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Volatile organic compounds in snow in the Quebec-Windsor Corridor

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[1] Volatile organic compounds (VOC) were determined in snow to investigate the role of the snowpack as an exchange medium for atmospherically active compounds of anthropogenic and biogenic origin. The major question was which VOC species occur in snow and how the species identity and selected concentrations are related to the sampling area and environmental conditions. Samples were collected using a standardized sampling protocol in two distinct areas in six locations (near Mont-Saint-Hilaire, 45°33′06″N, 73°03′03″W (semirural) and Mont Tremblant, 46°20′11″N, 74°30′36″W (rural) in the heavily populated Quebec-Windsor Corridor, Canada, with different characteristics regarding location and proximity to urban centers. A solid-phase microextraction (SPME) procedure was employed for analysis, and VOC were identified using a gas chromatography method with mass spectrometric detection (GC/MS). Results revealed a broad spectrum of VOC in snow samples, including ethers, aldehydes, and aromatic and halogenated compounds, all of them active precursors for atmospheric reactions. Quantification was carried out for 11 aromatic and/or oxygenated compounds. Concentrations were found to be between 1.0 ± 0.2 ng/L (ethylbenzene) and 2.67 ± 0.06 μg/L (acetophenone), and limits of detection varied between 0.30 ng/L (benzene) and 78.2 ng/L (benzaldehyde). Principal component analysis was carried out to assess similarities between the sampling locations based on the types of species identified and concentration profiles. We discuss the implication of our results for atmosphere-snowpack interactions of VOC including back trajectory calculations for the sampling dates.

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1. Introduction

[2] Volatile organic compounds (VOC) play an important role in a multitude of atmospheric processes, especially the production of tropospheric ozone via reaction with NO_x and OH radical chemistry [*Atkinson*, 2003]. They are emitted in large quantities from anthropogenic and biogenic sources; their chemistry and interactions have been the subject of numerous studies, because of their involvement in atmospheric oxidation processes, aerosol formation, and their impact on climate change [*Guenther et al.*, 1995; *Dassau et al.*, 2002; *Thompson*, 1992]. Furthermore, VOC are found in most compartments of the environment and pose a serious environmental and health hazard, which makes them the subject of regular monitoring programs [*Hashimoto et al.*, 2001; *Bocchini et al.*, 1999]. The densely populated Quebec-Windsor Corridor (QWC) stretching from Lake Erie to the St. Lawrence River Valley in southeastern Canada is of prime importance for the study of VOC chemistry, because of the high level of commercial activity and high population numbers [*Reid et al.*, 1996]. Elevated ozone levels, especially in large cities such as Toronto and Montreal, led to the establishment of management plans for VOC and nitrous oxides (NO_x) [*McKendry*, 1993]. Accurate measurements and correct assessment of fluxes between sources and sinks are a necessity [*Grannas et al.*, 2007].

[3] Because of their ubiquity in the environment VOC indeed occur in snow and hence their accurate determination in the snowpack is highly desirable for impact assessment [*Grannas et al.*, 2002]. Although a considerable part of the Earth's surface is covered with snow for several months of the year, little work has been published on the snowpack as a potential source and/or sink for VOC and other organic compounds [*Chebbi and Carlier*, 1996]. The main focus has been on selected compounds (formaldehyde, acetaldehyde, acetone) relevant for major atmospheric reaction pathways, but a broad discussion of occurring species is not available [*Sumner and Shepson*, 1999]. This is also true for structurally complex compounds that could either act directly in atmospheric processes or act as precursors undergoing reactions. Available VOC data for snow are still scarce, but are desirable for incorporation into models to accurately estimate VOC fluxes. *Domine and Shepson* [2002] have summarized measurement and model calculation data with contributions from *Grannas et al.* [2002] and

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Yang et al. [2002]: Concentrations measured over snow and comparison with predictions from gas phase chemistry calculations showed underestimation of measurement data, e.g., by a factor of 3 for formaldehyde and a factor of 2 for acetaldehyde. Subsequent reaction partners and products are also underestimated by calculations, e.g., OH radical concentrations (factor of 10) and ozone (factor of up to 400). The authors' major conclusion is that known but also new snow-air processes need to be investigated to understand and model atmospheric processes correctly. This includes reaction products from oxidized organic matter that occur in the boundary layer after release from the snowpack [*Domine and Shepson*, 2002]. Anthropogenic and biogenic VOC are ubiquitous and found in urban as well as remote areas of the planet [*Desideri et al.*, 1998; *Sumner and Shepson*, 1999].

[4] VOC occur at considerable concentrations and their impact should therefore be properly assessed [*Clement et al.*, 2001]. Compounds chosen for quantification in the presented study (see Table C1, which provides a list of compounds and concentrations detected) are of prime importance for climate and environmental issues [*Derwent et al.*, 1996]: Aromatics (e.g., benzene, toluene, xylenes) are major anthropogenic toxic pollutants originating from traffic and industrial sources [*Iovino et al.*, 2009]. The benzene/toluene concentration ratio is a widely recognized parameter to assess the aging of an air parcel and, therefore, its distance from the emission site [*Karl et al.*, 2009; *Gelencser et al.*, 1997]. This is due to the higher reactivity of toluene with the OH radical, which is a key molecule in tropospheric removal processes for organics in general [*Wang et al.*, 2009]. The oxygenated species acetophenone and benzaldehyde are water soluble and the latter is readily degraded by microorganisms and nitrate radical assisted photochemistry [*Caralp et al.*, 1999]. Most species have atmospheric lifetimes of several days, which makes them good tracers for atmospheric transport phenomena [*Atkinson*, 1990].

[5] The objective of this study was to provide analytical data on the VOC content of snow and contribute to the evaluation of its potential to act as a source or sink for VOC, be they directly atmospherically active or precursors for atmospheric reactions [*Guimbaud et al.*, 2002; *Viskari et al.*, 1997; *Swanson et al.*, 2005]. It was important to provide a broad picture of occurring compounds to complement already available information on the few previously measured selected compounds [*Valsecchi et al.*, 1999; *Houdier et al.*, 2002; *Hutterli et al.*, 2002; *Sumner and Shepson*, 1999; *Sumner et al.*, 2002]. In order to make the determination simple and suitable for field work in even remote environments, solid-phase microextraction with gas chromatography and mass spectrometric detection (SPME-GC/MS) was chosen, because of its simplicity and ability to detect a wide range of compounds at trace levels [*Kos and Ariya*, 2006; *Kolb and Puttmann*, 2006; *Lord and Pawliszyn*, 2000]. Samples were collected at a rural semiremote site and in the immediate surroundings of the city of Montreal in southwestern Quebec, Canada. Analysis was performed using a modified procedure that allowed for greater sensitivity for headspace and liquid phase analysis compared with an earlier work [*Kos and Ariya*, 2006]. The obtained data provide a detailed qualitative and quantitative picture of species and conclusions give insight on how VOC and their concentrations listed in Figure 1 vary in the snowpack with location and environmental conditions at the time of sampling.

2. Experimental Setup

2.1. Sampling and Storage

[6] A standardized sampling protocol was established for precleaning, sampling and storage to minimize sample contamination and ensure comparability. Glassware was rinsed with ethanol (Fisher Scientific, Nepean, Canada) to remove soluble organic impurities and ultrapure water (Millipore, Etobicoke, Canada). Washing with phosphate-free detergent, soaking overnight in 10% hydrochloric acid (Fisher) followed before a rinsing step with ultrapure water and drying at 125°C (Lindberg, Asheville, North Carolina). Ethanol was not detected in any of the samples or blanks. Sterile equipment for single use was individually packaged and used as provided.

[7] Care was taken to avoid contamination from the sampling personnel and access to the site from downwind and leaving a distance between parked vehicles and sampling location of 2 km. Clean suit, face mask and gloves were worn. Sterile 220 mL containers (Fisher) were filled with snow using a fresh sterile spoon (Fisher) for each location. The first 10 cm of the snowpack from the surface were collected including field blanks consisting of ultrapure water. Addition of tracers during sampling was not feasible due to the inhomogeneous nature of snow. Frozen samples were transported in the dark using ice packs in commercial coolers and stored in a freezer at −18°C upon arrival at the laboratory and no melting was performed until analysis. Seven samples were collected at each site including a field blank.

2.2. Sampling Areas and Locations

[8] Samples were collected in two areas at six different locations in southwestern Quebec, Canada. For sampling locations see Figures 2a and 2b. The sites reflect two environments with different degrees of anthropogenic influence (see below). All sampling equipment was temperature-equilibrated before sampling started. Temperature and snow depth measurements were averaged from five measurements taken throughout the duration of sampling. They are specific for the sampled location itself. Detailed ancillary data for all sampling locations and areas are listed in Table 1. Sampling area data (first two columns in Table 1) were reported by Environment Canada (EC) from stations in Sainte-Madeleine (45°37′N, 73°7′W) for the Mont-Saint-Hilaire area and Saint-Come (46°16′N, 73°45′W) situated in the Tremblant area (http://www.climate.weatheroffice.ec.gc.ca/, accessed 31 August 2006). Wind data at sampling location were estimated.

