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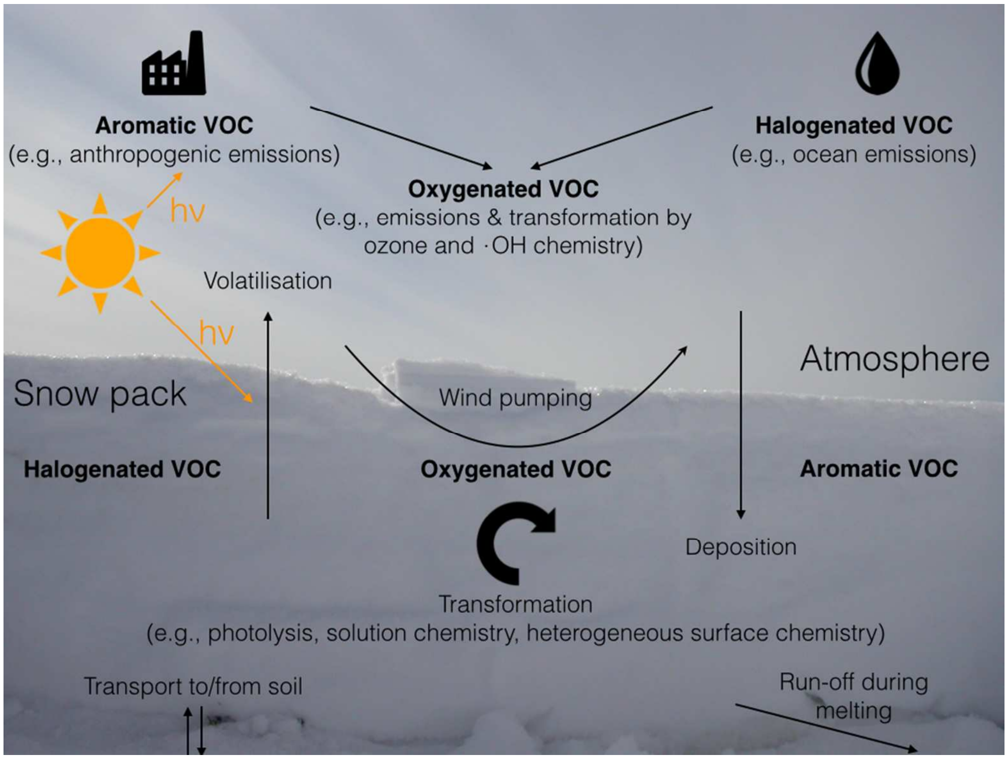

Table of contents entry: Colour graphic
361x270mm (72 x 72 DPI)

Concurrent measurements of aromatic, oxygenated and halogenated VOC in the High-Arctic snow pack and air with solid-phase microextraction gas chromatography.

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Measurements of volatile organic compounds (VOC) in snow are scare, despite the fact that VOC in the snow pack affect the gas-particle transfer with the atmosphere, atmospheric oxidation and aerosol formation. We present robust, yet sensitive methodology for the determination of VOC in snow on site. Data for 18 organic species in snow and air were obtained during field studies in Alert, NU, CANADA and the Ocean-Atmosphere-Sea Ice-Snowpack field campaign in Barrow, AK, USA. Results were evaluated with other environmental and meteorological data to show the method's ability to track changes of VOC concentrations with environmental conditions. We discuss the method's expandability by use of different adsorbents for optimized selectivity and sensitivity for environmental monitoring.

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# Volatile organic compounds in Arctic snow: Concentrations and implications for atmospheric processes

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The role of volatile organic compounds (VOC) in the snowpack for atmospheric oxidation, gas-particle transfer and aerosol formation remains poorly understood, partly due to a lack of methodology and unavailable data. We deployed solid phase micro-extraction (SPME) gas chromatography with flame ionization detection for measurement of halogenated, aromatic and oxygenated VOC in the snow pack in Alert, NU, Canada, a High Arctic site. Halogenated, aromatic and oxygenated VOC in the snow pack were measured. Maximum concentrations in snow were 39 ± 6 $\mu$g/L (styrene), indicating a potential VOC contribution to atmospheric oxidation and aerosol formation. Concurrently sampled air had concentrations of up to 1.0 ± 0.3 ng/L (trichloroethene). Back trajectory data showed a change of air mass source region during a depletion event of several VOC in snow (e.g., trichloroethene and benzene). Snow profiles showed an enrichment of most compounds close to the surface. During a second study in Barrow, AK, USA VOC were quantified in snow and frost flowers in the Montreal lab. In Barrow work was carried out as part of the extensive OASIS (Ocean–Atmosphere–Sea Ice–Snowpack) field campaign. Maximum VOC concentrations were up to 1.3 ± 0.1 $\mu$g/L (acetophenone). Bromoform in frost flowers averaged 0.19 ± 0.04 $\mu$g/L, indicating the potential to contribute to bromine generation through photolysis.

## 1 Introduction

The snow pack has been recognised as an important matrix for (photo) chemical and biological reactions of organic compounds[1]. It provides a large surface area consisting of interstitial air, water and ice that readily exchanges chemical and biological species with the atmospheric boundary layer (ABL). Previous reports described snow pack exchange and transformation processes that included trace gas exchange, scavenging, photolysis and adsorption[1,2]. More recently, biological transformations have been considered[3]. The complex structure of snow, which is a temporally and spatially highly dynamic structure makes it challenging to study. Apart from open questions regarding the contaminant profile, significant knowledge gaps exist regarding the location and transfer processes of contaminants in the snow matrix, which was recently addressed in a review by Bartels-Rausch *et al.*[4]. Snow effectively provides a photobiochemical platform for the exchange and transformation of organic species[5]. These reactions potentially change the oxidative capacity of the lower troposphere with important implications for climate processes, including atmospheric oxidation and aerosol formation[6,7]. Despite these results that highlight the importance of snow for atmospheric processes, it remains a rarely investigated matrix for volatile organic compounds (VOC) of anthropogenic and biogenic origin. Currently, the only compound exchanged between air and snow with a demonstrated impact on the oxidative capacity is the more volatile formaldehyde[8]. However, VOC are major contributors to atmospheric reactions[9] and aromatic, halogenated and oxygenated species together with nitrous oxides ($NO_x$) can drive ozone ($O_3$) and hydroxyl radical ($\cdot$OH) production in the troposphere[10]. Lifetimes of aromatic VOC in the troposphere are comparatively long compared to short ($C_1$ to $C_3$) carbon chain volatile species, e.g., up to 9 d for benzene in a polluted atmosphere[11]. However, aromatic and longer carbon chain (e.g., $C_6$) VOC are potentially important since they provide a reservoir for reactive carbon species.

The snowpack provides ice and water surfaces for a different set of processes than atmospheric reactions, including photochemical and biological interactions[2,12,13]. The resulting products are potentially relevant for atmospheric chemical processes upon re-volatilisation[14] by wind and melting. Snow pack data exist mostly for inorganic compounds, e.g., bromine and precursors[9], $NO_x$, hydrogen peroxide[15], and selected organic species e.g., formaldehyde[16], dicarboxylic acids[17], selected $C_2$-$C_7$ hydrocarbons[9], glyoxal and acetaldehyde[18]. Reports indicated that the range and number of compounds found in the snow pack is indeed diverse and

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large[18–22]. The number of studies so far that dealt with VOC in snow is relatively small and provided limited information on concentrations and potential reaction pathways[23]. Recent work focused on the determination of persistent organic pollutants[24–27]. Data presented here was obtained as part of the OASIS (Ocean–Atmosphere–Sea Ice–Snowpack) 2009 campaign in Barrow, AK. Other work related to organics carried out at the same time included the investigation of soluble chromophores and humic-like substances (HULIS) in snow[28–30]. Individual species were also determined primarily in air, but due to the use of proton transfer reaction mass spectrometry an unambiguous identification was not attempted[31]. VOC species in air and snow were also determined at sampling sites in Switzerland[32–34] using headspace-solid-phase dynamic extraction (HS-SPDE) with gas chromatography mass spectrometry (GC/MS) and an automated sampler with gas chromatography flame ionisation detection (GC/FID). Further measurements in the Quebec-Windsor corridor in Canada employed solid phase micro-extraction (SPME) with GC/MS[35]. Kippenberger *et al.*[36] determined higher carboxylic acids in snow samples from the Fee glacier in Switzerland using solid-phase extraction (SPE) and liquid chromatography coupled with time of flight mass spectrometry (LC-TOF). Earlier work on the determination of saturated and unsaturated organic acids in snow has been reported by Narukawa *et al.*[21]. A summary for different species and methods was provided by Blas *et al.*[37].

