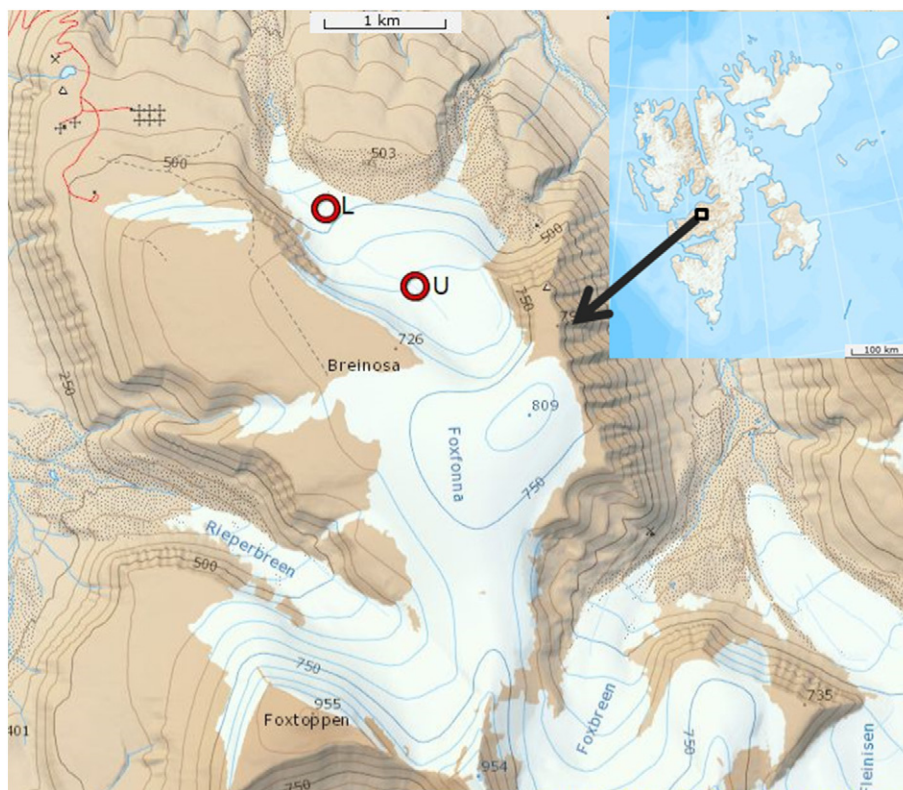


Fig. 1. Sampling locations on Foxfonna glacier, Svalbard: lower (L) and upper (U). (Source of the map extracts: toposvalbard.npolar.no; printed by courtesy of Norwegian Polar Institute.)

7683B, an Agilent Technologies 7890A gas chromatograph with a capillary column ZB-5MS and an Agilent Technologies 5975C mass spectrometer. Other parameters of the used analytical procedure are listed in Table 1. The congeners determined can be found in Table 2.

All data were subject to strict QC (quality control) procedures. The analytical procedures were validated against CRM (certified reference materials): QC1223 (low level PAHs in acetone) and QC1033 (PCBs in water-WP), both by Sigma-Aldrich Chemie GmbH, Munich, Germany. All the obtained values for PAHs and PCBs in CRM were within the interval of confidence. Reproducibility and recovery were high (80%–105%)

Table 1
Parameters used in the laboratory analysis of PAHs and PCBs.

Parameter	Description
Temperature programme of the GC	Initial temperature at 40 °C, then increase to 120 °C (by 40 °C per minute), then increase to 280 °C (by 5 °C per minute)
Carrier gas	Hellium, inlet pressure 70 kPa
Deionised water	Mili-Q® Ultrapure Water Purification Systems (Millipore®)
PAHs external (calibration) standards	A mixture of 16 PAHs (2000 µg mL ⁻¹ each) in dichloromethane (Resteck Corporation, USA): acenaphthylene, acenaphthene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene and pyrene
PCBs calibration (external) standards	A mixture of PCBs (5 µg mL ⁻¹ each) in isooctane (Resteck Corporation, USA): PCB 28–2,4,4' trichlorobiphenyl; PCB 138–2,2',3,4,4',5' hexachlorobiphenyl; PCB 153–2,2',4,4',5,5' hexachlorobiphenyl; PCB 101–2,2',4,5,5' pentachlorobiphenyl; PCB 118–2,3',4,4',5, pentachlorobiphenyl and PCB 180–2,2',3,4,4',5,5' heptachlorobiphenyl
Internal standard	40 µL isotopically marked PCB 28 and PCB 180 mixture as well as 20 µL of deuterated mixture of PAHs: naphthalene and benzo[a]anthracene (per 500 mL of sample)

with relative standard deviation (RSD) of 5%–10%. Average recoveries of standards in the following validation studies were in range: 70%–85%, and the recoveries of internal standards were 80%, 85%, 82% and 80%, for naphthalene-d8, benzo[a]anthracene-d12, PCB-28 C13 and PCB-180 C13, respectively. Replicate samples and reference solutions were run after every five samples to assure the precision of each run. All blanks were analysed in the same setup as for the samples, using the same reagents. Internal standards were used for quantitative analysis. Thanks to the isotope marking of the internal standards (naphthalene-d8, benzo(a)anthracene-d12; PCB-28 C13 and PCB-180 C13), we calculated the relative response factors (RRF), a characteristic value of a specific pair of an analyte and an internal standard, depending on the conditions of the analysis (Rome and McIntyre, 2012).

Organic acids, alike PAHs and PCBs, were analysed in GUT, using an ion chromatograph DXICS3000 system, Dionex Corporation, USA, fitted with an AC Claim TM Organic Acid column (5 µm, 4.0 × 250 mm, Dionex Bonded Silica Products), with 6 mL min⁻¹ flow rate, UV-Vis detection and 5 µL injection volume. The following acids were determined: oxalic, tartaric, malic, lactic, acetic, citric and succinic; however, only tartaric and oxalic acids were detected in most samples. Blank levels were determined and subtracted from results, at 0.0076 (±0.0025, 1 SD) mg L⁻¹ and 0.0076 (±0.0035, 1 SD) mg L⁻¹, for oxalic and tartaric acid, respectively. Also in GUT, formaldehyde and phenols were determined spectrophotometrically, using ready-made test kits by Merck Millipore.

Cell counts were derived from flow cytometry measurements performed with Partec CyFlow® SL device (with a 20 mW, 488 nm argon ion laser), in the Department of Geography, UoS. Staining procedure followed (Van Nevel et al., 2013), a result of optimisation performed by Hammes et al. (2012), with the use of SybrGreen II stain. Cells were defined as particles fluorescing in the waveband 536/40 nm (FL1) in stained samples, with a minimum signal of 1% intensity of the 3 µm beads (noise signal threshold following manufacturer's

Table 2

Determination range, LOD and LOQ of the used analytical methods for each determined compound. LOD and LOQ were determined at triple and tenfold instrumental noise signal level of a blank sample, respectively. Blank correction of results was used for oxalic and tartaric acid, stained cells, TOC and DOC.