[9] The (semirural) mountain of Mont-Saint-Hilaire (45°33′06″N, 73°03′03″W) is a nature reserve situated about 50 km east of Montreal. A major highway passes 1.10 km to the northeast, representing a major source of VOC due to traffic emissions. A total of 14 samples (including two field blanks) were collected in two different locations. Sampling sites were populated by shrubs and small trees, which broke through the snow cover at the time of sampling. Some

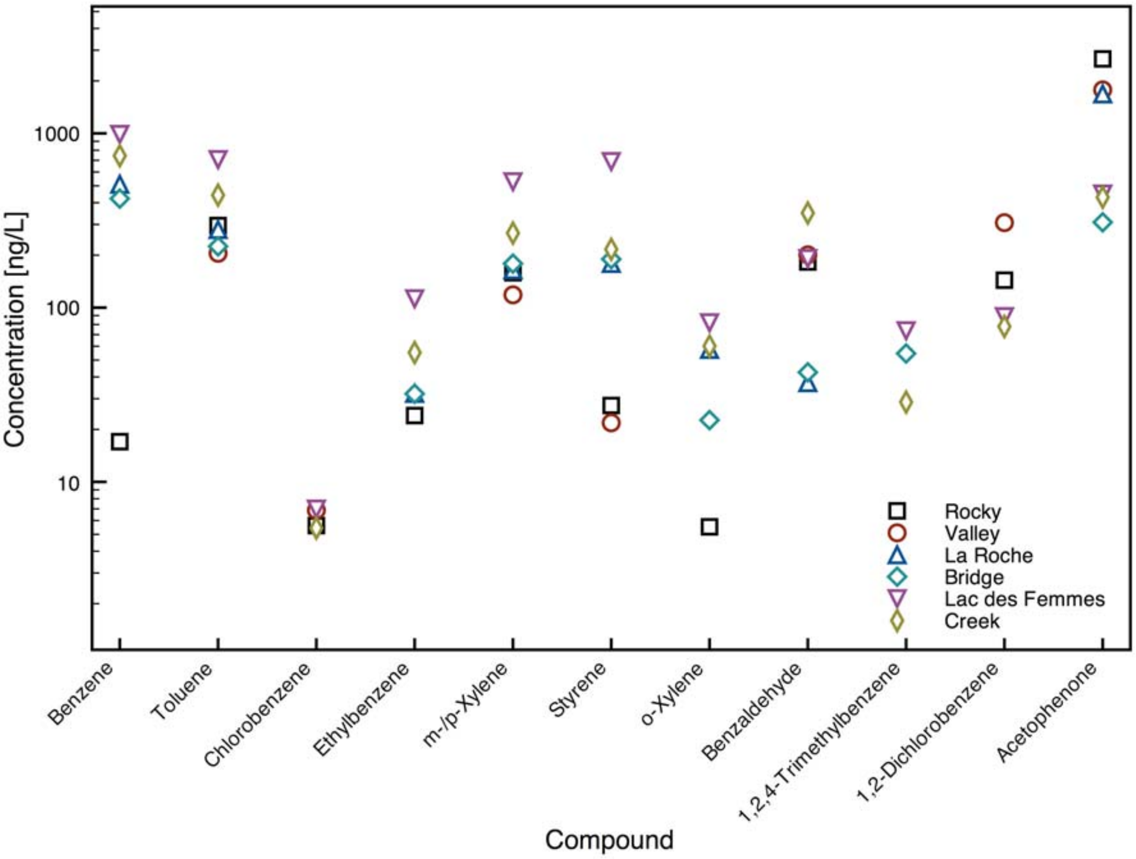

Figure 1. Concentrations in the liquid phase for 11 quantified compounds at six sampling locations (two from the Mont-Saint-Hilaire area and four from the Tremblant area). Error bars were removed due to the log scale. Uncertainty data (±3s) and limits of detection are available in Tables C1 and C2 in Appendix C.

animal tracks were found near the sampling locations, which itself was free of tracks and biomaterial. Meteorological conditions were sunny with good visibility (estimated as $\geq$50 km), slight westerly wind and a few cirrocumulus clouds. Samples from (rural) Tremblant Park, a protected area of 1510 km^2 situated about 145 km northwest of Montreal (46°20′11″N, 74°30′36″W) were taken around Petit Lac Monroe and Lac des Femmes. Anthropogenic influence is limited compared with Mont-Saint-Hilaire consisting mostly of recreational activities. No motorized vehicles and boats are operated in the park apart from traffic on the access road, which is very light in winter. Twenty-eight samples were collected at four locations. Sites were shaded by trees and sunny conditions prevailed with a few cirrocumulus clouds but no or slight wind. For detailed measured and estimated numerical data, see Table 1.

2.3. Snow Properties

[10] Sampling was performed in early spring and during the day temperatures usually were already well above freezing, even at higher altitudes (Table 1). Therefore, estimated snow water content (liquid water present in percent by weight) was high, resulting in a high degree of agglomeration. Determination of snowpack properties was performed by visual inspection using a magnifying glass. The snowpack was in an advanced stage of ripening with a highly structured surface, presumably from repeated freezing and thawing cycles. For locations “Rocky” and “La Roche” the first 3 cm from the snow surface were hard and packed followed by a layer down to 10 cm where individual grains could not be recognized. Sampling ended there. At locations “Valley”, “Bridge” and “Lac des Femmes”, “Creek” the snowpack started with several centimeters of partially melted snow, followed by a hard layer and then depth hoar. All of the latter locations were probed at air and snow temperatures at or around 0° and in lower lying areas (Table 1).

2.4. SPME-GC/MS

[11] For analysis, the contents of three containers were pooled after melting at a sample temperature <7°C to minimize volatilization. 140 mL were used for SPME analysis. After melting samples were transferred to gas tight vials, which were still cold to minimize loss of VOC. Vials were sealed with PTFE lined silicon septa (Chromatographic Specialities, Brockville, Canada) and equilibrated to room temperature. Compounds were preconcentrated on a SPME fiber using a 65 μm divinylbenzene coated polydimethylsiloxane (PDMS) fiber (Supelco, Bellefonte, Pennsylvania) for adsorption of analytes. Regular conditioning and cleaning procedures were carried out by heating the fiber to 250°C to avoid contamination. A pair of two fibers was used through-

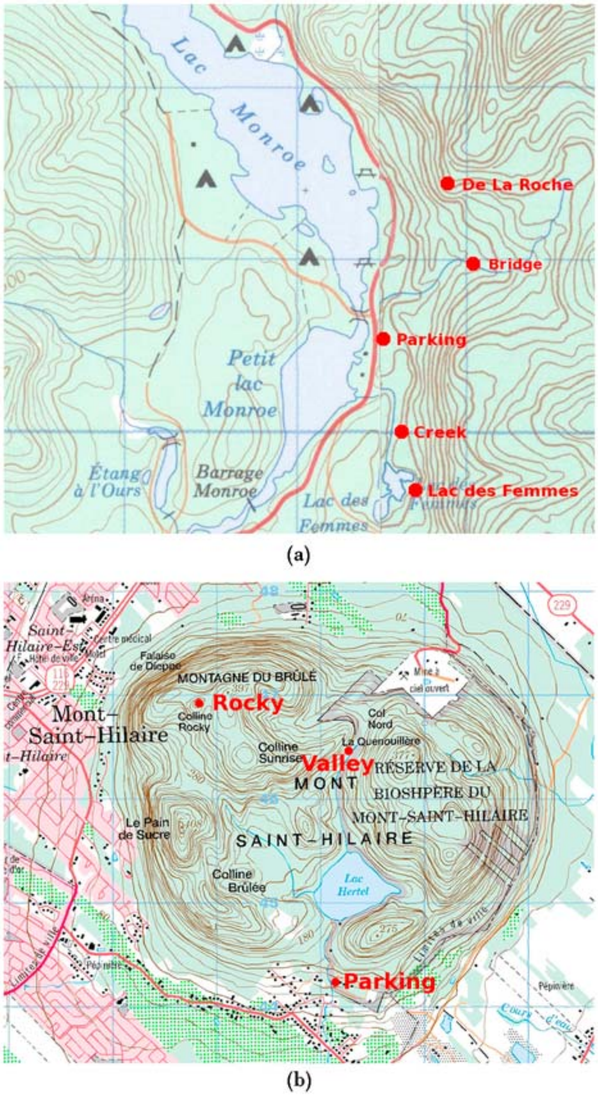

Figure 2. Map of sampling locations in the (a) Tremblant (46° 20′11″N, 74° 30′36″W) and (b) Mont-Saint-Hilaire (45° 33′06″N, 73° 03′03″W) areas; copyrighted topographic maps are reproduced under license from Her Majesty the Queen in Right of Canada, with permission of Natural Resources Canada. Scale: 1:50,000.

out the study. Ultrapure water field blanks that were treated like the samples were used for blank experiments. After melting the liquid phase was probed by immersion of the fiber for 120 min followed by immediate transfer to the GC injector port for desorption, separation and analysis. Headspace analysis was carried out in a similar fashion by exposing the fiber to the gas space above the liquid in the gas-tight vial. Detailed measurement conditions and data analysis procedures are described in an earlier article focusing on analytical methodology [*Kos and Ariya*, 2006]. General SPME application notes and theory are available from *Scheppers Wercinski* [1999] and *Pawliszyn* [1997].

