Determination of a wide range of volatile and semivolatile organic compounds insnowbyuseofsolid-phasemicro-extraction (SPME)

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Abstract

Quantification and transformation of organic compounds are pivotal in understanding atmospheric processes, because such compounds contribute to the oxidative capacity of the atmosphere and drive climate change. It has recently been recognized that chemical reactions in snow play a role in the production or destruction of photolabile volatile organic compounds (VOC). We present an environmentally friendly method for determination of VOC and semi-VOC in snow collected at three sites— remote, urban, and (sub-)arctic. A solid-phase micro- extraction (SPME) procedure was developed and (semi-) VOC were identified by gas chromatography with mass spectrometric detection (GC–MS). A broad spectrum of (semi-)VOC was found in snow samples, including aldehydes, and aromatic and halogenated compounds. Quantification was performed for 12 aromatic and/or oxygenated compounds frequently observed in snow by use of neat standard solutions. The concentrations detected were between 0.12 (styrene and ethylbenzene) and 316 μg L^{-1} (toluene) and limits of detection varied between 0.11 (styrene) and 1.93 μg L^{-1} (benzaldehyde). These results indicate that the SPME technique presented is a broad but selective, versatile, solvent-free, ecological, economical, and facile method of analysis for (semi-)VOC in natural snow samples.

Introduction

Atmospheric chemical processes are driven mainly by photochemical reactions. The energy for these reactions is provided by solar radiation, the intensity of which is regulated by scattering and absorption processes. Aerosols, especially, contribute to attenuation of solar and terrestrial irradiation, although not homogeneously, because of their uneven distribution throughout the atmosphere [1]. A large fraction of volatile organic compounds (VOC) is emitted by anthropogenic and biogenic sources. The chemistry of VOC is the focus of much current research, because of their potential effect on atmospheric oxidation and aerosol formation, and consequent impacts on climate change through direct and indirect alteration of solar and terrestrial irradiation [2, 3]. Several studies have reported VOC emissions. Mueller [4], for example, estimates anthropo- genic emissions are approximately 142 Tg $year^{-1}$, with alkanes contributing 52 Tg $year^{-1}$ and aromatic compounds 42 Tg $year^{-1}$. In urban areas, anthropogenic VOC comprise a large proportion of total VOC, with a variety of compound types observed, including alkanes, alkenes, and aromatic compounds [5]. In more remote areas, biogenic emissions contribute to the VOC spectrum, especially where large amounts of biomass are present. Vegetation, soil, volcanic activity, and oceans are the main natural sources [6].

It has been suggested that the snowpack is a potential reservoir and reaction medium for volatile organic com- pounds [7–9]. Indeed, several studies report measurements of formaldehyde [7], C_2–C_7 hydrocarbons [8], acetone and acetaldehyde [9], elucidating the role of the Arctic snowpack in the storage of VOCs. Franz and Eisenreich have measured polychlorinated biphenyls (PCB) and poly- cyclic aromatic hydrocarbon species (PAH) at a suburban site near Minneapolis/St Paul, MN [10]. Since the 1970s ice-cores have been investigated to monitor climatic developments, transport phenomena, and the increasing effect of anthropogenic compounds in remote areas [11], with the focus on long-term studies of climate developments, e.g. reconstruction of the oxidation capacity of the atmosphere [12]. Waddington et al. [13] have described the airflow in polar firn and the impact of snow ventilation on reversibly deposited species. Deposition and release of chemical species, especially volatile compounds, could occur in the snow pack; important conditions affecting concentrations of chemical species include the effective surface area, permeability, convection (natural or forced), and micro- topography. Snow deposition could cause volatilization and co-deposition of chemical species, resulting in the snow layer acting as a sink for compounds [14]. Chemical species associated with wind-blown snow are well exposed to the atmosphere and UV radiation and could therefore undergo photochemical conversion. The snow surface it- self might, moreover, even promote photochemical con- version [15]. There have been few published studies describing the exchange and reaction of a large number of VOC between snow and the atmosphere [16], with the exception of some semi-volatile organic compounds in the Arctic [17], mainly because of the lack of suitable analytical methodology. Desideri et al. [18] have reported very low concentrations (in the lower ng L^{-1} range) of hexane-extractable compounds in Antarctic snow and these measurements give a good idea of the types of compound that can be found in snow in even very remote regions of the Earth. Although detection limits for the method are high,

only compounds present at high concentrations will have a potentially significant impact on the photochemical and microbiological activity occurring in snow, when a sufficient amount of reaction products are formed, and it is within this context the method will be used. For potentially toxic and bioaccumulating compounds, however, lower detection limits might still be required.