Compound name	Determination range	Blank levels	LOD	LOQ	CV [%]	unit
Total organic carbon (TOC)	0.00003 to >50	0.021	0.00003	0.00012	<1	mg L ⁻¹
Dissolved organic carbon (DOC)	0.00003 to >50	0.065 ^a	0.00003	0.00012	<1	mg L ⁻¹
Organic acids:	0.1–20	0.0076	0.01	0.03	0.5–2.5	mg L ⁻¹
Formaldehyde	0.02–8.00	<LOD	0.01	0.03	5	mg L ⁻¹
Sum of phenols	0.025–5.00	<LOD	0.025	0.075	5	mg L ⁻¹
PAHs:						
Naphthalene	0.35–200	<LOD	0.35	1.05	0.5–5.0	ng L ⁻¹
Acenaphthylene	0.4–100	<LOD	0.4	1.2	0.5–5.0	ng L ⁻¹
Acenaphthene	0.4–100	<LOD	0.4	1.2	0.5–5.0	ng L ⁻¹
Fluorene	0.6–100	<LOD	0.6	1.8	0.5–5.0	ng L ⁻¹
Phenanthrene	0.35–200	<LOD	0.35	1.05	0.5–5.0	ng L ⁻¹
Anthracene	0.45–200	<LOD	0.45	1.35	0.5–5.0	ng L ⁻¹
Fluoranthene	0.75–200	<LOD	0.75	2.25	0.5–5.0	ng L ⁻¹
Pyrene	0.6–100	<LOD	0.6	1.8	0.5–5.0	ng L ⁻¹
Chrysene	0.5–100	<LOD	0.5	1.5	0.5–5.0	ng L ⁻¹
Benzo[a]anthracene	0.55–50	<LOD	0.55	1.65	0.5–5.0	ng L ⁻¹
Benzo[b]fluoranthene	0.8–50	<LOD	0.8	2.4	0.5–5.0	ng L ⁻¹
Benzo[k]fluoranthene	0.75–50	<LOD	0.75	2.25	0.5–5.0	ng L ⁻¹
Benzo[a]pyrene	0.35–50	<LOD	0.05	1.05	0.5–5.0	ng L ⁻¹
Indeno[1,2,3-cd]pyrene	1.4–50	<LOD	1.4	4.2	0.5–5.0	ng L ⁻¹
Dibenzo[a,h]anthracene	0.9–50	<LOD	0.9	2.7	0.5–5.0	ng L ⁻¹
Benzo[g,h,i]perylene	1.1–50	<LOD	1.1	3.3	0.5–5.0	ng L ⁻¹
PCB (all congeners from this study, i.e. PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153 and PCB-180)	0.35–100	<LOD	0.35	1.05	0.5–5.0	ng L ⁻¹
Cell count (stained)	257 to >100,000	211	257	677	13	Counts mL ⁻¹

^a Filtering blank.

recommendations). A cross-check against 18 MΩ and UV-sterilised water blanks (stained) showed cell counts of 0.211 ± 0.097 (1 SD, $n = 11$) L⁻¹, which was interpreted as the background level of the laboratory facility, and used for blank-correction of all obtained counts. The accuracy of the absolute counting procedure was monitored using CountCheck® beads by Partec in the low and medium concentration range, obtaining a relative standard error (RSE) of 9.3% from $n = 7$ independent measurements (24.850×10^6 counts L⁻¹ and 82.660×10^6 counts L⁻¹, respectively).

Organic carbon (OC), both total (TOC) and dissolved (DOC), were determined with the Sievers M5310 C Portable TOC Analyser (GE Power, Water & Process Technologies), also in UoS. DOC was defined as the TOC of 0.7 μm filtrate (Whatman GF/F). In samples with visible particulates, their TOC content was determined also by combustion of Whatman GF/F filterpapers with the suspended matter in 450 °C. TOC was then obtained as a sum of water and dry matter content. Particulate organic carbon (POC) was defined as the difference between TOC and DOC.

The data obtained in this study was characterised by the following quality assurance parameters (Table 2). Especially the PAHs and PCBs were determined from 500 mL water samples, which may have increased the limits of detection and quantification (LODs and LOQs). However, otherwise it would not be possible to sample the thinner snow or ice layers.

The laboratory analysis was performed at the earliest opportunity, which was approximately 4 months past sample collection for organic acids and between 6 and 18 months for PAHs and PCBs. The high detected levels of PAHs however, show that even if losses to adsorption occurred, the relative levels of PAHs were still a reliable source of information for the collected samples, and hence there is a major focus placed on those in the following analysis. Unfortunately, the 4 months may have been a long time for the measurement of the organic acids, since we obtained very high concentrations of tartaric acid. Therefore, this component was treated with extra caution in the interpretation, as possibly influenced by post-sampling microbial activity.

2.3. Theoretical data on physical properties of the determined compounds

Theoretical data on the physical properties of the sampled compounds was collected from the existing literature. The properties of each compound, namely water solubility and water-octanol partitioning coefficient (K_{ow}), are reported in Table 3 for the measured organic compounds. The included values will be used in the further considerations on the compound fate in snowpack, solid ice and liquid water.

3. Results

The snowpack evolution differed slightly between the upper and lower site, as in particular there occurred a gain of total snow water equivalent (SWE) in the upper site between the first and second snowpit, while in the lower site there was a continuous decline in SWE (Fig. 2). This could reflect the altitude affecting the form and quantity of precipitation, as well as melt intensity, in the period 06/06–22/06, when light snowfalls occurred (on 13/06, 14/06 and 17–19/06). The gaps between field dates in both sites corresponded to periods without precipitation. Therefore, the chemical changes in each of those snow profile sites will be described separately below, the lower and upper sites being pictured on Figs. 3 and 4, respectively. In those figures, there can be found also the division of stratigraphical layers as sampled. In the lower site, already at the first occasions two ice layers were noted (at depths 38–39 cm and 54–56 cm), as well as a wet layer at the depth of 74–76 cm. Then, it evolved to contain two ice layers, almost neighbouring, near the bottom of the snowpit on 24/06/2014 (between the depths of 53 and 57 cm). In the upper site snowpit, the initial structure was more unified, with the dominant hardness between 4 fingers and 1 finger in hand test scale. In the next sampled stage, two ice layers were formed, at the depths of 21 cm and 40 cm. The final stage at both sites was almost unified snow structure, differentiated only by the level of water saturation. The capillary water rise level was found at 10 cm and 20 cm depth, at the lower and upper site, respectively.



Table 3

Water solubility and related properties of the analysed compounds (PubChem, 2004; Ritter et al., 1995; Tobiszewski and Namieśnik, 2012).