[12] GC/MS measurements and data analysis were performed using a Hewlett-Packard gas chromatograph with quadrupole mass spectrometric detection (GC/MS, HP GC 6890 and MSD 5973, Agilent Technologies, Mississauga, Canada). The most important improvement to the method presented earlier was the use of splitless injection for increased sensitivity and thus better limits of detection (LOD). It was possible to avoid hanging water drops after retraction of the fiber by immersing the fiber fully, but not the protective needle thus reducing the overall amount of water entering the system significantly. After 3 min of desorption the injector port was purged with 25 mL/min of carrier gas to flush out any retained contaminants.

[13] Eleven aromatic compounds with concentration data displayed in Figure 1 were quantified using standard solutions (a stock solution of mixed standards was prepared in methanol, subsequent dilutions for working standards were made with ultrapure water). Standards were prepared and treated in an identical manner as the samples with regard to the SPME procedure and conditions of GC/MS measurements; that is, headspace and liquid phase fiber adsorption measurements were carried out and peak area data were determined for each standard.

[14] Calibration curves were set up with at least five standards (n = 5) and blanks for the liquid in a concentration range from 0.01 to 100 μg/L. Compound names and LODs are listed in Table C2 in Appendix C. Blank measurement variation was always <5%, n = 20, minimum distinguishable signal was calculated to be the mean with 3 standard deviations (3s) added. Sample peak area data from headspace and liquid phase measurements were then matched with the respective calibration curve after subtraction of the blank signal. Overall a better sensitivity was obtained for liquid phase measurements for quantification.

[15] Identification of compounds was carried out using a spectral deconvolution program (AMDIS 2.6, NIST, Gaithersburg, Maryland) and MS Search 2.0 (an MS library, NIST) [*Zhang et al.*, 2006; *Bleasel et al.*, 2003]. The extraction of spectral information removed peaks identified as column bleeding and, therefore, increased the reliability of identification, but also resulted in more accurate quantitative data. Extracted spectra were carefully checked against raw data for removal of analyte fragments. Additional data used to support identification included retention times from standard runs and comparison with previous sample runs. Could the identity not be established with the above methods, the compound was not reported. This was the case for predominantly biogenic compounds with a large number of potential isomers, e.g., limonene, α- and β-pinene, whose presence was nevertheless confirmed. These compounds are listed separately in Table B1 in Appendix B.

2.5. Back Trajectory Calculations

[16] In order to determine the source region of the air masses passing areas and locations before the sampling event back trajectories were calculated for both sampling locations using the NOAA HYSPLIT model (R. Draxler and G. Rolph, Hysplit (Hybrid Single-Particle Lagrangian Integrated Trajectory) model, 2003, http://www.arl.noaa.gov/ready/hysplit4.html) (hereinafter Draxler and Rolph, HYSPLIT model, 2003). The HYSPLIT model was run using the NCEP Global Data Assimilation System (GDAS1), a 3 hourly, global, 1° latitude-longitude data set and back trajectories were calculated for the previous 72 h. A new trajectory was started every 3 h for a total of 24 at the altitude of the sampling location. Model vertical velocity

Table 1. Ancillary Data

	Sainte-Madeleine[a]	Saint-Come[a]	Rocky	Valley	La Roche	Bridge	Lac des Femmes	Creek
Date	18 Mar	5 Apr	18 Mar	18 Mar	5 Apr	5 Apr	5 Apr	5 Apr
Sampling started[b] (UTC)			1715	1850	1715	1830	2040	2140
Sampling ended[b] (UTC)			1810	1940	1800	1920	2115	2220
Altitude (m)	30	244	400	220	630	510	420	400
Maximum air temperature (°C)	+1.5	+12	NA[c]	NA	NA	NA	NA	NA
Minimum air temperature (°C)	−14	−0.5	NA	NA	NA	NA	NA	NA
Mean air temperature (°C)	−6.3	+5.8	−2.8 ± 0.55	+1.0 ± 0.41	+4.9 ± 0.33	+7.0 ± 0.89	+7.3 ± 0.71	+4.8 ± 0.22
Wind speed (km/h)	20[d]	NA	l	g	n	n	l	n
Wind direction (°C)	250[d]	NA	270	270			270	
Cloud cover (%)	10–40[e]	NA	5	40	10	0	20	20
Total rain (mm)	traces	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total snow (mm)	traces	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Snowfall: date: (mm)	01 Mar: 26	02 Apr: traces	NA	NA	NA	NA	NA	NA
Rainfall: date: (mm)	16 Feb: 0.6	03 Apr: 10	NA	NA	NA	NA	NA	NA
Snow on ground (cm)	35	30	90	60	49	48	42	37
Snow temperature, 0 cm[f] (°C)	NA	NA	−1.0	−0.1	0.0	+0.2	+0.2	+0.1
Snow temperature, 15 cm (°C)	NA	NA	−3.0	−1.9	−0.2	−0.2	−0.2	−0.3
Layer thickness[g] (cm)	NA	NA	3s, 7h	3s, 2h, 5s	3h, 7s	7s, 3h	3s, 2h, 5s	10s

[a] Meteorological conditions obtained from Environment Canada stations for sampling areas Mont-Saint-Hilaire (Sainte-Madeleine) and Tremblant (Saint Come).

[b] Measurements at individual sampling locations (Rocky-Creek) in 2005.

[c] NA, not available.

[d] Wind speed as obtained from Montreal Airport hourly data; data on location estimated. Abbreviations: n, none; l, light; g, light gusts.

[e] Cloud cover obtained from Montreal Airport hourly data; data on location estimated.

[f] Temperature during sampling. Data provided for air and for snow at 0 cm (surface) and 15 cm depth; n = 5).

[g] Snow layer properties for 0–10 cm. Abbreviations: h, hard; s, soft.

was employed. Results for the locations "Rocky" and "La Roche" are displayed in Figure 4 in section 3.5, and back trajectories for the other sampling locations in both areas look similar to the origin of air masses.

3. Results and Discussion

[17] Both sampling areas are located in the QWC to assess the contributions of the snowpack toward the VOC budget in the region during the winter and early spring. Results are especially relevant, because of the influence of VOC chemistry and concentrations on air quality in this densely populated area [*Miller et al.*, 2009]. Together with remarks regarding the methodology used, we report on species detected and quantification data for 11 selected species important for atmospheric chemistry, environmental processes and air quality.

[18] We evaluate results from different sampling sites to investigate how types of compounds detected and concentrations are dependent on the immediate environment at the sampling location (e.g., snow properties, hillside, catchment, human presence). We also compare data with already published material from the QWC and other regions. These data were acquired with the same method [*Kos and Ariya*, 2006].

[19] Finally we assess the influence of the VOC input provided by air masses passing the sampling area shortly before the sampling event. For reference, sampling site details and ancillary measurements are listed in Table 1.

3.1. Analytical Method

[20] Compounds identified and quantified in snow samples from both, headspace and liquid phase experiments are presented in Figure 1 and Table 2. SPME is a technique that enables probing of the liquid phase and the above headspace of a gas tight sample vial and detection limits are a function of volatility and matrix effects [*Beranek and Kubatova*, 2008; *Scheppers Wercinski*, 1999]. For a comprehensive investigation, both phases were probed for this study and compounds detected in both phases represent the majority for all samples. Some volatile compounds were detected in the headspace only (e.g., heptanal) and a few in the liquid phase only (e.g., methylisobutylketone). SPME is an established extraction technique, especially for aqueous samples that exhibits similar performance to traditional solvent intensive extraction methods [*Pawliszyn*, 1997]. Numerous comparison studies were conducted, illustrating the performance and reliability of the methodology [*Lara-Gonzalo et al.*, 2008; *Bocchini et al.*, 1999; *Nilsson et al.*, 1997]. An example for detected species by phase is given in Table A1 in Appendix A. For all data presented graphically, exact concentrations including the variability of duplicate measurements (±3s) are listed in Table C1 in Appendix C. Our results underline the technique's unique capability to provide data on a wide range of VOC in snow in a convenient, efficient and environmentally benign manner.