Regarding the impact of halogenated compounds, bromine chemistry has been suggested to be instrumental in understanding tropospheric ozone depletion events in the Arctic and its impact on the global ozone budget[38,39]. In addition to snow, frost flowers have received increased attention from researchers in recent years[40]. The large surface area of frost flowers facilitates exchange with the atmosphere[28,41,42]. Results are also of relevance for atmospheric concentrations of halogenated organic species in the Arctic[43,44]

Grannas *et al.*[8],[45] provided a comprehensive overview of current research on snow photochemistry dealing with halogens and organics. Dramatic observations were made including ozone depletion events[46,47] during polar sunrise and the related bromine explosion[48], illustrating the sensitivity of the Arctic environment to changes in the chemical composition of the air-snow interface. Recently Granfors *et al.*[49] studied the halocarbon content of young sea ice and frost flowers and acknowledged that brominated halocarbons including bromoform provide a small contribution to the atmospheric bromine load.

The major underlying challenge is that the mass balance of organic species in the snow pack is still poorly understood, despite strong indications that organics and their reaction products contribute to atmospheric chemistry oxidation reactions and aerosol formation. Concentrations and processes governing production and destruction of organics are not well understood, partly due to a lack of analytical methodology and subsequent lack of data[8].

Solid phase microextraction (SPME) is a solvent-less extraction technique that uses analyte adsorption to a polymer fibre from solution or its headspace[50]. It is widely used for analysis of aqueous samples[51–53]. We previously used SPME for snow analysis in mid-latitudes[19,35]. The presented GC/FID method was modified from a lab-based GC/MS method[19] and the choice of model compounds largely based on detection in snow during earlier studies. The mostly identical GC set-ups (with MS in the lab and FID detectors in the field) provided comparison data from snow samples and added confidence about the correct identification of compounds using the field-based GC/FID system. Studies employing SPME in an environmental context are widely available[54–56]. However, the usage of SPME under extreme environmental conditions such as in the High Arctic is not well characterized.

### 1.1 Objectives

The objective of the presented study was to provide much needed VOC data in snow in the Arctic regions by deploying SPME-GC/FID methodology in the field at a remote High Arctic site in Alert, NU, Canada for the first time. The concurrent determination of 18 halogenated, oxygenated and aromatic VOC (see Appendix table A.2) in surface snow and in snow depth profile samples under extreme and remote Arctic conditions was carried out. Concurrent air samples collected were analysed for the same selection of VOC species following a previously reported method[57]. Data sets from Alert were analysed in the context of local ozone concentrations and Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) back trajectory data. Data were also compared with sample concentrations collected at the Arctic site of Barrow, AK, USA. The latter were analysed at the McGill Atmospheric Chemistry laboratory in Montreal, QC, Canada employing GC/MS. The implications of the findings for atmospheric processes are discussed.

## 2 Experimental

In this study we provide gas chromatography (GC) data with both, flame ionisation (FID) and mass spectrometric (MS) detectors to help close the stated knowledge gap about VOC in snow. GC/FID was employed close to the field in a High-Arctic environment due to its simple set-up and moderate power requirements. GC/MS was used in a laboratory environment. Sensitivity, robustness of field instrumentation, ease-of-use and minimisation of solvent use were important criteria for measuring species concentrations in extremely remote environments, while retaining comparability with lab-based methods.

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### 2.1 Sampling and Storage

Data presented here were obtained from two sampling sites: Alert, NU on Ellesmere Island (82° 29' N, 62° 20' W) and Barrow, AK (71° 17' N, 156° 47' W). Adjacent meteorological facilities provided complementary data.

At both sites equipment used for sampling was either single use or pre-cleaned glassware prepared before departure and shipped to the field site. Clean suits and shoes, face-masks and gloves were worn during all sampling events. Pre-cleaned 1 L brown glass bottles, which were foil wrapped and fitted with Teflon lined lids (Wheaton) were filled with snow using an individually wrapped HDPE spoon for each event (Fisher). Surface snow was sampled from the first 10 cm starting at the surface at randomly chosen locations. A blank container filled with ultra-pure water was treated identically to quantify any contamination from the surrounding air or equipment. Laboratory blanks were also measured in an analogous fashion. Snow remained frozen until analysis to minimise reactions caused by melting and degradation[58].

In Alert, sampling and analysis was carried out between May 22 and June 2, 2006 (Julian days: JD 142-JD 153). The study location was close to the Alert meteorological station with a focus to avoid local contamination from the military base by sampling upwind, approximately 7 km away from the base on a flat plateau (Appendix figure A.1). Test runs at the base itself revealed high pollution levels with target molecules due to fossil fuel burning (data not shown), the main reason the sampling area was moved upwind to avoid local pollution sources. Access to the site was by truck parked downwind with the final leg of approximately 500 m carried out on foot in accordance with on-site regulations. All equipment was transported with a hand pulled sled to sampling sites. For selected sites in Alert, depth profile samples were collected from a snow pit dug with a pre-cleaned aluminium shovel. Samples were treated identically to all other snow samples, but collected and assessed independently. Depth profiling was completed over the course of no more than 3 hrs.

Air samples in Alert were collected in electro-polished canisters (AeroSphere) using stainless steel transfer lines (Supelco) with a battery powered teflon-membrane pump (KNF-Neuberger) and filtered through a 0.45 $\mu$m PTFE membrane. All canisters were pre-cleaned and evacuated before departure by four flushes with ultra high purity helium (Matheson) followed by evacuation to $1.3 \times 10^{-6}$ bar and heating to 120 °C over a period of 4 hours. For sampling, the inlet was positioned 20 cm above the snow surface and the canister was over-pressurized to 3 bar for leak detection during transport. Sampling of a canister was complete after approx. 15 min. Canisters were then stored at 20 °C (room temperature) until transfer by air to Montreal, Canada, for subsequent analysis. For each snow sample an air sample was collected within 30 min of snow sampling. Each canister provided several subsamples for analysis.

Snow samples collected in Alert were analysed on site. For transfer to the close-by improvised laboratory space, snow samples were packed into commercial coolers (Coleman) and transferred to the analysis site within 3 hrs (30 min transfer time). Further storage continued in a freezer at $-20$ °C until analysis was performed within 48 hrs.

In Barrow samples for organics analysis were collected from March 4 to 20, 2009. A field dedicated to snow studies in the clean air sector was used for all sampling events and experiments were carried out as in Alert. Frost flower sampling was carried out as part of a sampling event on Mar 20, 2009 on sea ice, also described by Beine *et al.*[28] and Douglas *et al.*[41] following the general snow sampling protocol used here. The sample was collected from a frost flower “field”, i.e., frost flowers grown on a flat area of sea ice, in a single location about 5 km northwest of Barrow. Frost flowers were characterised as “old frost flowers” having coatings from increased vapour phase deposition[41]. A total of 900 mL frost flower sample, minimising (but not completely eliminating) brine content by carefully lifting frost flowers off the surface with a pre-cleaned single-use HDPE shovel were transferred into a 1 L brown glass bottle. Samples collected in Barrow were shipped to Montreal for analysis after dividing the sample into 3 subsamples. To minimize transport and storage effects, all samples were kept frozen until analysis[35]. Samples were stored in a $-20$ °C freezer using commercial coolers, until time of shipment. Once shipped out by airfreight (Barrow to Montreal transit time: 41 hrs), the maximum temperature upon arrival in the laboratory at McGill University in Montreal was $-5$ °C, where storage continued in a freezer at $-20$ °C until analysis was initiated by melting.