Compound	Water solubility [mg L ⁻¹] at 25 °C	Log K _{ow} at 25 °C
Naphthalene	31	3.37
Acenaphthylene	16	4
Acenaphthene	3.8	3.92
Fluorene	1.9	4.18
Phenanthrene	1.1	4.46
Fluoranthene	0.2	8.9
Pyrene	0.13	8.8
Anthracene	0.04	4.49
Benzo[a]anthracene	0.011	5.8
Benzo[e]pyrene	0.007	6.44
Chrysene	0.0019	5.73
Benzo[b]fluoranthene	0.0015	5.78
Benzo[a]pyrene	0.0015	6.35
Benzo[k]fluoranthene	0.0008	6.5
Dibenzo[a,h]anthracene	0.0005	6.5
Benzo[g,h,i]perylene	0.00014	6.63
Indeno[1,2,3-c,d]pyrene	0.00019	6.7
Trichlorobiphenyl (e.g. PCB-28)	0.015–0.4	5.5–5.9
Pentachlorobiphenyl (e.g. PCB-101, PCB-118)	0.004–0.02	6.2–6.5
Hexachlorobiphenyl (e.g. PCB-138, PCB-153)	0.004–0.0007	6.7–7.7
Heptachlorobiphenyl (e.g. PCB-180)	0.000045	6.7–7.0
Phenol	82.8	1.46
Formaldehyde	400	0.35
Oxalic acid	220	–0.81
Tartaric acid	1000	–0.76

PubChem. 2004. National Center for Biotechnology Information, U.S. National Library of Medicine, database [online] Available from: <https://pubchem.ncbi.nlm.nih.gov/> (Accessed 28 November 2016).

Ritter L, Solomon KR, Forget J. 1995. Persistent organic pollutants. An assessment report on: DDT - Aldrin - Dieldrin - Endrin - Chlordane - Heptachlor - Hexachlorobenzene - Mirex - Toxaphene - Polychlorinated Biphenyls - Dioxins and Furans.

Tobiszewski M, Namieśnik J. 2012. PAH diagnostic ratios for the identification of pollution emission sources. *Environmental Pollution* 162: 110–119. DOI: [10.1016/j.envpol.2011.10.025](https://doi.org/10.1016/j.envpol.2011.10.025).

In the lower snowpit of Foxfonna glacier in the period 06.06.2014–24.06.2016, 11% of the SWE has been removed (from 375 to 334 mm w.e.), and 52% of the TOC load (86 mg m⁻²; see also Table 4). Subsequently, during the period 24.06–08.07.2016, another 67% of the initial SWE melted out, leaving only 83 mm w.e. This second period corresponded to a loss of 60 mg m⁻² TOC from the snow profile (37% initial TOC load). Therefore, there remained 22% of the initial SWE and 11% of the initial TOC load.

The main losses of organic substances in the first part of the melting period were in the components from PAHs and PCBs groups, as well as formaldehyde, in contrast to an increase in the loads of short chain organic acids, accompanied with an increased number of stained cells (especially oxalic acid load grew by 167%). The second melting period brought a marked loss of the short chain organic acids mass (exceeding

90% reduction), and a significant decrease in the formaldehyde, stained cells and PCBs content (by 70%, 70% and 67%, respectively; see Table 4), while a slight increase in PAHs load was noted in that period (24%). A striking increase was also noted for the sum of phenols (236%). The final snow cover in 2014 included mainly phenols (14 mg m⁻²), formaldehyde (4.5 mg m⁻²), oxalic and tartaric acids (4 mg m⁻² and 0.1 mg m⁻², respectively), but the highest percentages of the initial chemical load were noted for phenols (299%), and then for oxalic acid and PCBs (16% and 15%, respectively).

The situation was somewhat different in the upper snowpit, which was subject to less melt and more accumulation from precipitation, and in the first period (05/06–22/06/2014) it even gained 11% of SWE, despite the reduction in snowpack depth (from 107 cm to 90 cm). This corresponds well with its location approximately 100 m higher and on a more levelled ground. Conversely, the second part of the melt season led to a reduction of 42% of the maximum SWE on 22nd June 2014. The TOC changes however, demonstrated a constant decrease: by 8% in the initial melting period and by another 54% of the first snowpit content in the second part of the melting season, leaving 47.2 mg m⁻² TOC on July 8th. In first part of the melting season (before June 22nd), the decrease was marked in the tartaric anion load (by 18%). On the contrary, the particulate components have increased their loads, and strikingly: POC, cell count and sum of PAHs increased by 167%, 191% and 101% of the initial load, respectively. Oxalic anion noted a smaller increase in that period, while the formaldehyde and sum of phenols cannot be compared to the initial stage due to lack of reliable measurement of this time point. The second part of the melting period in the upper site brought yet further increase in the load of POC (20%), as well as growth in the tartaric acid load (by 80% of the initial value), but a drop in many other chemical and biological components of the snowpack: –146% of the initial cell load (–50% of the intermediate value), –93% of the oxalic acid from the first snowpit (–77% of the intermediate one), and –87% of PAHs load from the beginning (–43% of the preceding measurement load). PCBs have not been detected in any of the upper site snowpits. Formaldehyde could only be compared between two last occurrences, and it has increased its load by 184%.

Superimposed ice (SI) contained variable amounts of the initial organic chemicals loads. In the upper site, it preserved 28% of the TOC deposited up to the beginning of melt (as found in the first snowpit), while in the lower only 12%. This may correspond to the higher water equivalent of this ice layer in the upper site, where it preserved 12% of the initial SWE, as opposed to 7% initial water equivalent in the lower site. Fig. 4 shows both SI layers had higher TOC concentrations compared to the initial snow cover, in particular as POC (for which SI stored 61% and 65% of the load found in the snowpit with highest SWE in the upper and lower site, respectively). The main enriched chemical group was PAHs. In the upper site, 18% of PAHs in the initial snowpit was preserved in SI, while for the lower this share amounted to 9%. Also PCBs in the upper site can be claimed to have increased their concentration in SI, where they were detected, unlike in any of the preceding snow covers; indeed the PCBs load in SI did not exceed the theoretical PCBs load of the

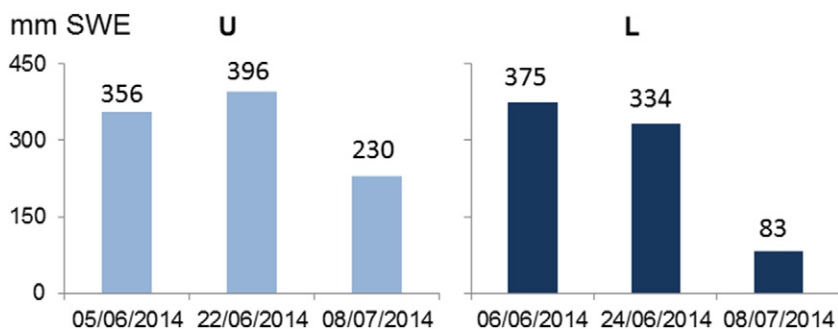


Fig. 2. Snow water equivalent (SWE) changes between the sampling dates in the investigated snowpit sites.