Several methods are available for determination of VOC in environmental samples. Sample preparation with solid- phase extraction (SPE) and purge and trap methods, then analysis by GC–MS, are among the most commonly employed procedures. A recent and interesting development, by Herbert et al. [19], is the use of dedicated snow samplers in combination with SPE for determination of persistent organic pollutants (POP) in snow. The use of (chlorinated) solvents, however, makes this approach difficult to apply in the field, although the snow samplers themselves are a convenient and less error-prone method for sampling snow. Grollert et al. [20] identified aliphatic alcohols, phenols, and phthalates in Alpine snow samples by using liquid–liquid extraction in combination with GC–MS–FID for detection and identification. Concentrations of compounds were in the low μg L^{-1} range, similar to the results presented here. Solid-phase micro-extraction (SPME), developed by Pawliszyn et al. [21], is a quick and efficient method of sample preparation. An overview of state-of-the-art methodology for determination of VOC in aqueous samples is given in Table 1. Most methods employ solid-phase extraction or purge and trap methods for analysis of aqueous solutions and require the use of substantial amounts of solvents or use of complex equipment. Use and transport of solvent increases environmental risk, especially in ecologically fragile areas, and transport of equipment is costly and requires facilities to run analyses near the sampling locations. Snow contains a wide range of compounds with different chemical properties (including aldehydes, esters, ketones, aromatic compounds, etc.) and several complementary analytical methods can be used to properly identify and quantify these different chemical groups. A consequence of sampling only a small number of compounds, or employing several analytical techniques for a wider range of compounds, is, however, the resulting lack of comparable analytical data, thus preventing more

Table 1 State of the art of methodology for the determination of VOCs in aqueous matrices

Author	Principle	Analytes	Note	Ref
Clement R.E., Yang P.W., Koester C.	–	–	Review on environmental analysis methods	[23]
Lavagnini I., Favaro G., Magno F.	Purge and trap with GC–MS	VOC in water	Non-linear and non-constant variance calibration curves	[24]
Schmidt T.C.	Purge and trap and GC–MS	Methyl *tert*-butyl ether and *tert*-butyl alcohol	Comparison of direct injection, headspace analysis, SPME	[25]
Lekkas T., Kostopoulou M., Petsas A., et al.	Purge and trap with GC–MS	VOCs and pesticides	Sampling and analysis of natural waters in accordance with EU directives	[26]
Hashimoto S. et al.	Purge and trap	VOCs	Various environmental matrices	[27]
Bocchini P. et al.	Comparison of purge and trap with SPME	55 VOCs	VOCs according to EPA method 524.2	[28]
Lacorte S., Viana P., Guillamon M., Tauler R., Vinhas T., Barcelo D.	SPE and GC–EI–MS	115 SVOCs, 41 VOCs, determined in 644 surface water samples	Analysis of natural waters in accordance with EU directives	[29]
Almeida C.M.M., Boas L.V.	SPME and GC–FID	Aromatic compounds in water	Method validation	[30]
Wardencki W., Michulec M., Curylo J.	SPME	Drinking water and other food matrices	Review of solid-phase micro-extraction methods in food analysis	[31]
Serrano A., Gallego M.	SPME and GC–MS	Benzene, toluene, ethylbenzene, and xylene isomers in water	Direct coupling of a headspace sampler with a mass spectrometer	[32]
Chvilickova I., Kuban V.	SPME and GC–MS	Monoterpene hydrocarbons in conifer needles	Headspace sampling	[33]
Tsai S.W., Chang C.M.	SPME and GC–MS	Aldehydes in water	On-fiber derivatization	[34]
Martínez E. et al.	Purge and trap	40 VOC in surface waters	Method performance evaluation	[35]

de- tailed characterization of given atmospheric processes. It would, therefore, be desirable to employ a single method that can simultaneously detect a large number of different species in a single run. Earlier reports have several disadvantages, especially with regard to field use and characterization of species. Petterson et al. [22] used a high-capacity sampler to characterize a limited set of snow samples; part of the sensitivity gain was, however, a result of the use of mass spectrometric selected ion monitoring(SIM), an approach which is not feasible for the survey presented here, because the range of compounds present is unknown. It is also worth noting that instrument

modifications and liquid nitrogen cooling make use in the field challenging, although still feasible.

We present herein an approach using solid-phase micro- extraction (SPME) for determination of VOC and semi-VOC, in snow-samples, in the low μg L^{-1}-concentration range. The objective of the work was broad chemical characterization of (semi-)VOCs found in snow samples from several locations with urban and remote environments. SPME has several analytical advantages, including suitability for in-situ monitoring in remote and ecologically sensitive environments. SPME was found to be adequate, because adsorption on the fiber is not limited to a specific compound (class); compounds within a certain polarity range are adsorbed and fiber polarity can be chosen on the basis of the analytes expected. Adsorbed compounds were determined in a single run; GC–MS was used for identification and quantification.