### 2.2 Determination of VOC

Snow and frost flower samples from both sampling locations were prepared for GC analysis employing SPME. A detailed description of the extraction of VOC from snow samples is available elsewhere[19]. Briefly, samples were melted into a pre-cleaned septum flask using glove bags filled with inert He (Matheson) to minimise cross-contamination from ambient air. A 65 $\mu$m polydimethylsiloxane divinylbenzene (PDMS-DVB) SPME fibre was introduced via the septum port and adsorption of VOC from the stirred sample took place for 120 min at ambient conditions. Direct transfer to the GC injector and separation completed the analysis process. Field, transport and laboratory blanks collected during both campaigns were measured in identical fashion and all signals were corrected accordingly.

For snow sample measurements in Alert, the set-up from a previous GC/MS lab-based study was optimised to facilitate measurements in the Arctic[19]: (a) The mass spectrometric detector was replaced with a flame ionisation detector (FID) for easy deployment in a remote environment and avoid the use of vacuum pumps with significantly higher and more stringent power requirements, (b) GC/FID and GC/MS retention times and mass spectra of all compounds to be determined were compared on both systems equipped with set-ups as similar as possible to ensure the reliability of identification, (c) a calibration curve for 18 aromatic, halogenated and oxygenated compounds was obtained from dilutions of a mixed standard stock solution, which was treated the same way as the samples. The content of individual 1 mL standard ampoules (Sigma-Aldrich) were mixed on site with ultra-pure water modified with 500 µL methanol to facilitate mixing. While it cannot be ruled out that the presence of methanol did not adversely impact sensitivity, the resulting limit of quantitation (LOQ; calculated as 10 times the standard deviation of the blank) data were suitable to track VOC concentrations in snow and air (see Appendix tables A.2 and concentration data in Appendix tables A.3 and A.4). Desorption time was kept at 3 min in split-less injection mode followed by flushing the injector with 25 mL/min of carrier gas. Injector temperature was 200 °C and samples were separated on a HP-5 column (5%-Phenyl-methylpolysiloxane, 30 m length × 250 $\mu$m internal diameter × 1.00 $\mu$m film thickness, Agilent). Ultra high purity (UHP) helium (Matheson) served as carrier gas with a flow rate of of 3.0 mL/min. Oven temperature was regulated to start at 50 °C and maintained for 3 min followed by an increase at a rate of 15 °C/min until 200 °C. This temperature was maintained for another 10 min, resulting in an overall runtime of 23 min. FID temperature was set to 250 °C.

For lab-based measurements of Barrow snow and frost flower samples in Montreal, a similar procedure was employed with the major difference being the use of a mass spectrometric detector (GC 6890 and MSD 5973, Agilent). Otherwise a set-up mostly identical to the above GC/FID instrumentation was maintained. Mass spectrometer operation details are available in a previous study[19].

Determination of VOC in air from Alert was also performed in Montreal. A home-built pre-concentration and cryo-focusing system was employed for analysis. Details of the set-up were reported previously[59]. Air samples were directly connected to a pre-concentration GC/FID system and VOC were trapped in a liquid nitrogen cooled trap. After re-volatilization by flash-heating VOC were cryo-focused on top of a GC column before separation and detection using a GC/FID system.

For air sample measurements a HP-5 column was employed under the following conditions: The injector was set to 200 °C in split-less injection mode (purged with 25 ml/min of carrier gas after 1 min). The GC temperature program started at 50 °C (held for 3 min), then 10 °C/min to 150 °C (held for 5 min), and 15 °C/min to 220 °C (10 min hold); the FID temperature was set to 250 °C. UHP helium (Matheson) served carrier gas with a flow rate of 3.5 mL/min. For calibration purposes, known amounts of neat standards were injected into a canister and diluted with UHP helium. The mixture was humidified by the addition of 100 $\mu$l ultra-pure water (Millipore). Compounds from snow runs and air samples were identified by retention time compared with standards and quantified by automatic integration with manual correction.

### 2.3 Calculation of Back Trajectory Data

Back trajectories were calculated using the NOAA Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model[60] for the Alert sampling location. The model was run using the NCEP Global Data Assimilation System (GDAS1), a 3 hourly, global, 1° latitude-longitude data set. Total runtime was 72 hrs, whereby a new trajectory started every 6 hrs for a total of 12 trajectories at 310 m AMSL, i.e., 100 m above the surface of the sampling location (210 m AMSL) to account for the shallow Arctic ABL. Model vertical velocity was employed.

## 3 Results

In Alert, measurements were carried out during the melt period of the seasonal snowpack under 24 hr sunlight conditions; see Appendix table A.1 for details. Appendix figure A.2 shows comparable temperatures at the start of the measurements (May 22/JD 142) for air and snow. On JD 145 and 146 air temperatures were low, while higher temperatures were observed for JD 149 and 150. Snow temperatures generally followed this behaviour, but with a strongly dampened amplitude due to the relatively small heat conductivity of snow. Measured snow depth data at randomly chosen sampling locations in Appendix table A.1 do not represent an averaged snow pack thickness. Additional data were provided from Alert meteorological station (see Appendix figure A.1). Wind speeds were generally low with only one occurrence of blowing snow.

Results for concentrations of 18 aromatic, oxygenated and halogenated compounds in surface snow, depth profiles and air sampled over 12 days from 22 May (JD 142) to 02 June 2006 (JD 155) in Alert, NU are reported. Samples in Barrow, AK were collected over a period of 17 days for total of 84 samples. Final concentrations used in figures and tables were calculated from analytical duplicate measurements (i.e., from the same subsample, thus representing method variability and a lower limit for between-subsample variability). Variability was reported as 3 standard deviations (3s). Error bars were omitted for clarity in figures, but provided in tabular data in the Appendix. The relative standard deviation was generally $\leq 15\%$.

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### 3.1 VOC Concentrations in Alert

Concentrations were obtained in Alert in air (black squares) and snow (red circles) for halogenated compounds (Figure 1) and aromatics (Figure 2). Concentrations for oxygenates acetone and acetophenone are shown in Figure 3. For aromatic species, concentrations in snow were highest for styrene (39 $\mu$g/L on May 22). Among halogenated species bromoform showed concentrations of up to 34 $\mu$g/L on May 26 (JD 146) and for oxygenates acetophenone concentrations were at a maximum with 1.0 $\mu$g/L on May 22. In snow, variation for bromoform was the highest (0.357-34 $\mu$g/L), whereas 1-chloro-2-bromopropane exhibited the least variation (0.031-0.141 $\mu$g/L). On May 30 (JD 150) concentrations for two halogenated (1-chloro-2-bromopropane and trichloroethane) and two aromatic (benzene and styrene) species in snow dropped to below the LOQ; see Figures 1 and 2. Concentrations rebounded the following day. For the unusually high styrene and bromoform concentrations measured, co-elution with other species cannot be ruled out, although the peak shape (no shoulders observed) and width in the GC/FID chromatograms do not suggest that this was the case.