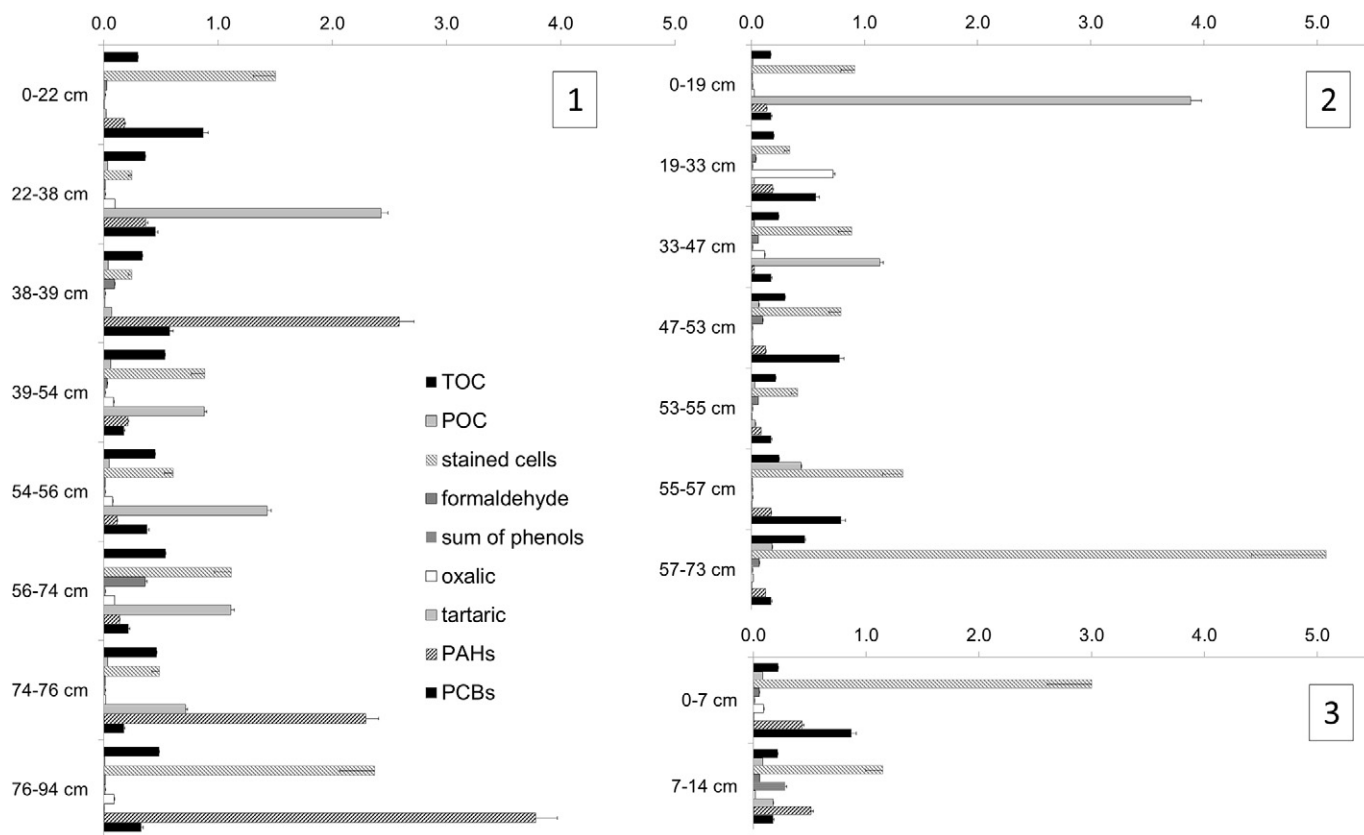


Fig. 3. The temporal changes in the lower site (L) snowpit composition, in the order given by graph numbers: 1 – initial snowpit on 06.06.2014, 2 – mid-melt snowpit on 24.06.2014, 3 – final snowpit on 08.07.2014 (for superimposed ice composition, see Fig. 4). Units differ for particular chemicals: TOC, POC, formaldehyde, sum of phenols and oxalic acid [mg L^{-1}], tartaric acid [$\times 10 \text{ mg L}^{-1}$], sum of PAHs [$\mu\text{g L}^{-1}$], sum of PCBs [ng L^{-1}], stained cells [$10^4 \text{ counts mL}^{-1}$]. Values <LOD shown as half of its value. For clarity, error bars are displayed only on one side of the value.

initial snowpit, if calculated using half of LOD as concentration. As for the other chemicals, phenols in the lower site and oxalic acid in both showed a similar percentage in SI to the share of water equivalent preserved, while the other compounds (formaldehyde and tartaric acid) noted a decrease, showing they were disproportionately removed from the refrozen layer. Finally, a strongly enriched element was also stained cells, however this effect was highly variable between two sites, showing 272% of the initial cell content in the upper site SI, and only 40% in the lower site.

4. Discussion

Generally, the water soluble pollutants were more abundant at the earlier and middle stages of melting snowpack development. However, high formaldehyde concentration in the later stage of the upper site is an exception. At least part of the formaldehyde in snowpack is deemed to be photochemically produced (from $\text{OH}\cdot$ radical reaction with hydrocarbons or other organic chemicals, including oxalic acid). However, formaldehyde is also prone to photochemical degradation. It may remain in the lower layers of snowpack, less exposed to sunlight, and so its presence at the late stages of melt is likely a result of fast melt in limited irradiation conditions (indeed only two days in the period between the second and third sampling were sunny), and perhaps also sealing the pore spaces that could let the HCHO escape into the atmosphere in gaseous form. The 60 times lower snow-air than water/air equilibrium constant for HCHO would facilitate it to tarry in the snowpack once it saturates with water. An additional source of formaldehyde in snow could be from algal production, however the vertical distribution of stained cells and formaldehyde are far from supporting this interpretation (Sumner and Shepson, 1999).