Fig. 1 Map of sampling locations

Experimental

Sampling and storage

Samples were collected at several urban and remote sites in the province of Québec and territory of Nunavut, Canada, to reflect different anthropogenic influence (the sampling locations are shown in Fig. 1). The samples from Nunavut (latitude: 74.70°, longitude: 95.05°) were taken well outside human settlements, and were thus little affected by anthropogenic activity except as a result of long-range transport. Conversely, anthropogenic influence was expected to dominate the sample taken in downtown Montreal (45.54°, 73.60°). Samples from the Gaspé Peninsula (49.12°, 66.49°) were taken in a vegetation rich, coastal area where the presence of large amounts of biogenic VOC could be

expected. Other samples were taken at a higher altitude with less vegetation. The Gaspé Peninsula is a thinly populated part of Québec—anthropogenic influence is present, but limited compared with the urban samples.

Twelve samples were collected on the campus of McGill University in downtown Montreal, Canada, on the university campus lawn. Sterile sample containers, volume 120 mL (Fisher Scientific, Nepean, ON, Canada) were pressed upside down into an area of snow covering a grassy patch on February 16, 2004, under clear skies with a temperature of −11°C, and an average westerly wind (3– 4 m s^{-1}). Non-powdered latex gloves were worn at all times during sampling of the snow samples. The container was taken out of the snow and closed immediately. Thirty-five more samples were taken at adjacent positions by the same procedure. Collected snow was from the surface (top ~7 cm) and the overall snow cover was measured to be 35 cm close to the sampling location. Samples were then transferred to the laboratory and stored in their sterile sampling containers at 4°C in the fridge. For analysis, the contents of three containers were pooled after melting.

Samples from the Gaspé Peninsula in eastern Québec were chosen from the total of 120 samples collected in the area of Mont Albert near Ste-Anne-des Monts on April 17 and 18, 2004. The surface temperature was between +3°C and 14°C during the day and 0°C at night with a northerly wind (2–4 m s^{-1}). Samples were taken at different depths in the snow (up to 1.0 m from the surface). One set of samples was taken 600 m above sea level (a.s.l.) and the second set 1,200 m a.s.l.. The former set was taken in a forested area and the sample consisted mainly of freshly fallen snow (i.e. the sample was collected during precipitation) whereas the latter set was from a region of higher altitude with less vegetation, where the snow was metamorphous and ice- structured (flake size 2 mm). Snow water content (liquid water present as percent by weight) was 30% to 50%. Samples were taken either in 500-mL sterile Teflon containers (Nalgene, Rochester, NY, USA) or in sterile 10-mL screw-cap vials (Fisher). All sample containers were stored in coolers filled with ice and these were stored in a fridge at 4°C.

Sampling on Cornwallis Island, Nunavut was conducted outside the settlement on the southern shoreline of North Lake situated north west of the village of Resolute Bay, on June 22, 2003 at 14:00 h. The sky was mainly overcast and the temperature was −0.2°C with a relative humidity of 90% and a westerly wind (6–7 m s^{-1}). Only surface snow from approximately the top 3 cm was collected, downwind. No strata were identified, because the state of metamorphism of the snow grains was highly advanced. Snow grains were rounded, with some cohesion, between 2 and 4 mm. Snow water content was approximately 45%. Snow was collected in 2-L Teflon bottles (Nalgene) previously cleaned by washing with acid and rinsing with ultra-pure water (Millipore, Etobicoke, ON, Canada). Between the sampling site and the storage facility in Resolute Bay, samples were wrapped in two layers of polyethylene (PE) bags and kept in a cooler, which itself was wrapped in a PE bag to avoid contamination from outside sources. Until transportation to Montreal, samples stayed in the cooler at −20°C. On June 26, 2003, samples were transported to Ottawa by air and the storage temperature did not exceed 4°C. On arrival in the laboratory the samples were kept frozen. For analysis, a solid subsample was taken with a clean spatula under sterile conditions and melted at room temperature in a tightly closed Pyrex container, immediately before analysis.