3.2. Concentration Levels in the Snowpack

[21] The most pronounced feature of Figure 1 is high concentrations (2.67 and 1.77 μg/L) of acetophenone in both samples from Mont-Saint-Hilaire. Concentrations are 4 to 5 times higher than the second most abundant compound 1,2-dichlorobenzene (0.30 μg/L in sample "Valley"). Benzene concentrations from Mont-Saint-Hilaire were lower than in Tremblant as were Styrene and o-xylene, showing that VOC concentrations differ between areas. The concentrations suggest that samples could potentially be classified by sampling area using species concentrations. We employed principal component analysis (PCA) of the concentration data to illustrate differences between the profiles of the 11 species displayed in Figure D1 in Appendix D [*Preisendorfer and Mobley*, 1988]. Three clusters made up

Table 2. Compounds Detected in Snow Samples Collected in the Sampling Areas of Mont-Saint-Hilaire and Tremblant

Rocky	Valley	La Roche	Bridge	Lac des Femmes	Creek
	Acetone	Acetone			
		Acetic acid-isobutylester		Acetic acid-isobutylester	
Acetophenone	Acetophenone	Acetophenone	Acetophenone	Acetophenone	Acetophenone
Benzaldehyde	Benzaldehyde	Benzaldehyde		Benzaldehyde	
Benzene		Benzene	Benzene	Benzene	Benzene
		n-Butylbenzene		n-Butylbenzene	
					Butylated hydroxytoluene
					Butyrolactone
Chlorobenzene	Chlorobenzene		Chlorobenzene	Chlorobenzene	Chlorobenzene
	Chloroform	Chloroform		Chloroform	
	Coumarin				
					p-Cymen-8-ol
	Decanal				
	5-Decanone				
1,2-Dichlorobenzene	1,2-Dichlorobenzene	1,2-Dichlorobenzene	1,2-Dichlorobenzene	1,2-Dichlorobenzene	1,2-Dichlorobenzene
	2,4-Dimethylheptane				
4,6-Dimethyl-2-heptanone	4,6-Dimethyl-2-heptanone	4,6-Dimethyl-2-heptanone	4,6-Dimethyl-2-heptanone	4,6-Dimethyl-2-heptanone	4,6-Dimethyl-2-heptanone
2,4-Dimethyl-1-heptene	2,4-Dimethyl-1-heptene	2,4-Dimethyl-1-heptene	2,4-Dimethyl-1-heptene	2,4-Dimethyl-1-heptene	2,4-Dimethyl-1-heptene
		Di-n-butylether	Di-n-butylether	Di-n-butyl-ether	
			Di-tertbutylether		
m-Ditertbutylbenzene	m-Ditertbutylbenzene	m-Ditertbutylbenzene	m-Ditertbutylbenzene	m-Ditertbutylbenzene	m-Ditertbutylbenzene
2,6-Ditertbutyl-p-10pt-benzoquinone	2,6-Ditertbutyl-p-10pt-benzoquinone	2,6-Ditertbutyl-p-10pt-benzoquinone	2,6-Ditertbutyl-p-10pt-benzoquinone	2,6-Ditertbutyl-p-10pt-benzoquinone	2,6-Ditertbutyl-p-10pt-benzoquinone
		2,4-Ditertbutylphenol		2,4-Ditertbutylphenol	
Ethylbenzene	Ethylbenzene	Ethylbenzene	Ethylbenzene	Ethylbenzene	Ethylbenzene
					Eucalyptol
	Heptanal	Heptanal	Heptanal	Heptanal	Heptanal
	2-Heptanone				2-Heptanone
3-Heptanone	3-Heptanone	3-Heptanone		3-Heptanone	3-Heptanone
Hexanal	Hexanal	Hexanal	Hexanal	Hexanal	Hexanal
2-Hexanone					
	3-Hexen-2-one				
Isopentylbenzene					
2-Methylacetate-2-butanol	2-Methylacetate-2-butanol				2-Methylacetate-2-butanol
				Hexanoic acid-ethylester	Hexanoic acid-ethylester
		2-Methyl-2-butanolacetate	2-Methyl-2-butanol-acetate	2-Methyl-2-butanolacetate	
2-Methyl-1-heptene			2-Methyl-1-heptene	2-Methyl-1-heptene	2-Methyl-1-heptane
4-Methylheptane			4-Methylheptane	4-Methylheptane	
4-Methyl-2-heptanone	4-Methyl-2-heptanone	4-Methyl-2-heptanone	4-Methyl-2-heptanone	4-Methyl-2-heptanone	4-Methyl-2-heptanone
				6 Methyl-2-heptanone	6-Methyl-2-heptanone
				4-Methyl-2-heptanol	
Methylisobutylketone	Methylisobutylketone	Methylisobutylketone		Methylisobutylketone	Methylisobutylketone
2-Methylnaphtalene					2-Methylnaphtalene
				2-Methyl-2-octanol	
	2-Methyl-1-pentene	2-Methyl-1-pentene	2-Methyl-1-pentene	2-Methyl-1-pentene	
			1-Methyl-2-pyrolodinone		
Naphtalene	Naphtalene	Naphtalene	Naphtalene	Naphtalene	Naphtalene
Nonanal		Nonanal	Nonanal	Nonanal	Nonanal
2-Nonanone					
3-Nonanone				3-Nonanone	3-Nonanone
	5-Nonanone				
				Octanal	

Table 2. (continued)

Rocky	Valley	La Roche	Bridge	Lac des Femmes	Creek
Orthoformic acid-triisobutylester		Orthoformic acid-triisobutylester	Orthoformic acid-triisobutylester		
2-Pentyl-1-pentene					2-Pentyl-1-pentene
	Pentane				
	Pyrrolidine				
Styrene	Styrene	Styrene	Styrene	Styrene	Styrene
Tertbutyl-ethylether					Tertbutyl-ethylether
Tertbutylisopropylether		Tertbutylisopropylether	Tertbutylisopropylether	Tertbutylisopropylether	Tertbutylisobutylether
	Tertbutylphenylether			Tertbutylphenylether	
Tetrachloroethylene	Tetrachloroethylene	Tetrachloroethylene	Tetrachloroethylene	Tetrachloroethylene	Tetrachloroethylene
	1,2,3,4-Tetrahydro-naphtalene			1,2,3,4-Tetrahydro-naphtalene	1,2,3,4-Tetrahydro-naphtalene
Tetrahydro-2,2,5,5-tetramethylfuran	Tetrahydro-2,2,5,5-tetramethylfuran	Tetrahydro-2,2,5,5-tetramethylfuran	Tetrahydro-2,2,5,5-tetramethylfuran	Tetrahydro-2,2,5,5-tetramethylfuran	Tetrahydro-2,2,5,5-tetramethylfuran
Toluene	Toluene	Toluene	Toluene	Toluene	Toluene
	2,2,4-Trimethylheptane				
1,2,4-Trimethylbenzene	1,2,4-Trimethylbenzene	1,2,4-Trimethylbenzene	1,2,4-Trimethylbenzene	1,2,4-Trimethylbenzene	1,2,4-Trimethylbenzene
m-/p-Xylene	m-/p-Xylene	m-/p-Xylene	m-/p-Xylene	m-/p-Xylene	m- & p-Xylene
o-Xylene	o-Xylene	o-Xylene	o-Xylene	o-Xylene	o-Xylene

of two sampling locations each emerged from the score plots of principal component (Prin) 1 versus Prin2. A comparison with the maps (Figures 2a and 2b) shows that sampling locations closest to each other were grouped together and a discrimination using the concentration profile is indeed possible for the presented data set. Concentration profiles seem to be reflecting local effects at the sampling location rather than the sampling area, e.g., for the "Tremblant" locations: Samples "De La Roche" and "Bridge" were sampled on the same hillside, whereas "Lac des Femmes" and "Creek" were collected from the same catchment. For the presented data, PCA results are a measure of the proximity of sampling locations. It should also be possible to assign the origin of an unknown snow sample, though requiring a larger data set of reference samples with known origin. These preliminary results show the potential of the discrimination method.

[22] Differing snow concentrations are caused by factors that are closely associated with the immediate environment of the sampled location [*Wania et al.*, 1998]. Microphysical snow properties and linked processes are important for the increasing or decreasing amount of species over time, especially during the snow melt in spring described here [*Meyer et al.*, 2009]. Deposition provides a baseline, which is then subjected to photochemical activity [*Sumner and Shepson*, 1999], microbiological transformation [*Pennisi*, 2003], (re-)volatilization [*Herbert et al.*, 2004] and losses to soil through percolation during snow melt [*Wania et al.*, 1998]. Formed reaction products in turn contribute to the overall VOC budget in the snowpack. Exposure time and intensity to sunlight and the microbiological load (bacteria and fungi) of the snowpack represent additional environmental factors that influence conversion rates. Photochemistry is responsible for the formation and reaction of oxygenates that play an important part in tropospheric ozone chemistry. It was suggested that the snow surface itself promotes photochemical transformation [*Pomeroy and Jones*, 1996].

[23] Overall these factors described in the literature lead to a differentiation of the VOC concentrations found in the snow, which allows for classification by PCA demonstrated above. They are dependent on the conditions in the immediate surroundings of the sampling location, e.g., exposure to sunlight due to sloping and orientation of the sampled hillside.