The more hydrophobic substances, i.e. PAHs and PCBs, and in the lower site also phenols, remained in the snowpack in proportionally higher concentrations than the hydrophilic species at the late melting stage (third sampling occasion), they were also trapped in the SI. This is curious since the SI is actually formed from the earlier portions of meltwater percolating down the snow profile and refrozen at its bottom. However, it would also include a layer of early snow that became saturated with this water before refreezing took place. Thus it is different from the composition of the last, waterlogged snowpits, and it accumulated a surprisingly high amount of relatively hydrophobic elements: POC, PAHs and PCBs (the latter in the upper site). This leads to a hypothesis, that these compounds, which would be difficult to leach with the first portion of meltwater, are more likely to be an inheritance from snow deposition history, particularly as in the lower layers of the studied snowpits, such components were also more abundant in the two lowest layers of each. In the case of Foxfonna, placed near a coal mine with some waste deposited in the vicinity, and near Longyearbyen heated with a coal power plant, this is likely an effect of the combination of coal combustion and raw material redistribution when the snow cover was thin and patchy. The high values in the upper layers, particularly of PCBs in the lower site, are more likely of different origin. These could result from intensified deposition of pollutants from long-range transport in the spring, known as the Arctic haze phenomenon. The lower contribution of PCBs to the upper site snowpit (below LOD) agrees with the general tendency for decreasing PCB concentration with increasing altitude in mountainous regions (UNECE, 2010).

A curious case is the behaviour of phenols, which increased their concentration in the lower site in the last stage of melt, yet were not visible in the upper site. Due to generally low levels of phenols in the snow profiles, this is difficult to interpret for certain, yet it has at least a

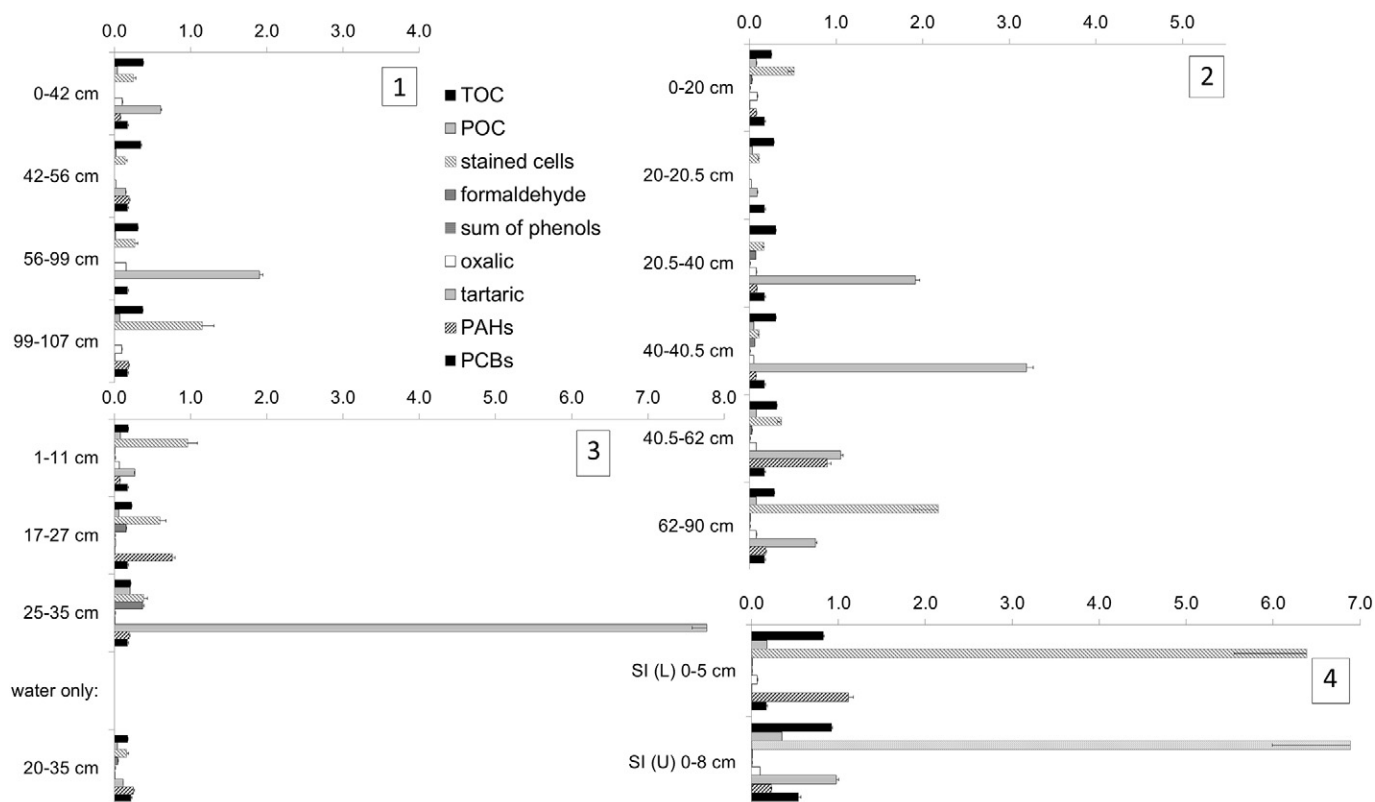


Fig. 4. The temporal changes in the upper site (U) snowpit composition, including the superimposed ice (SI) composition in both sites: 1 – initial snowpit on 05.06.2014, 2 – subsequent snowpit on 22.06.2014, 3 – final snowpit on 08.07.2014, 4 – superimposed ice (SI) composition on 20.07.2014. Units differ for particular chemicals: TOC, POC, formaldehyde, sum of phenols and oxalic acid [mg L^{-1}], tartaric acid [$\times 10 \text{ mg L}^{-1}$], sum of PAHs [$\mu\text{g L}^{-1}$], sum of PCBs [ng L^{-1}], stained cells [$10^4 \text{ counts mL}^{-1}$]. Values <LOD shown as half of its value. For clarity, error bars are displayed only on one side of the value.

hypothetical explanation. Since phenols are a group of compounds, they could express different chemical composition (and therefore properties) in both sites, i.e. the more volatile (and more hydrophilic) phenols would be transported more easily into higher altitudes through the atmosphere. Then, the snowpit profile more abundant in the hydrophobic fraction of phenols (the lower one) would accumulate them in contrast to the upper one.

There was a clear domination of hydrophilic over hydrophobic organic compounds in the recognised proportion of organic matter mass in the Foxfonna snowpacks, yet the majority of TOC detected in the samples was not chemically characterised (Fig. 5). On average 19% of the TOC in snow was POC, while most of the snowpack OC was in dissolved state. However, according to Meyer and Wania (2011), those well-soluble chemicals will be also removed from snowpack first, therefore towards the end of the melt season the remainder of OC will be mostly hydrophobic. Surprisingly, the relative proportion of TOC as hydrophilic compounds rather increased in the studied snowpack (attuned to the physical presence of liquid water). However, the last sampled snowpits also contained the highest proportion of the TOC as POC (48%), while

the earliest snowpits in both sites contained on average only 7% POC. Superimposed ice contained a relatively small proportion of the hydrophilic compounds characterised and a moderate proportion of POC in TOC (30%).