Sample preparation

All glassware and accessories were washed with detergent, and rinsed thoroughly with ultra-pure water (Millipore Corporation) and ethanol, then dried overnight at 125°C in an oven (Lindberg, Asheville, NC, USA). Ethanol was not detected in any of the samples. Use of acetone for rinsing and cleaning was strictly avoided, because it was one of the potential target molecules. Samples (20 mL) transferred to Pyrex vials were used for all experiments. The sampling vial was filled to the septum to avoid loss of analytes to the headspace [35]. Repeatability experiments were performed in triplicate, each carried out using a new subsample. A small Teflon-covered sterilized stirring bar was used, and the vial was sealed with an open-top cap fitted with a Teflon-lined silicone rubber septum (Chromatographic Specialties, Brockville, ON, Canada), with the Teflon liner facing the solution. The septum was pre-pierced with a needle to facilitate introduction of the SPME fiber into the vial through the Teflon lining. SPME was performed with a commercial kit (Supelco, Bellefonte, PA, USA) using a divinylbenzene (DVB)-coated polydimethylsiloxane (PDMS) fiber with a film thickness of 65 μm. The polarity of this fiber was a good compromise for adsorbing polar compounds and analytes with aliphatic character [36]. The fiber was conditioned in a GC injector port at 250°C, in split mode, to avoid column contamination. Conditioning was performed for a minimum of 10 min. The fiber was also regenerated overnight at 250°C at regular intervals to remove any contamination build-up. A single fiber was used throughout the entire study and neither a decrease in adsorption efficiency nor cross-contamination was observed—demonstrated by standard and blank runs. Field blanks consisted of Milli-Q water that was treated like the samples, i.e. placed in sampling containers at the sampling location, opened for the duration of sampling, transported with samples to the laboratory, and analyzed identically with sampling/transport blanks. Laboratory blanks that focused on the sample preparation and melting procedure were also analyzed regularly. Addition of compounds during

sampling to measure recovery after sampling and storage was not feasible, because the inhomogeneous nature of snow does not enable even distribution of the added compound. Addition and recovery of chlorobenzene-d5 (Sigma) was performed to evaluate losses because of matrix effects. Differences between recoveries of com- pounds from standards and collected samples were usually
±5%, indicating no significant matrix effects.

After sample preparation and melting, the fiber was fully immersed in the liquid sample for 40 min and then immediately transferred to the GC injection port for GC–MS analysis. The headspace was sampled for 180 min before GC–MS analysis, immediately after liquid sample analysis. Adsorption time was optimized and the best signal strength was obtained for the sampling time used, despite the expectation of a shorter adsorption time, because equilibrium should be reached more quickly. GC–MS analysis always immediately followed the adsorption procedure, to avoid losses of volatile components with low affinity for the fiber. Headspace analysis was conducted to take advantage of the reduced water content and possibly detect volatile compounds with sufficient sensitivity. It could also yield information on matrix effects in the liquid sample by comparing results from headspace and immersion techniques [36].

Gas chromatography with mass spectrometric detection

Measurements were performed with a Hewlett–Packard gas chromatograph with single-quadrupole mass spectrometric detection (GC–MS, HP GC 6890 and MSD 5973, Agilent Technologies, Mississauga, ON, Canada). Before injections any water drops hanging from the tip of the needle were removed with a wipe (Kimberly-Clark, Mississauga, ON, Canada) without touching the needle itself. The fiber was manually inserted into the injector via a pre-pierced septum (Thermogreen, Supelco, Ann Arbor, MI, USA). The needle was fully inserted into the injection port, ensuring repeatable insertion depth and exposure of the fiber in the middle of the liner, where temperature conditions are uniform. The injector was used in split mode (split ratio 200:1 with a split flow rate of 15 mL min^{-1}), to reduce the water content during runs, and a desorption time of 5 min was chosen at a temperature of 200°C. After desorption, the fiber was reconditioned at 250°C in a different GC injection port with a split flow rate of 50 mL min^{-1}. An HP 5-MS column (5% phenyl poly- dimethylsiloxane, length 30 m, internal diameter 0.25 mm, film thickness 0.25 μm; Agilent) was used with a flow rate of 1.5 mL min^{-1} and a pressure of 13 psig, resulting in an overall average velocity of 45 cm s^{-1}. Ultra pure Helium (Matheson Tri-Gas, Montgomeryville, PA, USA) was used as carrier gas, at a flow rate of 1.5 mL min^{-1}. The oven temperature program started at 50°C, maintained for 3 min. The temperature was then increased at a rate of 15° min^{-1} to 200°C, which was maintained for another 10 min, resulting in an overall run time of 20 min. All measure- ments were made by scanning a mass range between 15 and 550 a.m.u.. A threshold was set to ignore masses with fewer than 150 counts. The MS was fitted with an electron-

Table 2 Compounds found in snow samples (liquid phase and headspace)