Concentrations of the same species in air collected concurrently were generally less variable than their snow counterparts. They do correlate well with surface snow concentrations, especially for benzene (correlation r=0.58) and toluene (r=0.79); see Appendix tables A.3 and A.4 for averaged concentration data used for calculations. The highest concentration in air was measured for trichloroethene at 1 ng/L on May 29 (JD 149). Several species, mostly halogenated species such as bromoform, but also ethylbenzene and 1,2,4-trimethylbenzene were detected, but found to be below the LOQ in air for most days sampled, but showed robust concentrations in snow, well above the LOQ. While concentrations in snow on May 30 (JD 150) were lower for most species, a drop of species concentrations in air was not observed. 1,3,5-Trimethylbenzene showed the highest concentration measured among organics (0.047 ng/L), closely followed by benzene (0.045 ng/L). Acetone concentrations were measured to be highest among oxygenates at 0.070 ng/L on May 30.

Depth profile data for (a) May 26 (JD 146) and (b) June 2 (JD 153) are depicted in Figure 5 (high concentration species), Appendix figure 6 (organohalides), and Appendix figure A.3 (other compounds). Randomly chosen sites from the sampling area had specific strata heights and snow properties. The sample from June 2 (JD 153) was characterized by highly amorphous snow. On May 26, concentrations for most compounds in snow showing a considerably lesser degree of metamorphism were constant for individual compounds over all strata with concentrations between compounds varying from <LOQ to 1 $\mu$g/L. Exceptions were benzene (showing surface enrichment), acetophenone, and bromoform (high concentration in layer 2 from the top). Depth profile data for aromatic and oxygenated compounds can be found in Appendix figure A.3.

Data obtained on June 2 (JD 153) on the other hand, indicate an enrichment in the surface layer for the majority of compounds; e.g., for toluene from 1.1 $\mu$g/L in the first layer dropping to < LOQ in subsequent deeper layers), trichloroethene (1.4 to 0.2 $\mu$g/L) and bromoform (16 to 9.0 $\mu$g/L). Close to the soil some compounds were enriched, e.g., toluene (< LOQ to 2.5 $\mu$g/L) and 1,2,4-trimethylbenzene (1.4 to 2.4 $\mu$g/L).

### 3.2 VOC Concentrations in Barrow

Figure 4 provides a summary of concentrations in snow samples for toluene, m/p-xylene and acetophenone. Concentrations were in the lower $\mu$g/L range and in the same order of magnitude compared to concentrations observed in Alert. While concentration ranges for toluene and m/p-xylene are very similar at 0.3 $\mu$g/L, acetophenone concentrations were four times higher at a maximum of 1.3 $\mu$g/L. Concentrations for bromoform were 0.2 $\mu$g/L in the frost flower sample, but not found in any of the snow samples.

### 3.3 HYSPLIT Model Data

Back trajectories from Alert identified two major areas of origin for the air masses 72 hrs before reaching the sampling location: The Lincoln Sea northwest of Alert on May 22 (JD 142) and a south-westerly source region (JD 149). Finishing May 27 (JD 147), a shift towards the North Pole took place (see Figure 7), but maintained the Arctic Ocean as the major source region. May 27 saw the introduction of air masses from the land based source regions over Ellesmere Island and the south-west. For May 29 and 30 (JD 149 and JD 150) virtually all air originated south-west of Alert (see Figure 7). Beginning May 31 (JD 151) the air mass area of origin shifted further to eastern Ellesmere Island, the Davies Strait and the Greenland coast. Additional back trajectory data up to June 04, JD 155 are provided in Appendix figure A.4.

## 4 Discussion

The employed SPME methodology in this study makes sample extraction relatively easy compared to more elaborate derivatisation and PTI methods, which is extremely beneficial for field work. Observed concentrations were generally well above the LOQ (see Appendix table A.2). This demonstrates that simple, solvent-less measurements are possible at the sampling site reducing the risk of transport and storage errors.

Previous reports reported data on some of the compounds discussed here, but using several different methodologies, making direct comparisons challenging. These measurements were carried out in Arctic, Antarctic and mid-latitude

Alpine environments. For details, see Table 1. Additional data using SPME methodology for compounds presented here were reported previously[19,35]. Poliakova *et al.*[61] determined a wide range of compounds using time-consuming conventional solvent extraction and GC/MS; methods that are generally restricted for use in the lab only. The presented study also provides new, not measured before concentration data for the following five compounds in High Arctic snow with concurrent measurements in air: Acetophenone, 1-chloro-2-bromopropane, dibromochloromethane, dibromomethane and trichloroethene.

Concentrations found in this study are generally within the same order of magnitude for available species data for both locations in Alert and Barrow (see data in Table 1 and Appendix table A.4). Exceptions include high concentrations observed for 1,2-dichlorobenzene (up to 20 $\mu$g/L) and styrene (up to 39 $\mu$g/L) with no comparison data available for the former and the latter showing concentrations in the order magnitude for mid-latitude snow[19]. Also, comparatively high concentrations of halogenated species were observed (e.g., chloroform and bromoform and dibromomethane), due to closeness of the sampling location to the Arctic Ocean. As a consequence, the Arctic snow pack represents a source and sink for bromine driven ozone chemistry[62].

Halogenated compounds were much more prevalent in snow (open circles) than in air (solid squares), with the exception of trichloroethene (Figure 1), found in both matrices. This highlights the role of snow as a reservoir for organic species at significant concentrations, which can be either exchanged with the atmosphere or dissolved and added to liquid run-off including transfer to soil during the melt season. Concentrations in surface snow are also subject to large fluctuations (e.g., bromoform) of up to two orders of magnitude on short time scales of around 24 hours. Temperatures below freezing for snow and air suggest transport to the atmosphere at this time of year (Appendix figure A.2). In conjunction with Arctic tropospheric ozone chemistry[63], snow provides a significant reservoir of readily accessible organohalides, especially for bromine containing species 1-chloro-2-bromopropane and bromoform reported here.

Aromatic species showed consistent concentrations in snow and air with higher variations of about one order of magnitude in snow and less in air (Figure 2). For most species, i.e., benzene and o-xylene rising and falling concentrations in snow were followed by concentrations in air suggesting a continuous exchange between the two matrices, since compared to organohalides, concentrations in air are considerably higher. The investigated aromatic species can be considered to be primarily of anthropogenic origin, resulting mostly from fossil fuel burning. They act as important precursors for secondary organic aerosol and a carbon source for tropospheric reactions and are generally photolabile[64] and contribute around 13% of organic compounds in surface snow[65] thus representing a significant reservoir for atmospheric processes[66].

A similar situation applies to the two oxygenated species showing air concentrations that follow concentrations detected in snow and similar concentration levels (Figure 3. Fluxes from the snow pack to the atmosphere have been observed for compounds such as acetone during exposure to the sun's radiation and are typically intermediate products in the oxidative breakdown of larger organic molecules, as the aromatic compounds above[17,67]. The snowpack is considered to be a significant source of acetone[68]. Acetophenone is an intermediate reaction product of the oxidation of condensed aromatics such as ethylbenzene[69] and naphtalene[70] hinting at a much higher organic compound load of the snow pack.

Depth-profile data on accumulation of organic species in the snow surface layer most likely suggests an exchange of species between the snow pack and air; see Figure 5 and Figure 6. Alternatively, the data may also reflect VOC concentration changes as a function of snow anisotropy. Temperature gradients caused by solar radiation lead to melting, freezing, condensation and sublimation processes of water and ice phases, which could significantly impact VOC concentrations in affected layers. Other transient effects that could result in VOC concentration changes are e.g., wind pumping, a forced flow of air through parts of the snow pack caused by surface pressure changes that result in VOC species being deposited into or volatilised from the snow pack. Photochemical activity of snow chemical species seems enhanced, which has been recognized as a major driver in snow pack chemistry[8,71]. The top layer was accessible for photochemistry[72] during 24-hr sunlight conditions. The detailed role of the investigated species in Alert as precursors for photochemical reactions still needs to be established and SPME-GC/FID could be a viable tool for these investigations.