A closer look at the hydrophobicity of pollutants as a driving factor in their distribution in subsequent snowpits can be taken with help of the classification of pollutant enrichment types in snowpack drawn by Meyer and Wania (2011). In brief, Type 1 refers to chemicals dissolved in water, with peak concentration in the initial melt event, Type 2, on the contrary, is characterised by a strong attachment to snow grain and organic matter, where the pollutant load is removed in one strong pulse only in the end of the melt season, Type 3 results from partitioning between snow grain surface (majority) and liquid water (minority), leading to an increasing concentration in meltwater until the end of the season, where maxima occur, and Type 4 is a mixture of the Type 1 and 2 enrichment (concentration peaks in the beginning and end of melt). Of the chemicals analysed here, we fitted representatives to the characteristics of Type 1, 2 and 4, according to the cited source or the partitioning data given therein. These were:

Table 4
Proportional changes in chemical/biological load of the species determined in the study.

% Change of total chemical/biological load [in mass per m^2]	TOC	POC	Stained cells	HCHO	Σ phenols	Oxalic acid	Tartaric acid	PAHs	PCBs
Lower site, period: 06–24/06/2014	–52%	+203%	+23%	–56%	both <LOD	+167%	+34%	–88%	–55%
Lower site, period: 24/06–08/07/2014	–77%	–70%	–70%	–70%	+236%	–94%	–98%	–1%	–67%
Lower site, final load as % load on 06/06/2014	11%	91%	37%	13%	299%	16%	3%	12%	15%
Upper site, period: 05–22/06/2014	–8%	+167%	+191%	n.d.	n.d.	+21%	–18%	+101%	both <LOD
Upper site, period: 22/06–08/07/2014	–58%	+8%	–50%	+184%	both <LOD	–77%	+97%	–43%	both <LOD
Upper site, final load as % load on 05/06/2014	38%	287%	146%	n.d.	n.d.	28%	162%	114%	all < LOD



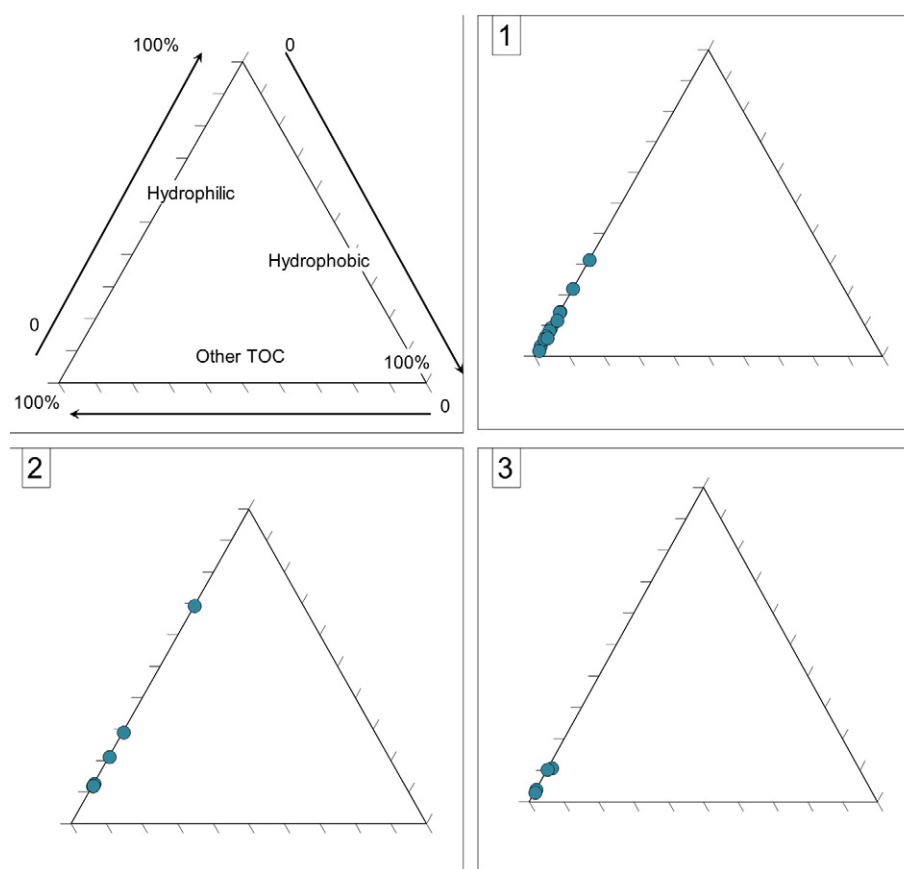


Fig. 5. Hydrophobic and hydrophilic compounds concentrations as parts of the general organic carbon content, as detected in: 1 – first snowpits in both sites, 2 – last snowpits in both sites, 3 – superimposed ice (5 samples from different locations).

- Type 1 – the definitely well-soluble formaldehyde and oxalic acid, as well as the best soluble of PAHs – naphthalene (for water solubilities, see Table 3);
- Type 2 – phenanthrene as mentioned in Meyer and Wania (2011) and pyrene, as it should be placed in the same region of the partitioning graph (Fig. 4 of the cited source);
- Type 4 – Fluorene and acenaphthene, both classified as such in the original paper.
- Type 3 was not identified among the measured compounds. The redistribution of the chosen compounds in the both snowpits is presented in Fig. 6.

The interpretation of Fig. 6 requires prior translating of the signature of those enrichment types in meltwater into the most probable state of the chemicals remaining inside the snow profile. Therefore, we would expect the above mentioned characteristics to lead to the following results:

- Type 1 chemicals should be rapidly removed from snowpack, only small residual remaining in the middle of melt period. First, they would be removed from upper layers, as the melt and rain water washes the profile starting from the top.
- Type 2 enrichment is expected to result in almost stable pollutant load in their initial location in the profile or their slow downward movement. Accumulation while refreezing is also possible, since it would slow down removal. High chemical loads are to be found either in the last, wet snowpit or in superimposed ice.
- Type 4 of pollutant behaviour would be a mixture of the two, hence part of the load should be removed rapidly, but may also be subject to refreezing or residual storage in various parts of the profile, especially where there is more particulate organic matter.

The comparison of those expected behaviours to the distribution of chemicals registered in the field, results in the following conclusions.