Sample "Resolute"		Sample "Gaspe-Low" (600 a.s.L.)		Sample "Gaspe-High" (1200 a.s.L.)		Sample "Montreal"	
Liquid Phase	Headspace	Liquid Phase	Headspace	Liquid Phase	Headspace	Liquid Phase	Headspace
Dimethyl sulfone	Dimethyl sulfone	Dimethyl sulfone	Dimethyl sulfone	2(3*H*)-Dihydro-3,5-dimethylfuranone	2(3H)-dihydro-3,5-dimethylfuranone	Acetone	Acetone
Benzene	Benzene	Toluene	Toluene	2,3-Diazabicyclo[2.2.1]hept-2-ene	2,3-Diazabicyclo[2.2.1]hept-2-ene	Diethyl ether	1,3-Butadiene
Dibromomethane	Trichloroethylene	Styrene	Hexanal	Dimethyl sulfone	1,1-Dichloroethene	Dichloromethane	Diethyl ether
Toluene	Dibromomethane	Benzaldehyde	Ethylbenzene	Chloroform	Dimethyl sulfone	Ethyl acetate	Acetic acid methyl ester
Chlorobenzene	Toluene	Acetophenone	1,3 and 1,4-Dimethylbenzene	Benzene	Chloroform	Chloroform	Dichloromethane
1,3 and 1,4-Dimethylbenzene	Paraldehyde		Styrene	Trichloroethylene	Benzene	Benzene	Ethyl acetate
Dibromoacetic acid methyl ester	Hexanal		Heptanal	Toluene	Trichloroethylene	Toluene	Chloroform
Diiodomethane	Acetic acid butyl ester		β-Ocimene	Paraldehyde	Dibromomethane	1,3 and 1,4-Dimethylbenzene	1-Ethoxy-2-methylpropane
Benzaldehyde	Chlorobenzene		Benzaldehyde	Dibromochloromethane	Toluene	Styrene	Benzene
1,2,4-Trimethylbenzene	Ethylbenzene		1,2,4-Trimethylbenzene	Chlorobenzene	Paraldehyde	1,2,4-Trimethylbenzene	Dibromomethane
1,2-Dichlorobenzene	1,3 and 1,4-Dimethylbenzene		1-Octanal	1,3 and 1,4-Dimethylbenzene	Dibromochloromethane		Toluene
1-Nonanal	Tribromomethane		1,2-Dichlorobenzene	Tribromomethane	Chlorobenzene		Paraldehyde
m-Di-*tert*-butylbenzene	Styrene		Limonene	Styrene	Ethylbenzene		Chlorobenzene
	Heptanal		Acetophenone	Diiodomethane	1,3 and 1,4-Dimethylbenzene		Ethylbenzene
	Diiodomethane		1-Nonanal	1,2,4-Trimethylbenzene	1-Nonene		1,3 and 1,4-Dimethylbenzene
	Benzaldehyde		1-Decanal		Tribromomethane		1-Nonene
	1,2,4-Trimethylbenzene				Styrene		Styrene
	β-Terpinene				1,2-Dimethylbenzene		Diiodomethane
	1-Octanal				Diiodomethane		β-Ocimene
	1,2-Dichlorobenzene				β-Ocimene		1,2,4-Trimethylbenzene
	p-Cymene				1,2,4-Trimethylbenzene		β-Terpinene
	1-Nonanal				β-Terpinene		Isoterpinolene
	1-Decanal				Isoterpinolene		1,2-Dichlorobenzene
	m-Di-*tert*-butylbenzene				*p*-Cymene		*p*-Cymene
					m-Di-*tert*-butylbenzene		*m*-Di-*tert*-butylbenzene

impact source, operated at 230°C, and the quadrupole temperature was 150°C. Mass spectra were analyzed with the NIST MS Search 2.0 program (NIST, Gaithersburg, MD, USA) after exporting data from the HP Chemstation software. Identification was performed by library search and comparison of the acquired spectrum with hits from the search program, based on the "match", "reverse match", and "probability" data. Only good matches (generally >900 out of 1,000) and high similarity for match/reverse match data were considered and differences in probability had to be 20%, or more, if no supporting data were available to confirm the identity of the compound. Differences between match/reverse match data for the next probable compounds were also taken into account. The AMDIS 2.6 spectral deconvolution program (NIST) provided additional information from mass spectra about the identity of overlapping peaks and smaller peaks with large contributions from column bleed. MS spectra were compared with regard to major fragments, relative fragment intensity, and retention time of peaks. Standard runs were used to confirm identity by retention time matching, if the mass spectrum was unclear, because characteristic fragments were missing. Isomer peak ratios were also used to establish the identity of compounds, if required. If the identity could not be established with these methods, the compound was not reported. Triplicate experiments showed the measurements were highly repeatable, despite the low concentrations observed.