[24] A comparison of concentrations with previous results obtained from an Arctic sample and data collected from snow samples from the Gaspé peninsula in April 2004 indicated a large variability of VOC concentrations in the top layer [*Kos and Ariya*, 2006]. Earlier results were in the lower μg/L range for a similar set of compounds (e.g., 32 μg/L in snow from the Gaspé peninsula). Data presented here were in the lower to mid ng/L range (e.g., 17 ng/L benzene in sample "Rocky"). However, variability was large for both data sets and concentrations were very similar for other species, e.g., 112 ng/L in sample "Lac des Femmes" and 310 ng/L ethylbenzene from the Gaspé peninsula. Consistent with qualitative results and concluding from results obtained in the earlier study, VOC concentrations varied considerably in the surface layer of the snowpack.

3.3. Chemistry of Quantified Species

[25] Concerning the chemistry of the quantified compounds the relevant question is, how the observed concentrations relate to atmospheric concentrations and what the major reasons for differences are: photochemistry [*Beine et al.*, 2008], biodegradation [*Amato et al.*, 2007] and accumulation via solubilization [*Mackay and Wania*, 1995] in the liquid phase are important mechanisms, the latter especially in wet, melting snow. Low water-soluble species that tend to reside in the interstitial air (e.g., aromatics) and selected species have been measured in the past, e.g., oxygenates [*Boudries et al.*, 2002], acetaldehyde [*Guimbaud et al.*, 2002], formaldehyde [*Hutterli et al.*, 1999] and ethene [*Bottenheim et al.*, 2002]. All measurements showed a positive flux from the snowpack to the atmospheric boundary layer suggesting that surface snow acts as a source for these species, especially during photochemical activity. No data are available for the compounds presented here, underlining the necessity for investigation of these species as precursors and definition of the reservoirs for these fluxes in the snowpack.

[26] Photochemistry in snow and involved species studied was reported recently [*Grannas et al.*, 2007]. Formic and acetic acid have been shown to be enriched in by 1 order of magnitude in firn interstitial air [*Dibb et al.*, 2002] and so were carbonyls from photochemical production of organics, e.g., formaldehyde [*Sumner and Shepson*, 1999]. Nitrate addition led to enhanced concentrations by enhanced OH-radical production. Together with the unique properties of snow that provides a large reaction surface on ice, liquid water and air phases the chemistry is quite different compared to atmospheric processes leading to the enhanced concentrations described [*Domine et al.*, 2007].

[27] Mixing ratios for some species discussed here were measured in past sampling campaigns in the atmosphere [*Gilman et al.*, 2009] and although dates and locations do not match the data presented here, concentrations in the snowpack were generally higher. This is in line with previous investigations cited above that determined positive fluxes of species with similar chemical functionalities (e.g., oxygenates) into the atmosphere due to enhanced photochemical production in the snowpack.

3.4. VOC Species and Functional Groups

[28] A large number of different compounds was detected in samples (e.g., in the "Creek" sample with 41 unambiguously identified compounds of predominantly anthropogenic (e.g., benzene) or biogenic origin (e.g., p-Cymen-8-ol); see Table 2). The spectrum of chemical functionalities of compounds found in all samples confirmed results of a previous study [*Kos and Ariya*, 2006].

[29] So far no comprehensive VOC data set using a single method has been published, except for interstitial air measurements of selected VOC [*Swanson et al.*, 2005] and higher molecular weight organics [*Satsumabayashi et al.*, 2001]. Knowledge of the overall chemical composition of snow is, therefore, quite limited and comparison is difficult [*Grannas et al.*, 2007]. Typically, oxygenated compounds were dominated by ketones and esters; ethers and aldehydes were also present (between 18 and 24 different species), followed by aromatics (11–17), aliphatics (1–6) and halogenated VOCs (2–3); see Table 2. A general overview of chemical functionalities present is given in Figure 3: Very few halogenated compounds were present above the detection limits, mostly chlorobenzene, tetrachloroethylene and 1,2-dichlorobenzene and sometimes chloroform (e.g., location "Valley"; Table 2. The number of oxygenated compounds provided a significant reservoir of photoreactive compounds contained in the snow either from deposition, but could also be resulting from reactions with peroxides [*Chu and Anastasio*, 2005].

[30] With multiple isomers not unambiguously identified, the number of compounds increased even further, e.g., by 25 at the location "Creek." The fraction of biogenic compounds was also increased significantly, e.g., *alpha*- and *beta*-pinene or limonene; see Table B1 in Appendix B. For the assessment of the full range of occurring VOCs it has to be noted, though, that there is a dependency of detected compounds on the polarity of the employed SPME fiber. Only compounds with similar polarity will adsorb to the fiber [*Scheppers Wercinski*, 1999]. Although a large number was detected, this represented a lower limit of the overall presence of species.

[31] Results from the Mont-Saint-Hilaire area ("Rocky" and "Valley"; Table 2) showed a similar number of identified compounds: 44 (identified) and 54 (including compounds with unknown substitution patterns). Similarly, 56 (identified) and 68 (including compounds with unknown substitution patterns) species were detected in samples collected in the Tremblant area. Sampling areas were quite different regarding their geographical location: Mont-Saint-Hilaire is 50 km east of Montreal with prevailing winds from the West and a major highway close by (1.10 km). Tremblant is 145 km north of Montreal and no major city upward of the prevailing winds from the West; see Figures 2b and 2a. These differences, however, are not reflected in the number and type of compounds detected, e.g., an expected lower fraction of anthropogenic species in Tremblant, which is more remote and not part of the Greater Montreal area. We employed principal component analysis (PCA) of the species type data from Figure 3 at their respective locations to determine similarities between locations (see Figure D2 in Appendix D). No clusters were formed and, therefore, no observable difference exists between sampling locations regarding the number of compounds with any chemical functionality.

[32] A comparison with results from an earlier study show a similar spectrum of compounds and chemical functionalities [*Kos and Ariya*, 2006]. Additionally, more halogenated species were present (e.g., diiodomethane and brominated methanes). This could be due to the coastal environment and the presence of open sea water as a source of halogens resulting in their detection in the snowpack [*Simpson et al.*, 2005], whereas the data presented here originate from land-based samples. The same sample preparation method was employed for both studies. Date of sampling, meteorological conditions and snow water content were also similar. The new results presented here, therefore indicate a large variability of species occurring in the snowpack and their dependence on the environment they were sampled in.

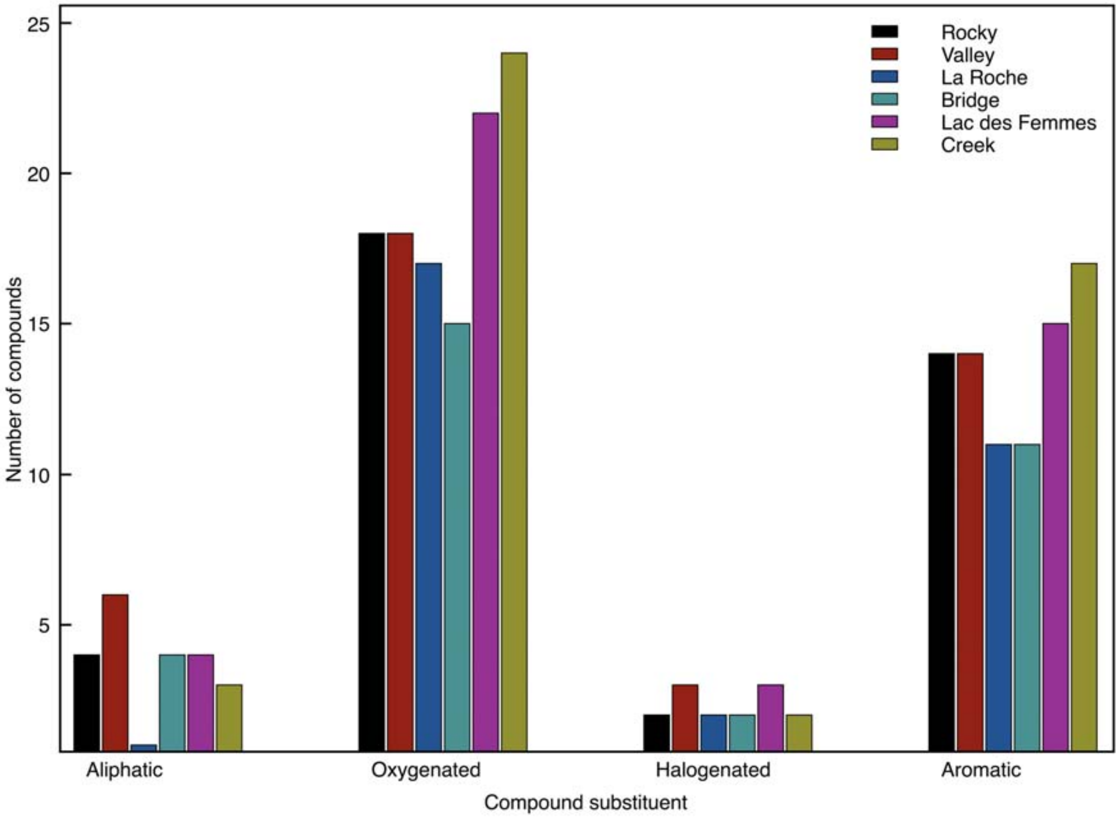

Figure 3. Number of compounds found at all sampling locations that were of aliphatic, oxygenated, halogenated, and aromatic character.