Atmospheric concentrations of organics are closely linked to oxidants such as hydroxyl radicals and ozone. Ozone is monitored in Alert on a regular basis; see Figure 1. Index (I) marks the beginning of sampling. A sharp drop of selected VOC concentrations in snow was observed on May 30, see index (II), which coincided with a rebound of ozone concentrations, thus hinting at an involvement of organics found in surface snow in atmospheric processes.

Concentration changes of organics and ozone are closely aligned with a change of the air mass source region as determined by HYSPLIT backtrajectory calculations. The initial polar source region shifted to mainly southwesterly sources on May 30 (JD 150) coinciding with the drop of organics concentrations in snow and rebounding ozone concentrations. Concentrations of 1-chloro-2-bromopropane and trichloroethene decreased to <LOQ in snow; see Figure 1 and Appendix tables A.3 and A.4 for numerical data. Previous studies reported that snow structure and temperature effects have an important

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influence on chemical processes occurring in the snow pack[73], thus suggesting a path forward for future studies of exchange processes[45].

The detection of bromoform in a frost flower sample from Barrow is notable and provides the basis for future detailed investigations. Findings of high bromoform concentrations in the lower Arctic troposphere, and in surface waters of the Arctic Ocean were previously reported by[39,74–77]. Concentrations of bromoform in sea water typically range from 39.5 to 276 pmol/L (10 to 69 ng/L). Highs coincide with micro-algal blooms, its major source, in summer and lows mark winter data for Antarctica[78]. Samples collected during spring time from Resolute Bay, Canada, showed bromoform concentration of 336 to 367 ng/L in sea ice and the snow-ice interface and 492 to 1260 ng/L for snowpack immediately overlying the sea ice[62]. Fresh snow typically showed concentrations of 2 orders of magnitude less, which was attributed to the photochemical activity of the species. Furthermore, it has been suggested that frost flowers could serve as a source for halogenated compounds, especially bromine species, notably BrO and bromide[40,42,48,79]. The role of frost flowers as accumulators of biological and chemical species, in addition to halogenated compounds, also needs to be investigated further in order to establish links between the behaviour of chemical species. Bromoform concentrations in Barrow are in line with reports about enrichment of organohalides through the wicking of brine[40].

The data presented here are part of a larger body of organics that were studied during the OASIS 2009 campaign and are listed here for reference. Species concentrations reported included formaldehyde[80], acetaldehyde, glyoxal, methylglyoxal and propionaldehyde[31,81] and, HUmic LIke Substances (HULIS)[29,30]. The latter could serve as precursors for smaller more volatile fragments through photooxidation[82] suggesting an avenue to explore in future studies. In frost flowers, organic compounds likely constitute the dominant absorbers exhibiting large absorption coefficients, suggesting increased photochemical activity due to enrichment through wicking of brine into the crystal lattice[28].

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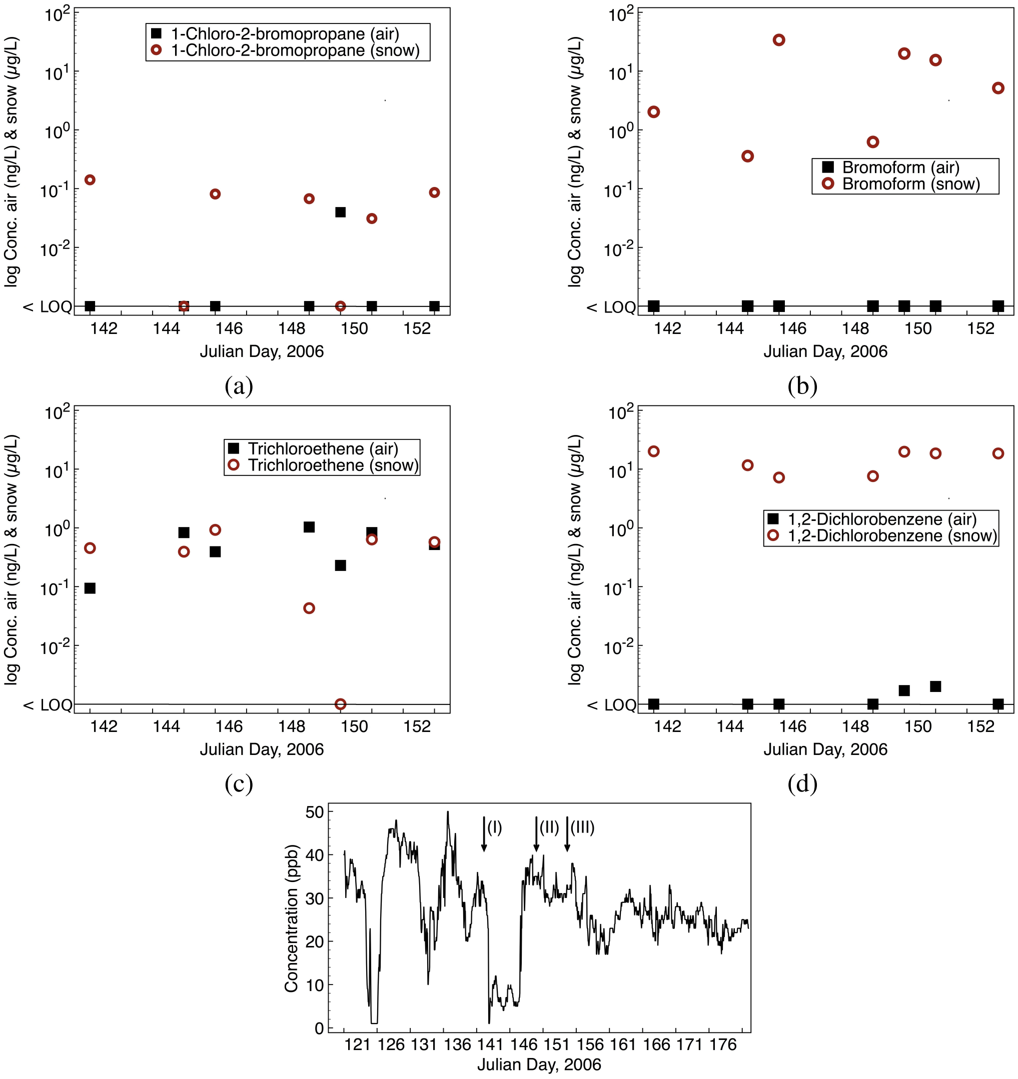
## 5 Graphics and Tables