Twelve aromatic compounds were quantified using standard solutions (a stock solution of mixed standards was prepared in methanol, subsequent dilutions to prepare working standards were made with Milli-Q water). Standards were prepared and treated in identically with the samples with regard to the SPME procedure and conditions for GC–MS analysis. Calibration plots were constructed with use of at least five standards and blanks for the liquid in the concentration range 1.00 to 500 μg L^{-1}, see Appendix for an example). Limits of detection (LOD) for the 12 quantified compounds are listed in Table 3. Blank measurement variation was always <5% (n=20, minimum distinguishable signal was calculated to be the mean with 3 standard deviations added).

Results and discussion

SPME procedures can easily be used with existing analytical instrumentation and GC–MS is an especially suit- able tool for identification of unknown compounds, even in complex samples, making SPME an efficient tool for product and screening studies. Quantification is possible if measurement conditions are strictly controlled throughout a measurement cycle.

Detected species

Data analysis of mass spectra obtained from peaks after direct immersion extraction with SPME revealed the presence of a large number of compounds in the samples (Table 2). The total ion chromatogram (TIC) recorded from the headspace of the "Montreal" sample shows good separation of 25 identified compounds (Fig. 2). Some column bleed occurred (e.g. at 6.3 min), mainly because of the aqueous matrix. For some peaks identification was not possible, because of the low number of counts of characteristic ions (e.g. at 2.4 min, 8.9 min), or the very similar mass spectra of potential compounds and isomers (e.g. at 10.9 min). Samples are dominated by oxygenated compounds (e.g. ethyl acetate, benzaldehyde, nonanal, acetophenone) with a large contribution from aromatic species (e.g. benzene, toluene and 1,3 and 1,4-dimethylbenzene), which are mainly of anthropogenic origin [37]. Among these, toluene and styrene were ubiquitous in the samples, although occurring at very different concentration levels (Tables 2 and 3). A check was therefore performed to ensure these two compounds did not arise as a result of contamination during sample preparation and analysis (e.g. septum leaching), using Milli-Q water from the laboratory and sampling blanks. Results from blank experiments and from analysis of sampling and storage blanks were not, however, indicative of contamination with these and other species during transport, storage, and sample preparation. Blanks were free from contamination, although column bleed occurred because of the aqueous matrix, and was easily identified.

The second-largest group of compounds identified was halogenated compounds, including chloroform, dibromo-methane, diiodomethane, and chlorobenzene. These com- pounds are mainly of anthropogenic origin, with some contributions from oceanic sources (e.g. dibromomethane [38]), and play an important part in atmospheric processes by reaction with HO radicals and photolysis. The total number of halogenated compounds was highest in the Gaspe sample taken at 1200 m a.s.l. ("Gaspe-High") with seven identified compounds. The "Resolute" sample contained five different halogenated compounds. The absence of halogenated species and the low number of aromatic compounds in the "Gaspe-Low" sample could be because of a large contribution from freshly fallen snow, and potentially short time span for efficient scavenging–accumulation of airborne organic compounds by snow, beyond the detection limit of the technique used. The "Gaspe- High" sample, on the other hand, was collected from aged snow and no precipitation was observed the day before sampling, possibly enabling accumulation of airborne VOC and further production of VOC in snow by photo- chemical and microbiological processes. It also seems worth noting that a small amount of acetone was found in the "Montreal" sample. The high volatility of the com- pound may have prevented a clearer signal being obtained in the total ion chromatogram (TIC), where it is barely visible, but the underlying mass spectrum at the expected retention time did confirm the presence of this compound. Acetone

is a compound of significant atmospheric interest believed to play a role in upper tropospheric oxidant chemistry [39].