3.5. Back Trajectories for Sampling Areas

[33] For the determination of source regions a model estimation using back trajectories is presented below to better understand contributions from deposition processes; see Figure 4 (Draxler and Rolph, HYSPLIT model, 2003). Organic species in seasonal snowpack typically reflect the history of multiple deposition (wet/dry) and removal events, e.g., melting and photochemistry [*Meyer et al.*, 2009]. Surface snow is especially exposed to atmospheric processes such as deposition events and primarily reflects recent events. Earlier deposited species already underwent processes for removal and reactions [*Albert and Shultz*, 2002; *Anderson and Neff*, 2008]. We therefore investigated the origin of air masses passing the sampling locations 72 h before the surface snow sampling event.

[34] Results for area Mont-Saint-Hilaire show that the air passing 72 h before sampling originates from the James Bay region to the north-northwest (Figure 4). Montreal, the only

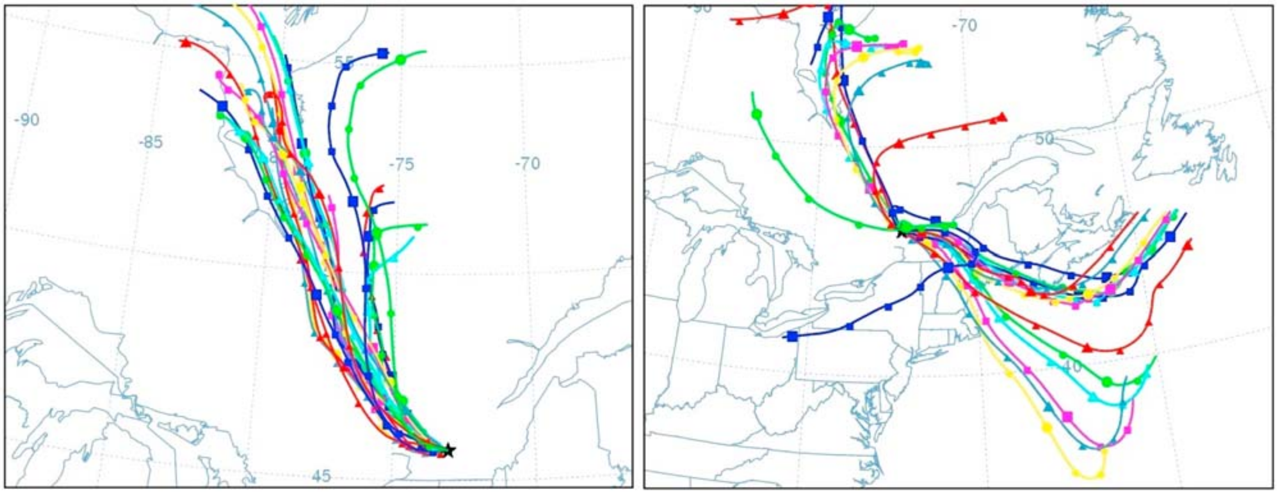

Figure 4. Seventy-two-hour back trajectories. (left) Location “Rocky” in area Mont-Saint-Hilaire. (right) Location “La Roche” in area Tremblant.

Table A1. Compounds Detected in the Liquid Phase and Headspace of a Snow Sample Collected in the Area of Mont-Saint-Hilaire, Location Rocky[a]

	Compounds
LQ and HS	Tertbutyl-ethylether, Benzene, Tertbutyl-isopropylether, Tetrahydro-2,2,5,5-tetramethylfuran, Toluene, Hexanal, Chlorobenzene, Ethylbenzene, m- & p-Xylene, 3-Heptanone, Styrene, o-Xylene, 4-Methyl-2-heptanone, 4,6-Dimethyl-2-heptanone, 1,2,4-Trimethylbenzene, Acetophenone, Naphtalene, Isopentylbenzene, 1,2-Dichlorobenzene
LQ only	Methylisobutylketone, 2-Hexanone, Benzaldehyde, Orthoformic acid-triisobutylester, 3-Nonanone, Nonanal, 2,6-Ditertbutyl-p-benzoquinone
HS only	2-Pentyl-1-pentene, 2-Methyl-1-heptene, 4-Methylheptane, 2-Methylacetate-2-butanol, Tetrachloroethylene, 2,4-Dimethyl-1-heptene, 2-Nonanone, m-Ditertbutylbenzene, 2-Methylnaphtalene

[a]Compounds listed in elution order. Abbreviations: LQ, liquid phase; HS, headspace.

urban area close to the trajectory is passed at its northeastern margin. Air masses passing over the Tremblant area 72 h prior to sampling originate from two principal source regions: The smaller amount from the James Bay region and the from heavily populated centers such as Boston and New York. Other source regions were over the state of Maine and the southern tip of Nova Scotia, most probably consist of less polluted air (Figure 4).

[35] This contribution from urban sources in the northeastern United States could account for the higher than expected VOC concentrations found in the more remote "Tremblant" samples. Atmospheric lifetimes of some investigated aromatics are typically on the order several days (see Table C2 in Appendix C) and long enough to be not completely transformed upon their arrival at the sampling site. They could readily be detected, whereas samples in Mont-Saint-Hilaire received cleaner air from an Arctic Source with concentrations of aromatic species below the detection limit. It has to be noted that air masses arriving at the sampling location to not represent the only source or sink for the detected compounds. Effects at the sampling location such as photochemical and microbiological transformations, location and removal processes (as discussed above, e.g., by increased solubility in the melted liquid phase) may contribute to higher or lower concentrations than expected. This is true for compounds such as styrene, which have a short atmospheric life time and that were detected at significant concentrations. Their presence cannot readily be explained by air mass movements and source regions as far away as described.

4. Conclusions and Future Work

[36] The data set provides consistent and comparable results obtained with a single method for a multitude of anthropogenic and biogenic compounds and 11 selected species with a high impact on climatic, environmental processes and air quality that were quantified. The major compound groups were oxygenated compounds (aldehyes and ketones), aromatics and relatively few halogenated (mostly chlorinated) species. Their potential to participate in photochemical reactions [*Matykiewiczova et al.*, 2007] and microbiological degradation [*Cote et al.*, 2008; *Nepotchatykh and Ariya*, 2002] also needs to be investigated in detail. Detected compounds had a similar qualitative profile for all sampling location and areas. Compared with previous measurements, the number of different halogenated compounds was very low in all samples [*Kos and Ariya*, 2006]. Their occurrence in the measured samples makes the snowpack a potential source or sink for these VOC contributing to the current gap of knowledge in organic snow chemistry [*Grannas et al.*, 2007]. Most compounds are reported for the first time in this comparable and consistent fashion. Halogenated compounds, including brominated and iodine species, however have previously occurred in larger numbers and we conclude that these species are present to a

Table B1. Additional Identified Compounds in Snow Samples From Six Sampling Locations[a]

Location	Compounds
Rocky	Dichlorobenzene, Methylacetophenone, Pentylbenzene, Trimethylpyridine, Heptanal, Methylbenzaldehyde, Methylnaphtalene, Trimethylbenzene
Valley	Dichlorobenzene, Methyl-benzaldehyde, Methyl-acetophenone, Methylbenzoic acid methylester, Trimethylbenzene, Dichlorobenzene, Tetramethylbenzene, Trichlorobenzene, Pentamethylbenzene, Methyl-naphtalene, Limonene
La Roche	α-Pinene, Trimethylbenzene, Propylbenzene, Camphor, Tetramethylbenzene, Bornylacetate, Methylacetophenone Methyl-benzaldehyde, Transpinocarveol, Borneol, Pentamethylbenzene, Pipteritone, 4-Methylheptane, 2-Methyl-1-heptene, Butanoic acid-ethylester, Ditertbutylether, Trimethylbenzene, β-Pinene, 6-Methyl2-heptanone, Camphene, β-Terpinene, Dichlorobenzene, Tetramethylbenzene, Limonene, 2-Nonanone
Bridge	Dichlorobenzene, Tetramethylbenzene, α-Thujene, α-Phellandrene, o-Cymene, Methyl-benzaldehyde, Trimethylbenzene, Methyl-styrene, Propylbenzene, Carene, β-Pinene, Dichlorobenzene, Tetramethylbenzene, Limonene, Bornylacetate, Methyl-naphtalene
Lac des Femmes	α-pinene, Propylbenzene, Trimethylbenzene, Dichlorobenzene, Methyl-benzaldehyde, Limonene, Methyl-naphtalene, 2,3-Dimethyl-3-hexanol, Tricylene, Methylacetophenone, Methyl-butylbenzene, 2,3-Dimethyl-3-norbornene, Trimethylbenzene, Carene, Dichlorobenzene, Tetramethylbenzene, Pentamethylbenzene, Bornylacetate
Creek	Trimethylbenzene, Dichlorobenzene, Camphor, Cymene, Methyl-benzaldehyde, Ethenyldimethylbenzene, Borneol, Methyl-acetophenone, Myrtenol, Thymol, Dibutyl-ether, Trimethylbenzene, α-Pinene, β-Pinene, Dichlorobenzene, Tertbutylbenzene, Limonene, α-Phellrene, Tetramethyl-benzene, Pentamethylbenzene

[a]Structural identity of these compounds could not be fully established.