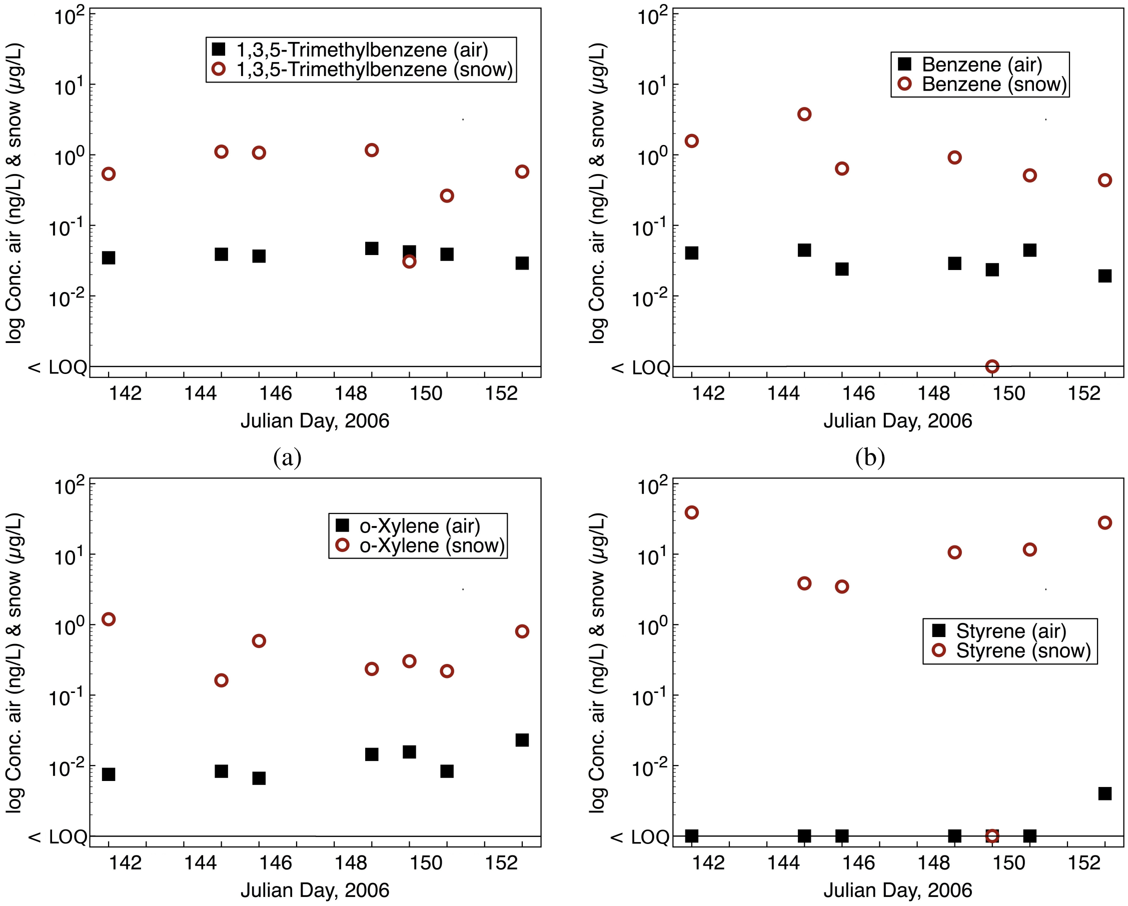
(a) (b)

(c) (d)

(e)

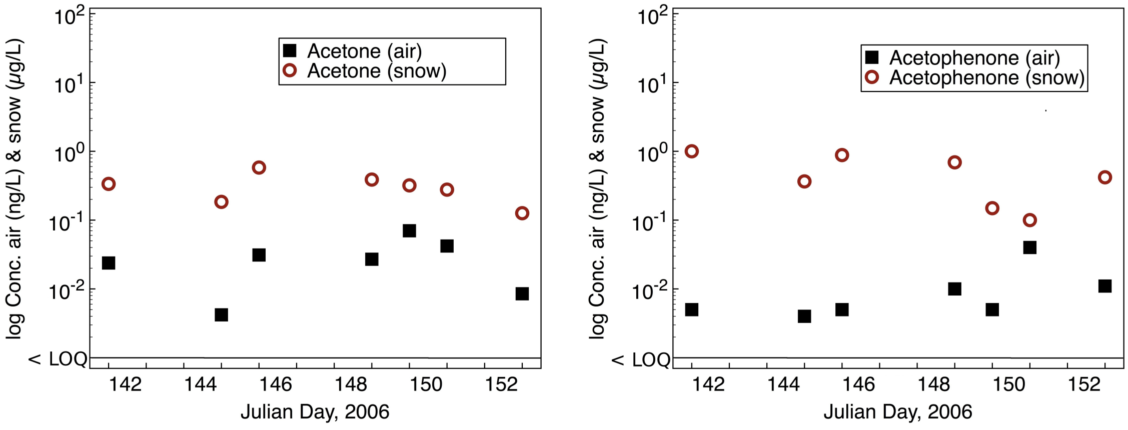
**Fig. 1** Averaged (melted) snow and air concentrations of organohalides (n=2): (a) 1-chloro-2-bromopropane; (b) bromoform; (c) trichloroethene and (d) 1,2-dichlorobenzene. Data located on the < LOQ line were detected, but not quantified. Error bars removed for clarity, but are listed in Appendix tables A.3 and A.4. Ground level ozone data (e) from May 1/JD 121 to June 30/JD 180. (I) Beginning of sampling on May 22/JD 142, (II) Depletion event for selected VOC on May 30/JD 150 and (III) End of sampling on June 2/JD 155. Ozone data provided by the Canadian Air and Precipitation Monitoring Network (CAPMoN).

Environmental Science: Processes & Impacts Accepted Manuscript



(a) (b) (c) (d)

**Fig. 2** Averaged (melted) snow and air concentrations for aromatics at the sampling site from duplicate measurements. (a) 1,3,5-trimethylbenzene, (b) benzene, (c) o-xylene and (d) styrene. Data points located on the <LOQ line were detected, but not quantified. Error bars removed for clarity, but in Appendix tables A.3 and A.4.



(a) (b)

**Fig. 3** Averaged snow and air concentrations for oxygenates at the sampling site from duplicate measurements. (a) acetone, (b) acetophenone. Error bars removed for clarity, but listed in Appendix tables A.3 and A.4.

Environmental Science: Processes & Impacts Accepted Manuscript

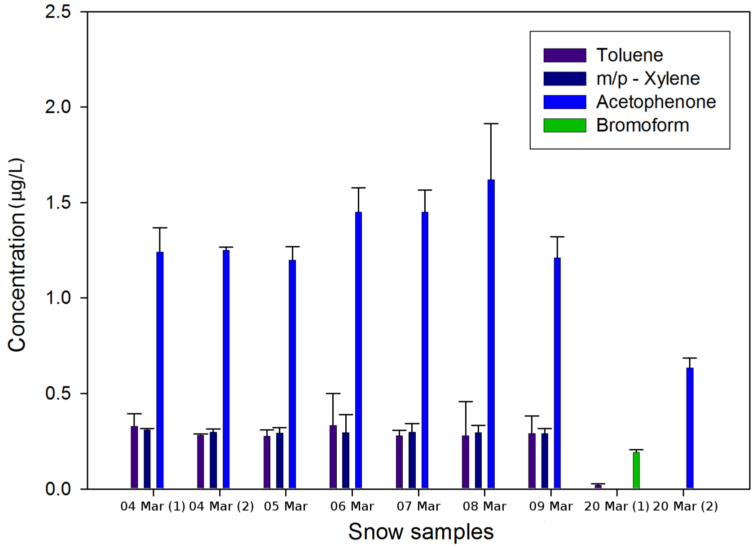
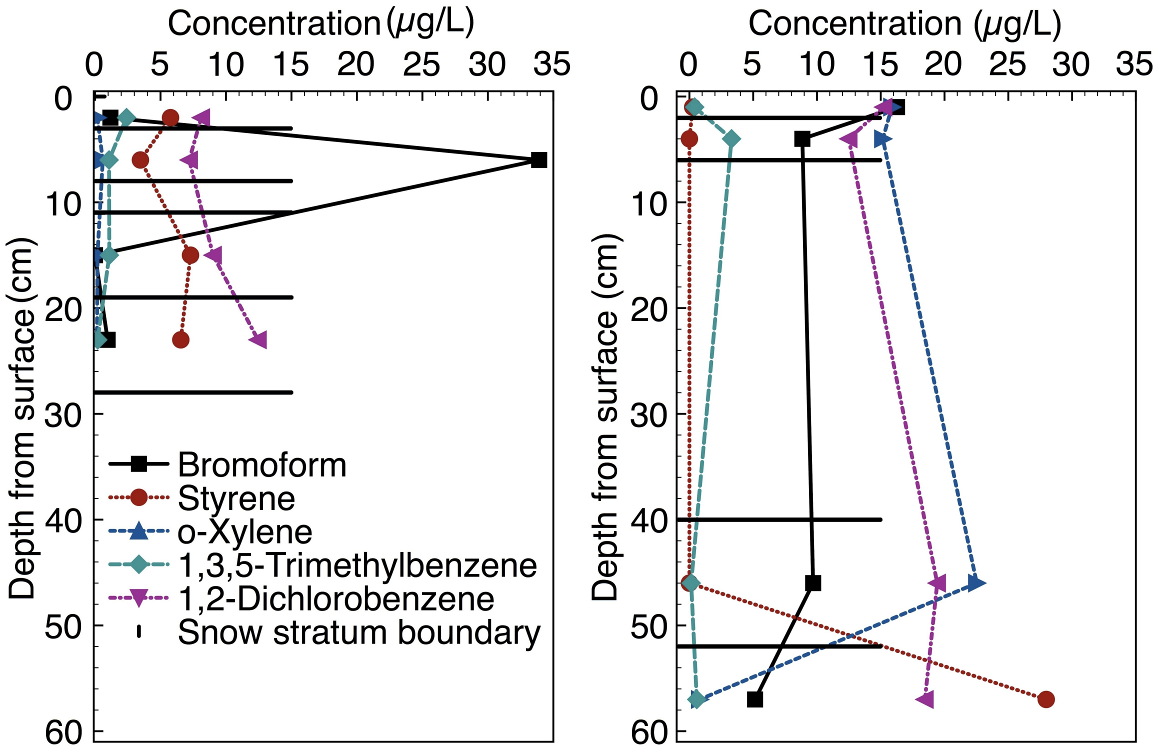