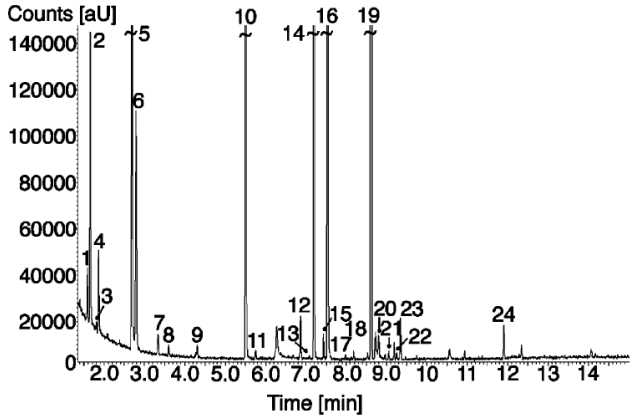

Fig. 2 Total ion chromatogram obtained from the headspace of the "Montreal" sample. Detected compounds were: *1*, 1,3-butadiene; *2*, diethyl ether; *3*, acetic acid methyl ester; *4*, dichloromethane; *5*, ethyl acetate; *6*, chloroform; *7*, 1-ethoxy-2-methylpropane; *8*, benzene; *9*, dibromomethane; *10*, toluene; *11*, paraldehyde; *12*, chlorobenzene; *13*, ethylbenzene; *14*, 1,3 and 1,4-dimethylbenzene; *15*, 1-nonene; *16*, styrene; *17*, diiodomethane; *18*, β-ocimene; *19*, 1,2,4-trimethylbenzene; *20*, β-terpinene; *21*, isoterpinolene; *22*, 1,2-dichlorobenzene; *23*, *p*-cymene, *24*: *m*-di-*tert*-butylbenzene

Table 3 Concentration (μg L^{-1}, ±3σ, n=3) of aromatic compounds in the liquid phase of snow samples

Compound	Montreal	Resolute	Gaspe-High	Gaspe-Low	LOD
Benzene	6.48±1.02	4.17±0.60	32.41±10.6	n.q.	1.22
Toluene	22.6±7.81	43.6±9.69	316±46.8	1.09±0.11	0.66
Chlorobenzene	n.q.	2.74±1.33	17.3±0.64	n.q.	0.40
Ethylbenzene	n.q.	2.65±1.28	0.31±0.06	0.22±0.02	0.20
1,3- and 1,4-Dimethylbenzene	8.59±6.01	0.65±0.01	1.04±0.43	n.q.	0.38
Styrene	7.82±1.32	0.22±0.04	2.44±0.11	13.4±5.90	0.11
1,2-Dimethylbenzene	n.q.	n.q.	0.16±0.09	n.d.	0.39
Benzaldehyde	n.q.	7.51±1.24	n.q.	12.8±4.56	1.93
1,2,4-Trimethylbenzene	4.59±2.26	5.41±1.91	17.1±5.23	n.q.	0.67
1,2-Dichlorobenzene	n.q. ±	4.35±1.87	1.03±0.42	n.q.	0.52
Acetophenone	n.q. ±	n.q.	n.q.	1.25±0.23	1.20

n.q., compound not quantified
LOD is the limit of detection in μg L^{-1}

The largest number of compounds was detected in the sample from the Arctic site in Resolute, the most remote environment studied. Anthropogenic influence and long- range transport are, however, certainly factors contributing to the species detected. The high persistence of com- pounds, the summer sampling time, and the advanced stage of metamorphism suggest the sampled snow was already aged, thus enabling organic species to be preserved for a long period or to undergo chemical transformation. The "Montreal" sample contains a common range of anthropogenic compounds emitted as a result of solvent use, fossil fuel burning, and car use (e.g. benzene, toluene, and dimethylbenzenes).

The results from the untreated samples demonstrate that a substantial number of species with very variable chemical

properties are stored in the snow (Table 2). Despite the large sample volume (20 mL), concentrations detected were low and some compounds remain unidentified, be- cause important fragments were missing, thus preventing reliable identification. Smaller volumes were tested with- out pre-concentration, but did not lead to a good signal strength. For all samples, aromatic compounds play a dominant role with substituted benzenes being the most abundant. Methyl-substitution is the most common, with one, two, or three methyl groups. Oxygenated compounds, for example ethyl acetate and benzaldehyde are also widespread.

Headspace analysis

Compounds in the headspace were expected to occur at even lower concentrations, which is why the adsorption time for the fiber was set to 180 min after preliminary experiments. Although equilibrium should be reached faster, because of higher diffusion coefficients in the gas phase (compared with extraction from the liquid phase), our observations showed that detectable amounts were adsorbed by the fiber only when the time of exposure of the fiber to the headspace was significantly increased. This is probably because of the time needed to reach equilibrium between the liquid and the gas phases (no external heating was applied) and matrix effects in the liquid phase. Qualitative headspace data are shown in Table 2 for untreated samples. Compounds found in the liquid phase are usually observed in the headspace also, although there are some exceptions: e.g. dibromoacetic acid methyl ester, which was only found in the liquid phase of the "Resolute" sample (Table 2). However, the headspace contains several compounds which are not usually found in the liquid phase (e.g. biogenic VOCs α and β-pinene, limonene, and *p*-cymene in the "Gaspe-High" sample). Despite high structural similarity it was possible to identify these compounds by comparison of mass spectral patterns and retention times. The results demonstrate the capability of the SPME method to provide a broad picture of the anthropogenic and biogenic VOC content of snow.