Table C1. Complete Data of VOC Concentrations[a]

Compound	Rocky	Valley	La Roche	Bridge	Lac des Femmes	Creek
Benzene	17.01 ± 2.543	n.q.	510.2 ± 118.3	422.2 ± 71.34	986.2 ± 199.0	744.1 ± 70.52
Toluene	295.8 ± 32.66	204.0 ± 60.64	280.5 ± 12.83	224.6 ± 27.37	707.1 ± 77.86	442.1 ± 30.18
Chlorobenzene	5.612 ± 1.915	6.875 ± 2.116	n.q.	n.q.	6.983 ± 1.622	5.436 ± 2.375
Ethylbenzene	24.02 ± 7.113	n.q.	32.18 ± 7.135	32.03 ± 6.561	112.5 ± 27.77	55.23 ± 6.188
m-/p-Xylene	158.6 ± 43.54	118.4 ± 32.37	164.8 ± 20.22	178.9 ± 27.63	527.9 ± 112.1	267.8 ± 25.16
Styrene	27.44 ± 4.817	21.82 ± 2.241	179.1 ± 38.77	189.7 ± 47.38	689.2 ± 28.37	216.1 ± 2.971
o-Xylene	5.521 ± 0.621	n.q.	57.55 ± 11.13	22.64 ± 5.028	81.93 ± 17.48	60.10 ± 17.81
Benzaldehyde	181.7 ± 32.23	200.9 ± 15.94	37.07 ± 7.258	42.54 ± 14.16	191.0 ± 64.08	349.0 ± 28.97
1,2,4-Trimethylbenzene	n.q.	n.q.	n.q.	54.56 ± 5.485	73.68 ± 21.64	28.69 ± 9.922
1,2-Dichlorobenzene	143.7 ± 39.31	307.3 ± 23.03	n.q.	n.q.	88.82 ± 19.96	77.85 ± 15.47
Acetophenone	2675 ± 686.2	1776 ± 31.04	168.3 ± 39.51	308.1 ± 66.62	448.5 ± 134.5	429.8 ± 43.01

[a] Concentrations are given in (ng/L); uncertainties represent 3s from duplicate measurements; n.q., not quantified.

Table C2. Quantified Compounds and Limits of Detection[a]

Compound	CAS Number	Retention Time (min)	LOD (ng/L)	Atmospheric Lifetime
Benzene	[71-43-2]	4.81	0.3	12 d[b] [*Atkinson*, 1994]
Toluene	[108-88-3]	7.77	3.2	2.4 d[b] [*Chan et al.*, 2006]
Chlorobenzene	[108-90-7]	9.38	0.7	19 d[b] [*Atkinson*, 1994]
Ethylbenzene	[100-41-4]	9.63	6.6	n.a.[c]
m-/p-Xylene	[108-38-3]/[106-42-3]	9.75	8.3	15/25 h[b] [*Kao*, 1994]
Styrene	[100-42-5]	10.1	0.6	6,[b] 23 h[d] [*Tuazon and Atkinson*, 1993]
o-Xylene	[95-47-6]	10.2	0.5	26 h [*Kao*, 1994]
Benzaldehyde	[100-52-7]	11.2	8.2	n.a.
1,2,4-Trimethylbenzene	[95-63-6]	11.6	25	n.a.
1,2-Dichlorobenzene	[95-50-1]	11.9	36	n.a.
Acetophenone	[98-86-2]	12.5	3.7	3.7 d[e] [*Atkinson and Aschmann*, 1989]

[a] LOD, limits of detection.
[b] Reaction with OH radical.
[c] Not available.
[d] Reaction with O_3.
[e] Atmospheric half-life.

far lesser extent in the current samples. Overall a high variability of concentrations in snow were observed giving rise to the speculation that the immediate environment and snow properties play an important role that needs to be investigated in detail. Furthermore, the presence of a liquid phase in the partially melted wet snowpack will also result in the solubilization of atmospheric constituents, and in an increase in their concentrations, stressing the importance of also comparing snow properties, when comparing concentrations in snow.

[37] Detected concentrations were in the lower ng/L range with some exceptions, notably acetophenone in samples from Mont-Saint-Hilaire with concentrations 1.5 μg/L. A few other species were found at concentrations >0.5 μg/L (e.g., benzene, toluene and styrene). Concentration profiles allowed for discrimination between individual profiles using principal component analysis with high similarities of locations close to each other. Standardized sampling and storage conditions have contributed to an improved comparability of data and an overall reduction in the analytical error.

[38] Ultimately answers to the following questions need to be provided after a detailed investigation of snowpack chemistry and snow physics: reasons why certain concentrations are observed for particular species and their variation with time and snow properties. Their connection with atmospheric concentrations need to be assessed to measure the impact of deposition and volatilization processes including modifications by photochemistry and biodegradation.

Appendix A: Liquid Phase and Headspace Extraction

[39] Appendix Table A1 lists VOC species identified in the snowpack that were extracted from the liquid phase and the headspace. In order to obtain a full picture both phases need to be extracted as some compounds could only be found either in the liquid phase or in the headspace. The majority, however, was found in both matrices confirming the validity of the analytical approach.

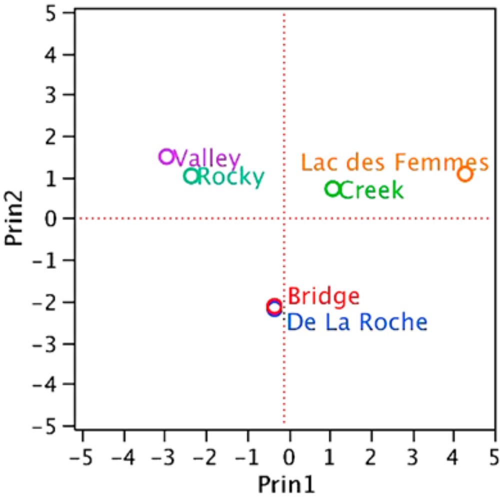

Figure D1. Principal component analysis of concentration data from all sampling locations.

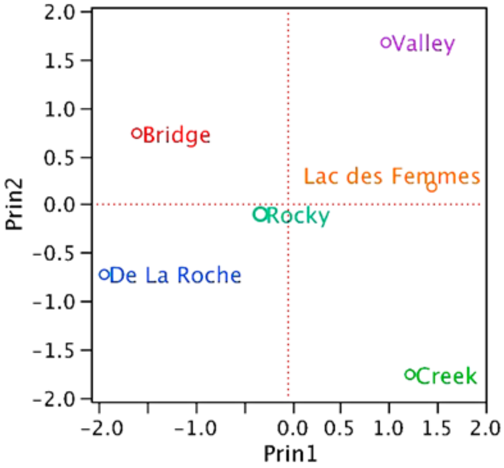

Figure D2. Principal component analysis of location-specific data describing the number of compounds of aliphatic, oxygenated, halogenated, or aromatic character as listed in Figure 3.

Appendix B: Compounds With Unidentified Isomers

[40] Basic structures of the following compounds were successfully identified and are listed in Table B1. However, several substitution patterns are possible and the correct isomer could not be identified. Identification of biogenic compounds (e.g., pinene, limonene) is especially difficult with unit mass resolution of the employed system, because of the high number of isomers and often weak signals. The presented data are highly useful, though, because it adds to the picture of the detected VOC spectrum of biogenic and anthropogenic compounds.

Appendix C: Full Set of Quantitative Data

[41] Table C1 shows all determined quantitative data in the liquid phase for 11 quantified compounds at 6 sampling locations (two from the Mont-Saint-Hilaire area and four from the Tremblant area). Table C2 illustrates methodology-related details of the quantified compounds, including retention times and limits of detection (LOD).

Appendix D: Principal Component Analysis Score Plots

[42] Principal component analysis (PCA) score/scor plots of concentration data are given in Figure D1, and plots describing the number of compounds of aliphatic, oxygenated, halogenated or aromatic character at each sampling location are given in Figure D2.

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References

Albert, M., and E. Shultz (2002), Snow and firn properties and air-snow transport processes at Summit, Greenland, *Atmos. Environ.*, *36*, 2789–2797.

Amato, P., M. Parazols, M. Sancelme, P. Laj, G. Mailhot, and A. Delort (2007), Microorganisms isolated from the water phase of tropospheric clouds at the Puy de Dome: Major groups and growth abilities at low temperatures, *FEMS Microbiol. Ecol.*, *59*(2), 242–254.

Anderson, P., and W. Neff (2008), Boundary layer physics over snow and ice, *Atmos. Chem. Phys.*, *8*, 3563–3582.

Atkinson, R. (1990), Gas-phase tropospheric chemistry of organic compounds: a review, *Atmos. Environ., Part A*, *24A*, 1–41.