**Fig. 4** Organics concentrations ($\mu$g/L) in snow samples and a frost flower sample collected in Barrow, AK. Snow sample labels provide the day of sampling; brackets the sampling event number in case that more than one sampling was collected per day. Snow sample labels are referenced to locations in Appendix table A.5.



(a) (b)

**Fig. 5** Depth profile data of snow pit samples for (a) May 26 and (b) June 2 for aromatic and halogenated compounds with high concentrations. Black vertical bars represent snow layers sampled. Legend applies to both graphs. Error bars removed for clarity, but all relative standard deviations for duplicate measurements were $\leq 15\%$.

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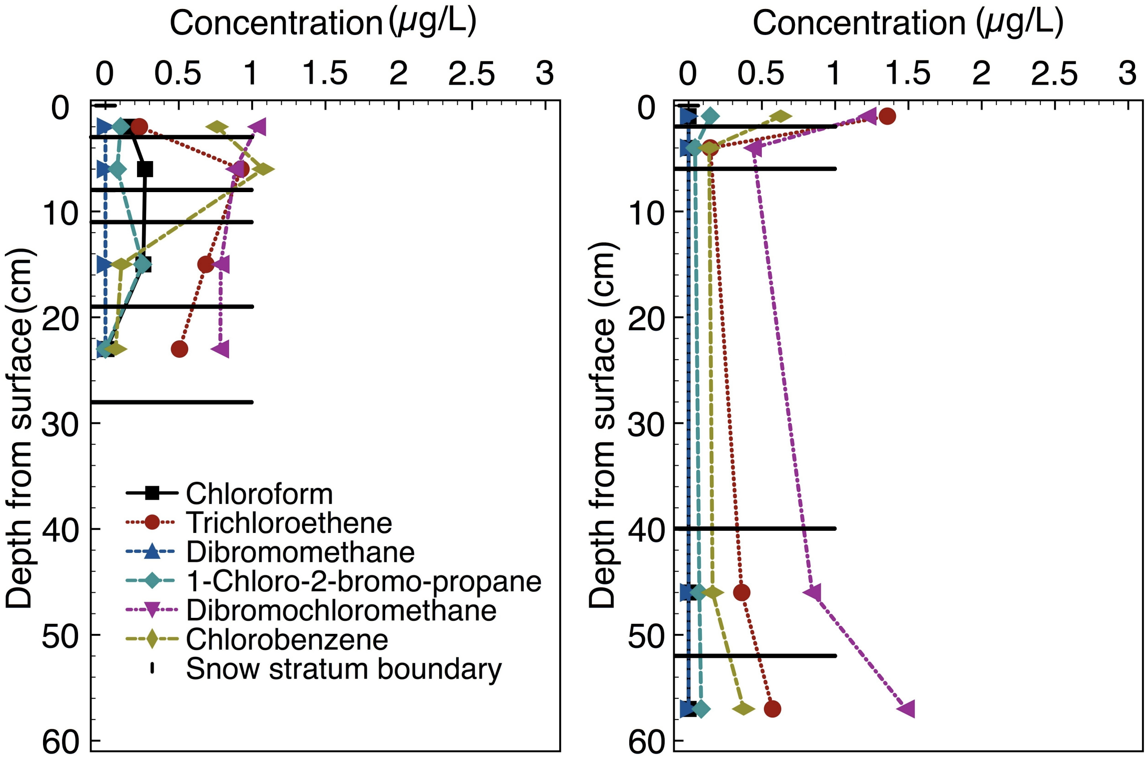
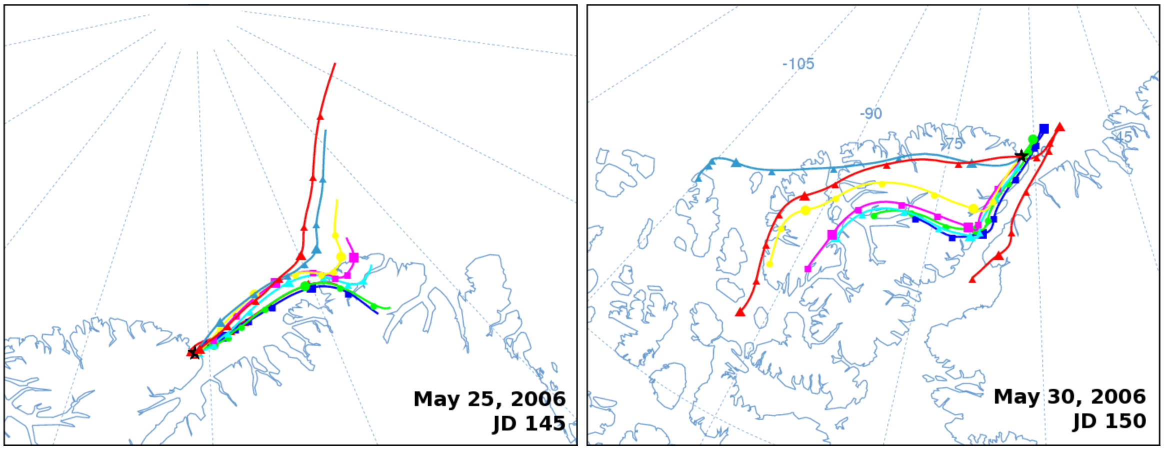


(a) (b)

**Fig. 6** Depth profile data of snow pit samples for (a) May 26 and (b) June 2 for halogenated compounds. Black vertical bars represent snow layers sampled. Legend applies to both subfigures. Error bars removed for clarity, but all relative standard deviations for duplicate measurements were ≤ 15%.



(a) (b)

**Fig. 7** HYSPLIT back trajectory data for sampling days: (a) May 25, JD 145, and (b) for May 30, JD 150, at the time of snow sampling. Model run duration was 72 hours with a new trajectory every 6 hours. GDAS1 data set used with a 3 hour resolution.