4.1. Type 1

Of the three selected compounds for this type, oxalic anion behaves furthest from the expected pattern, as it increases its concentration >7 times in the upper layers of the lower snowpit. In the upper snowpit, however, it experienced a more steady decrease in load. The noted growth may be associated either with microbial activity or photochemistry (see Bikkina et al., 2015 for the photochemical origin pathways). However the first may be supported with sufficient cell counts detected to have an influence, there was no correlation found between the oxalic anion concentrations and cell counts in snow layers ($r = -0.10$, $p < 0.60$). Also formaldehyde increased its load, although slower, but in both snowpits. Both these compounds noted the increases in the upper snow layers, which confirms the likely photochemical origin (Sumner and Shepson, 1999), as it could not be explained by atmospheric deposition (estimated for $<0.5 \text{ mg m}^{-2}$ in the whole sampling period, 06/06–20/07/2014). Therefore, the expected fast elution was likely observed only in the lower layers, while the content of higher layers could be replenished. Naphthalene was also classified here, although much less water soluble than the other contaminants listed above, and it has complied to an extent with the forecasted behaviour, at least in the lower site. The upper site showed a surprisingly high load accumulated in the lower layers of the 22/06/2014 snowpit, not possible to explain by its relatively small deposition ($<3.7 \mu\text{g m}^{-2}$ in the whole sampling period). In the lower site, its load significantly decreased during the first period of melt, although residual naphthalene was also observed in the upper, not inundated water layers, until the

last stage recorded, and in the upper site it was even present in the waterlogged bottom of the snowpit. Naphthalene concentration in snow layers did not significantly correlate with POC ($n = 29$, $r = -0.0313$, $p = 0.872$), so its remaining in the snowpit until late in the season could not be associated with organic matter affinity of naphthalene, but perhaps only snow grain affinity. The SI contained relatively small amounts of Type 1 chemicals (in the lower snowpit mostly naphthalene, and in the upper – oxalic acid), as did also wet layers.

4.2. Type 2

Surprisingly, pyrene had been removed rather efficiently by the second stage of melt in the lower snowpit, and phenanthrene remained present only in the upper layers then, where it could not be residual. In the upper snowpit, both chemicals were not detected at the initial stage of sampling, and showed a small concentration during the next stage. A likely source of both chemicals would be, atmospheric deposition, although for phenanthrene it could not explain the significant increases in the lower snowpit. In the glass containers, set up on the glacier to collect controls for atmospheric deposition, phenanthrene deposition for the whole period between 06/06/2014 and 20/07/2014 was estimated for $<130 \text{ ng m}^{-2}$, while pyrene noted a much higher deposition, $<1780 \text{ ng m}^{-2}$. Interestingly, both these chemicals were scarce within ice layers, but more abundant in wet layers, especially pyrene, which is also stored in SI, and this effect was repeated in both investigated sites. This leads to a hypothesis that its presence in the refrozen meltwater layer is linked to its presence in the stagnant water before, while it has no connection to particulate organic matter (neither phenanthrene nor pyrene correlated with POC in snow layers, the coefficients

being low, negative, and not statistically significant in the group of $n = 29$ snow layers).

4.3. Type 4

The behaviour of the two chosen representatives of this group matched closely the distribution changes observed for Type 2, especially if fluorene and pyrene concentrations are compared. Acenaphthene, showing redistribution pattern between the two observed for pyrene and phenanthrene, was less abundant in wet layers than pyrene and did not occupy the SI layer as much, either; the difference was most pronounced in the snow layer where the water table was set at the time of the last snowpit sampling. Therefore, acenaphthene could be claimed to be removed quicker and thus resemble its more water soluble counterparts, or maybe just lacking the ability remain on the water table surface, e.g. through adsorption to the floating fraction of the particulate matter.

Considering the curious composition of the superimposed layer, we also compared it, in the upper snow profile, to the stagnant water that has accumulated in the bottom of the snowpit on the last survey date (8th July 2014). Their concentrations of phenanthrene, pyrene, fluorene and acenaphthene were strikingly similar, and in fact the concentrations of all measured chemicals correlated on the level of $r = 0.9985$ with a $p < 0.01$ ($n = 27$ chemical compounds). This would suggest a similar source of chemicals for both types of layers, perhaps even resulting from a water surface mechanism. That would explain why superimposed ice was enriched in the less expected hydrophobic compounds rather than the hydrophilic ones, which should be more abundant in meltwater that feeds the SI layer.

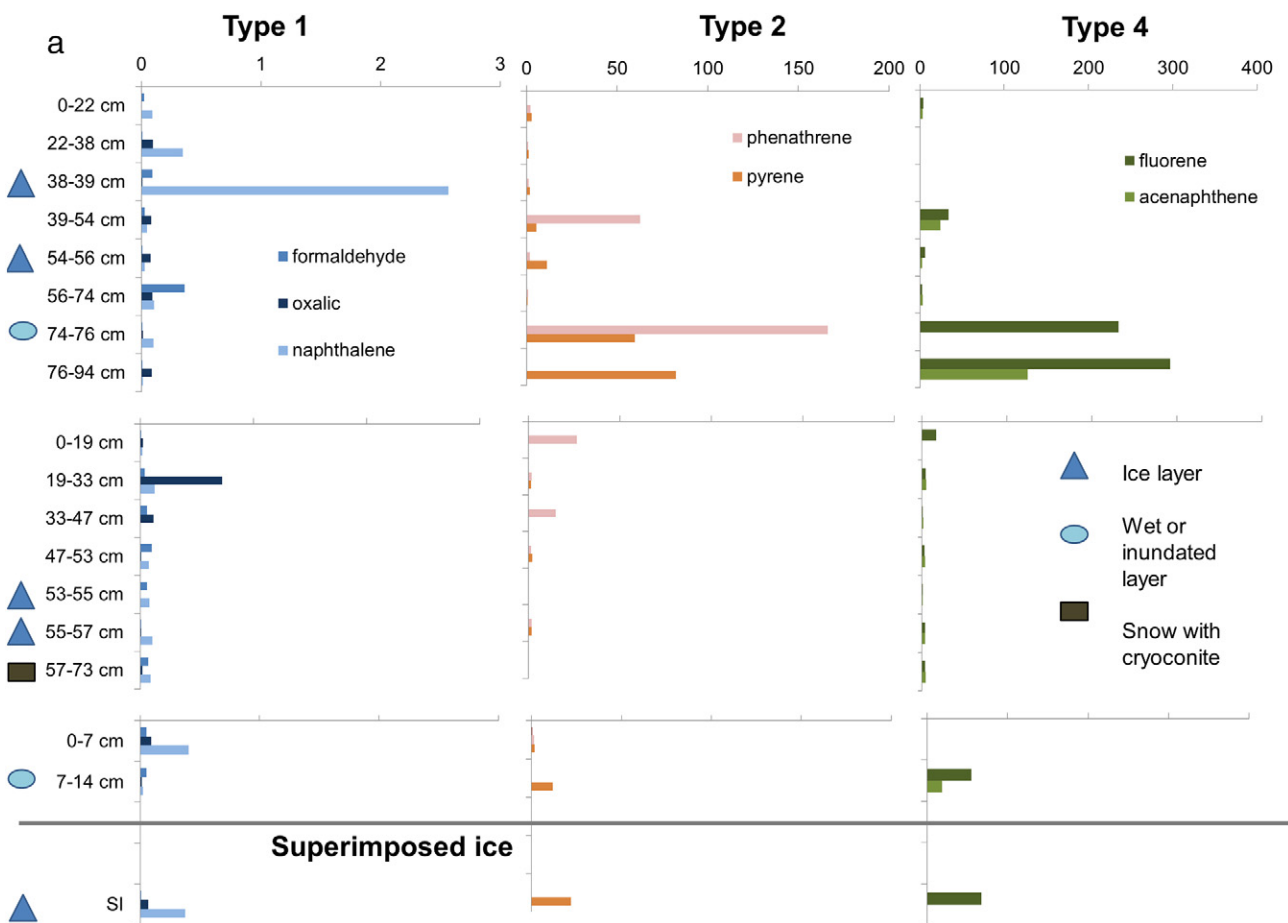


Fig. 6. Distribution in the melting snowpits at both sites (6a – lower site, 6b – upper site), for specific elution enrichment types of chemicals. Top axes in mg L^{-1} (for formaldehyde and oxalic acid), $\mu\text{g L}^{-1}$ (for naphthalene) and ng L^{-1} (for other PAHs).