Quantification of aromatic compounds

Quantification of 12 compounds in the liquid samples showed concentrations were low for most of the aromatic compounds investigated, but the high linearity and repeatability of the calibration plot, with a very low blank value, enabled quantification of most of the aromatic compounds detected. Triplicate experiments were per- formed on all liquid samples to determine repeatability. For each measurement a new sub-sample was used, so the results reflect the variation within the sample and take the sample matrix at the sampling location into account. The relative standard deviation (RSD) was between 1.24% (chlorobenzene in "Gaspe-High") and 23.3% (1,3 and 1,4-dimethylbenzene in "Montreal"). When looking at mean RSD values for individual compounds for all samples, data vary from 6.81% for toluene to 18.5% for ethylbenzene with 4 out of 6 (the mean RSD of 1,2,4-trimethylbenzene was 12.8%) being below a mean RSD of 10%. Results from quantification experiments are shown in Table 3. By far the most abundant quantified compound was toluene with concentrations between 22.6±7.81 and 316±46.8 μg L^{-1} (except for "Gaspe-Low", 1.09±0.11 μg L^{-1}). All other concentrations were typically below 40 μg L^{-1} (e.g. benzene in all samples), with typical concentrations below 10 μg L^{-1} for most compounds. Very low concentrations, <5 μg L^{-1} for all detected compounds, including toluene, were observed in the "Gaspe-Low" sample, which in accordance to the small number of species detected in samples, because of a large contribution from fresh snow. The other samples contained aromatic compounds (benzene and toluene were most abundant) with concentrations up to 30 μg L^{-1} (e.g. benzene in the "Gaspe-High" sample). Quantification of aromatic com- pounds in the headspace was attempted, but lack of peak- area repeatability led to unreliable quantification results. Previous reports have indicated the possibility of head- space quantification and research is continuing [40]. The results from the liquid sample do, however, demonstrate that SPME can be used to quantify a large number of environmentally relevant aromatic compounds at low μg L^{-1} levels with a satisfactory repeatability for real- world samples, for which matrix effects usually have a substantial effect on the measurements.

Conclusions and future work

This study has demonstrated the potential of SPME in combination with GC–MS for identification and quantification of VOC and semi-VOC in the lower μg L^{-1} range in snow. Our results revealed the presence of a broad range of (semi-)VOC in snow samples, including aldehydes, and aromatic and halogenated compounds, that are recognized as primary or intermediate species in (photo)chemical reactions in snow or in the atmosphere; their quantification will therefore contribute to the understanding of snow as a source and/or sink for (semi-)VOC. The identified and quantified compounds represent a typical profile of anthropogenic and some biogenic compounds found in the

atmosphere. Not all the compounds detected could be identified, however. Use of other SPME fibers of higher or lower polarity will provide additional information on VOC content. Increasing the amount of sample even further could also improve sensitivity, if partition coefficients for the investigated compounds between the fiber and the water matrix are high enough and fiber capacity is not a limiting factor. Therefore, improvements might only be observed for some less polar compounds. Ongoing studies focus on an improved quantification procedure capable of quantifying more compounds. A unified sampling and storing procedure will eliminate variations caused by different sample treatments. The use of more standards will facilitate quantification of more compounds (especially halogenated substances); such data are crucial for assessing the environmental impact of the compounds observed. The potential of SPME for automation and in- situ measurements will also be used to improve accuracy, precision, and sample throughput. Small equipment size and solvent-free operation substantially reduce transport costs and the environmental impact of on-site use. SPME is easy to use and inexpensive, and selectivity, reliability, and sensitivity are good for a wide range of compounds. After adsorption, extracts can be stored and/or transported on the fiber for a limited time. This method can be used in the field without major modification with existing portable field samplers, thus enabling reduction of storage errors, because of potential elimination of sample containers in some situations. Automation and in-situ measurements would be of great value to preclude uncertainties associated with sampling, storage, and sample preparation [41]. To assess the performance of the entire method (from sampling to detection) a validation exercise with an independent established technique (e.g. purge and trap) would be highly desirable.

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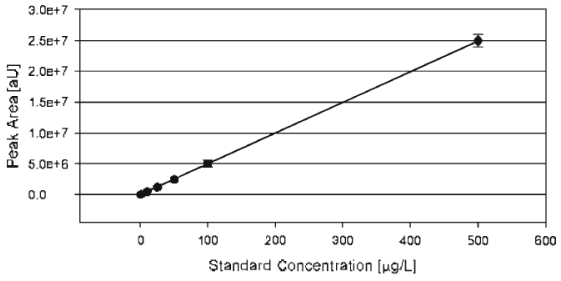
Appendix Calibration plot for ethylbenzene (n=5, error bars represent ±3σ, r=0.9994)



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