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**Table 1** VOC data in snow from previous studies; sampling months were Jan(uary), Feb(ruary), Mar(ch), Apr(il); concentration units were converted to $\mu$g/L with significant figures reported as in reference; sample preparation abbreviations: DNSAOA – DaNSyl-Acetamido-Oxy-Amine derivatisation; PTI – Purge and trap; HS – Headspace; SPDE – Solid-phase dynamic extraction; separation and detection system abbreviations: HPLC-FLD – High performance liquid chromatography with fluorescent detection; GC/MS – Gas chromatography with mass spectrometric detection; GC/FID – Gas chromatography with flame ionisation detection

| Compound | Sampling location | Month | Sample Preparation | Technique | Conc. range ( $\mu$g/L) | Reference |
|---|---|---|---|---|---|---|
| Acetone | Alert, NU | Feb & Apr | DNSAOA | HPLC-FLD | 1.5-3 ppbw | 83 |
| Ethylbenzene | Valdez, AK | Mar | PTI | GC/MS | 1.0-1.1 | 84 |
| | Dubendorf, CH | Jan & Feb | Tenax | GC/MS | 0.13-2.7 | 85 |
| | Jungfraujoch, CH | Feb & Mar | Carbotrap B/Carbosieve | GC/FID | 0.17-0.29 | 32 |
| | Jungfraujoch, CH | Feb & Mar | SPDE | GC/FID | 0.086-0.112 | 34 |
| | Jungfraujoch, CH | Feb & Mar | HS-SPDE | GC/FID | 0.074-0.29 | 33 |
| m-/p-Xylene | Valdez, AK | Mar | PTI | GC/MS | 3.0-3.3 | 84 |
| | Dubendorf, CH | Jan & Feb | Tenax | GC/MS | 0.17-7.4 | 85 |
| | Jungfraujoch, CH | Feb & Mar | Carbotrap B/Carbosieve | GC/FID | 0.104-0.169 | 32 |
| | Jungfraujoch, CH | Feb & Mar | SPDE | GC/FID | 0.105 | 34 |
| | Jungfraujoch, CH | Feb & Mar | HS-SPDE | GC/FID | 0.026-0.169 | 33 |
| o-Xylene | Valdez, AK | Mar | PTI | GC/MS | 0.4-1.1 | 84 |
| | Dubendorf, CH | Jan & Feb | Tenax | GC/MS | 0.067-1.5 | 85 |
| | Jungfraujoch, CH | Feb & Mar | Carbotrap B/Carbosieve | GC/FID | 0.166-0.238 | 32 |
| | Jungfraujoch, CH | Feb & Mar | SPDE | GC/FID | 0.124 | 34 |
| | Jungfraujoch, CH | Feb & Mar | HS-SPDE | GC/FID | 0.060-0.238 | 33 |
| 1,3,5-Trimethylbenzene | Valdez, AK | Mar | PTI | GC/MS | 0.4-0.8 | 84 |
| | Jungfraujoch, CH | Feb & Mar | Carbotrap B/Carbosieve | GC/FID | 0.042-0.068 | 32 |
| | Jungfraujoch, CH | Feb & Mar | HS-SPDE | GC/FID | 0.031-0.074 | 33 |
| 1,2,4-Trimethylbenzene | Valdez, AK | Mar | PTI | GC/MS | 0.4-1.3 | 84 |
| | Jungfraujoch, CH | Feb & Mar | HS-SPDE | GC/FID | 0.030-0.477 | 33 |
| Toluene | Jungfraujoch, CH | Feb & Mar | Carbotrap B/Carbosieve | GC/FID | 0.397-0.558 | 32 |
| | Jungfraujoch, CH | Feb & Mar | SPDE | GC/FID | 0.206-0.236 | 34 |
| | Jungfraujoch, CH | Feb & Mar | HS-SPDE | GC/FID | 0.397-0.651 | 33 |
| Benzene | Jungfraujoch, CH | Feb & Mar | HS-SPDE | GC/FID | 0.069-0.148 | 33 |
| Trichloroethene | Jungfraujoch, CH | Feb & Mar | HS-SPDE | GC/FID | 0.026-0.131 | 33 |
| Chloroform | Italy | | PTI | GC/MS | 0.0127 | 86 |
| | Antarctica | | PTI | GC/MS | 0.236 | 86 |
| Bromoform | Italy | | PTI | GC/MS | <0.001 | 86 |
| | Antarctica | | PTI | GC/MS | <0.001 | 86 |
| | Resolute Bay, NU | | Tenax | GC-ECD | 0.492-0.126 | 62 |

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## 6 Conclusions and Future Directions

Since the measurement of volatile organic compounds in snow has been very scare, this work aimed at acquiring VOC concentration data to assess the role of organic species in the Arctic snow pack as identified as a high priority by Grannas et al.[8] with optimized, field-ready SPME-GC/FID methodology. We successfully optimised and deployed highly sensitive SPME-GC/FID methodology for the determination of selected VOC in snow. The methodology was based on robust and cost-effective equipment that was well suited for on-site measurements in remote locations. MS based techniques have considerably higher and more stringent power requirements for the operation of vacuum pumps[87,88]. We demonstrated successful operation in a remote High Arctic environment by determination of 18 VOC species in snow and frost flower samples at two High Arctic sites. The method was solvent-less, easy-to-use and minimized storage and transportation time. The importance of these compounds in the snow pack has been shown to affect the gas-particle transfer with atmosphere, atmospheric oxidation, the formation of aerosols and influence aerosol-cloud interactions, which is indeed the largest uncertainty in the climate sciences. The presented methodology has the ability to contribute to an improved understanding of these processes.

It has to be noted that this robust yet sensitive SPME-GC/FID methodology has potential for further development of field measurement applications. The availability of SPME fibres with a range of polarities and the use of an electron capture detector (ECD) provides a variety of expandable, flexible and field-deployable platforms for the characterisation of a wide range of aliphatic, halogenated and oxygenated organic species. Additionally custom adsorbents, including nano particles[89,90], and on-fibre derivatisation[91,92] increase sensitivity and selectivity. The method also allows for the in-depth study of single or several species to investigate their contribution to atmospheric reactions and the measurement of snow-atmosphere fluxes in the field. Identification and quantification of unknown species is possible by GC/MS[19,35]. As shown, adsorbent-based pre-concentration and extraction can be easily adapted for use with instruments such as GC/FID and GC/MS.

Concentrations of 18 VOC determined in Arctic snow and air were determined to be in the µg/L range in snow and ng/L range in air with generally higher concentrations found for halogenated species due to the closeness of ocean-based sources. The findings highlight the need to account for snow in the study of atmospheric reactions and fluxes of VOC. Large fluctuations of selected organohalide concentrations on a 24-hour timescale suggest an active role of the snow pack as a readily available source and sink, directly affecting availability of VOC for atmospheric chemistry. Furthermore, we identified concentrations of bromoform at $0.19 \pm 0.042\ \mu$g/L in a frost flower sample from Barrow, AK. The occurrence of other bromine-containing precursors in snow from Alert, NU hints at the ability of the snow pack and frost flowers to contribute to the bromine budget of the cryosphere. Upon the release of organohalides such as bromoform to atmosphere, through processes including their emission from open leads or release upon snowmelt, they can undergo photolysis and partake in the photochemical tropospheric reactions.

Aromatic species such das benzene and toluene are tracers of anthropogenic activity and provide a carbon reservoir for atmospheric processes including the formation of secondary organic aerosol and photochemical reactions. Aromatic and oxygenated species concentrations hint at an overall high load of organics in the snow pack that could play a major role during melting season, either by volatilisation or as melt run-off.

The potential for exchange of the determined species with the Arctic ABL is further supported by the determination of enrichment of species in surface snow from depth profile measurements, which is especially significant for photolabile compounds affecting the oxidative potential of the atmosphere. Compounds with longer atmospheric lifetimes investigated here provide a significant reservoir of carbon species for multi-step photolytic reactions.

The Arctic snow pack and frost flowers contain significant amounts of important organic species. Studies of individual snow compartments (ice, water, brine and interstitial air) with their interfaces are desirable to assess their reactivity, mobility and exchange with the atmosphere.

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