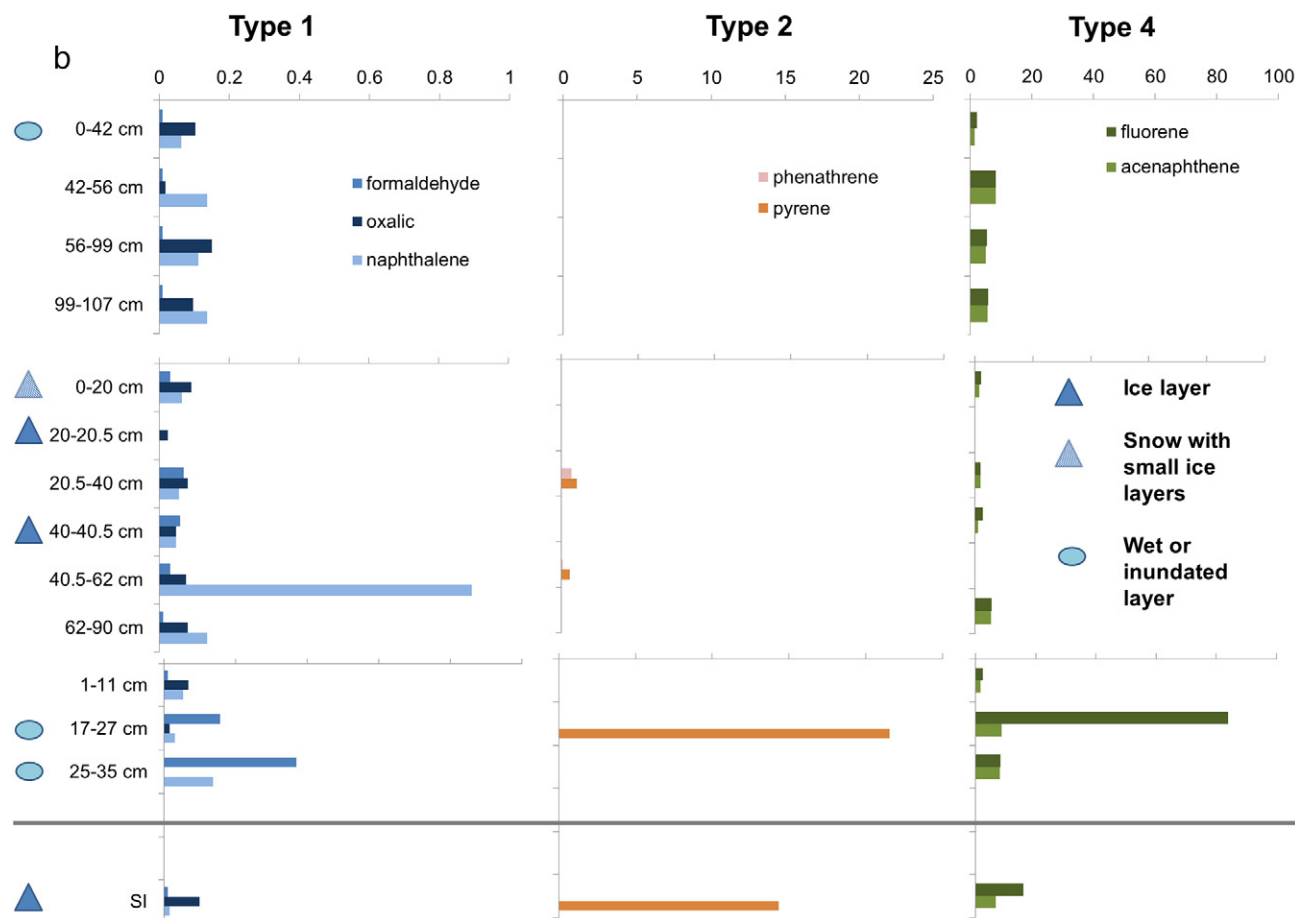


Fig. 6 (continued).

5. Conclusions

An observation of the temporal development of snow composition, in respect to their organic chemicals composition and properties, shows several characteristics that warrant a further study. The majority of the snow organic matter of the Foxfonna glacier was dissolved, and among the determined compounds, most were hydrophilic, with water solubilities exceeding 10 g L^{-1} ; among the other compounds also prevailed those with proportionally higher water solubilities. An important component of the snow accumulated on the glacier was also POC, especially at the later stages of melt.

The pollutant characteristics, and their hydrophobic or hydrophilic behaviour, alongside other partitioning effects in the snowpack, were successful in predicting some of the pollutant behaviour observed. The biggest difference from the expectations was within the spectrum of highly soluble and otherwise highly reactive compounds, e.g. formaldehyde and oxalic acid. Their distribution was most likely influenced by photochemical production. The other point, where the elution model by Meyer and Wania (2011) provided only limited explanations is the water table inside the snow profile. In this area some chemicals have been strongly enriched (especially fluorene and pyrene), perhaps as a result of connection to floating particles. This mechanism would also make the chemical composition of superimposed ice and thin ice lenses in snowpack significantly different. We conclude, that the changes in partly melting snowpack, the remainder of which could then be incorporated into glacial ice, the POC and the hydrophilic components become enriched. Conversely, the water soluble and reactive compounds are the least reliable components of ice records, and their share would be lower in glacial ice formed in times of increased melt. Perhaps the

hydrophilic to hydrophobic matter ratio is a promising characteristics for assessing past melt rates from ice records sampled in subpolar glaciers, since the hydrophobic compounds would be enriched in layers exposed to melt.

Acknowledgements

This study was solely funded by the National Science Centre of Poland (NCN) [grant number 2012/05/N/ST10/02848]. The fieldwork logistics was supported by UNIS and its students, especially R. Stankova and C. de Vries, as well as J. Johnson and J. Bartlett from the University of Sheffield (UoS). The laboratory analysis and initial data processing was aided by P. Żuchowska at Gdansk University of Technology; help in the laboratory was also given by R. Quartly (UoS). N. Austen volunteered proofreading.

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