Atkinson, R. (1994), Gas-phase tropospheric chemistry of organic-compounds, *J. Phys. Chem. Ref. Data Monogr.*, *2*, 216 pp.

Atkinson, R. (2003), Kinetics of the gas-phase reactions of OH radicals with alkanes and cycloalkanes, *Atmos. Chem. Phys.*, *3*, 2233–2307.

Atkinson, R., and S. Aschmann (1989), Rate constants for the gas-phase reactions of the OH radical with a series of aromatic-hydrocarbons at 296 +/− 2-k, *Int. J. Chem. Kinet.*, *21*(5), 355–365.

Beine, H., A. Colussi, A. Amoroso, G. Esposito, M. Montagnoli, and M. Hoffmann (2008), HONO emissions from snow surfaces, *Environ. Res. Lett.*, *3*(4), 045005, doi:10.1088/1748-9326/3/4/045005.

Beranek, J., and A. Kubatova (2008), Evaluation of solid-phase microextraction methods for determination of trace concentration aldehydes in aqueous solution, *J. Chromatogr. A*, *1209*(1–2), 44–54.

Bleasel, M., S. Aldous, and N. Davies (2003), Distinction between melanins derived from different precursors using pyrolysis/gas chromatography/mass spectrometry and the NIST mass spectral search algorithm, *J. Anal. Appl. Pyrol.*, *70*(2), 649–663.

Bocchini, P., C. Andalo, D. Bonfiglioli, and G. Galletti (1999), Solid-phase microextraction gas chromatography/mass spectrometric analysis of volatile organic compounds in water, *Rapid Commun. Mass Spectrom.*, *13*(21), 2133–2139.

Bottenheim, J., H. Boudries, P. Brickell, and E. Atlas (2002), Alkenes in the arctic boundary layer at Alert, Nunavut, Canada, *Atmos. Environ.*, *36*, 2585–2594.

Boudries, H., J. Bottenheim, C. Guimbaud, A. Grannas, P. Shepson, S. Houdier, S. Perrier, and F. Domine (2002), Distribution and trends of oxygenated hydrocarbons in the high arctic derived from measurements in the atmospheric boundary layer and interstitial snow air during the Alert2000 field campaign, *Atmos. Environ.*, *36*, 2573–2583.

Caralp, F., V. Foucher, R. Lesclaux, T. Wallington, and M. Hurley (1999), Atmospheric chemistry of benzaldehyde: UV absorption spectrum and reaction kinetics and mechanisms of the C6H5C (O)O-2 radical, *Phys. Chem. Chem. Phys.*, *1*(15), 3509–3517.

Chan, L., K. Chu, S. Zou, C. Chan, X. Wang, B. Barletta, D. Blake, H. Guo, and W. Tsai (2006), Characteristics of nonmethane hydrocarbons (NMHCS) in industrial, industrial-urban, and industrial-suburban atmospheres of the Pearl River Delta (PRD) region of South China, *J. Geophys. Res.*, *111*, D11304, doi:10.1029/2005JD006481.

Chebbi, A., and P. Carlier (1996), Carboxylic acids in the troposphere, occurrence, sources, and sinks: A review, *Atmos. Environ.*, *30*, 4233–4249.

Chu, L., and C. Anastasio (2005), Formation of hydroxyl radical from the photolysis of frozen hydrogen peroxide, *J. Phys. Chem. A*, *109*(28), 6264–6271.

Clement, R., P. Yang, and C. Koester (2001), Environmental analysis, *Anal. Chem.*, *73*(12), 2761–2790.

Cote, V., G. Kos, R. Mortazavi, and P. Ariya (2008), Microbial and "de novo" transformation of dicarboxylic acids by three airborne fungi, *Sci. Total Environ.*, *390*, 530–537.

Dassau, T., et al. (2002), Investigation of the role of the snowpack on atmospheric formaldehyde chemistry at Summit, Greenland, *J. Geophys. Res.*, *107*(D19), 4394, doi:10.1029/2002JD002182.

Derwent, R., M. Jenkin, and S. Saunders (1996), Photochemical ozone creation potentials for a large number of reactive hydrocarbons under European conditions, *Atmos. Environ.*, *30*, 181–199.

Desideri, P., L. Lepri, R. Udisti, L. Checchini, M. Del Bubba, R. Cini, and A. Stortini (1998), Analysis of organic compounds in antarctic snow and their origin, *Int. J. Environ. Anal. Chem.*, *71*(3–4), 331–351.

Dibb, J., M. Arsenault, M. Peterson, and R. Honrath (2002), Fast nitrogen oxide photochemistry in Summit, Greenland snow, *Atmos. Environ.*, *36*, 2501–2511.

Domine, F., and P. Shepson (2002), Air-snow interactions and atmospheric chemistry, *Science*, *297*(5586), 1506–1510.

Domine, F., A. Taillandier, and W. Simpson (2007), A parameterization of the specific surface area of seasonal snow for field use and for models of snowpack evolution, *J. Geophys. Res.*, *112*, F02031, doi:10.1029/2006JF000512.

Gelencser, A., K. Siszler, and J. Hlavay (1997), Toluene-benzene concentration ratio as a tool for characterizing the distance from vehicular emission sources, *Environ. Sci. Technol.*, *31*(10), 2869–2872.

Gilman, J., et al. (2009), Measurements of volatile organic compounds during the 2006 TexAQS/GOMACCS campaign: Industrial influences, regional characteristics, and diurnal dependencies of the OH reactivity, *J. Geophys. Res.*, *114*, D00F06, doi:10.1029/2008JD011525.

Grannas, A., et al. (2002), A study of photochemical and physical processes affecting carbonyl compounds in the arctic atmospheric boundary layer, *Atmos. Environ.*, *36*, 2733–2742.

Grannas, A., A. Bausch, and K. Mahanna (2007), Enhanced aqueous photochemical reaction rates after freezing, *J. Phys. Chem. A*, *111*(43), 11,043–11,049.

Guenther, A., et al. (1995), A global model of natural volatile organic compound emissions, *J. Geophys. Res.*, *100*(D5), 8873–8892, doi:10.1029/94JD02950.

Guimbaud, C., et al. (2002), Snowpack processing of acetaldehyde and acetone in the arctic atmospheric boundary layer, *Atmos. Environ.*, *36*, 2743–2752.

Hashimoto, S., T. Tanaka, N. Yamashita, and T. Maeda (2001), An automated purge and trap gas chromatography-mass spectrometry system for the sensitive shipboard analysis of volatile organic compounds in seawater, *J. Sep. Sci.*, *24*(2), 97–103.

Herbert, B., C. Halsall, L. Fitzpatrick, S. Villa, K. Jones, and G. Thomas (2004), Use and validation of novel snow samplers for hydrophobic, semivolatile organic compounds (SVOCS), *Chemosphere*, *56*(3), 227–235.

Houdier, S., et al. (2002), Acetaldehyde and acetone in the arctic snowpack during the Alert2000 campaign: Snowpack composition, incorporation processes and atmospheric impact, *Atmos. Environ.*, *36*, 2609–2618.

Hutterli, M., R. Rothlisberger, and R. Bales (1999), Atmosphere-to-snow-to-firn transfer studies of HCHO at Summit, Greenland, *Geophys. Res. Lett.*, *26*(12), 1691–1694.

Hutterli, M., R. Bales, J. McConnell, and R. Stewart (2002), HCHO in antarctic snow: Preservation in ice cores and air-snow exchange, *Geophys. Res. Lett.*, *29*(8), 1235, doi:10.1029/2001GL014256.

Iovino, P., R. Polverino, S. Salvestrini, and S. Capasso (2009), Temporal and spatial distribution of BTEX pollutants in the atmosphere of metropolitan areas and neighbouring towns, *Environ. Monit. Assess.*, *150*(1–4), 437–444.

Kao, A. (1994), Formation and removal reactions of hazardous air-pollutants, *J. Air Waste Manage.*, *44*(5), 683–696.

Karl, T., E. Apel, A. Hodzic, D. Riemer, D. Blake, and C. Wiedinmyer (2009), Emissions of volatile organic compounds inferred from airborne flux measurements over a megacity, *Atmos. Chem. Phys.*, *9*, 271–285.

Kolb, A., and W. Puttmann (2006), Methyl tert-butyl ether (MTBE) in snow samples in Germany, *Atmos. Environ.*, *40*, 76–86.

Kos, G., and P. Ariya (2006), Determination of a wide range of volatile and semivolatile organic compounds in snow by use of solid-phase microextraction (SPME), *Anal. Bioanal. Chem.*, *385*(1), 57–66.

Lara-Gonzalo, A., J. Sanchez-Uria, E. Segovia-Garcia, and A. Sanz-Medel (2008), Critical comparison of automated purge and trap and solid-phase microextraction for routine determination of volatile organic compounds in drinking waters by GC, *Talanta*, *74*(5), 1455–1462.

Lord, H., and J. Pawliszyn (2000), Evolution of solid-phase microextraction technology, *J. Chromatogr. A*, *885*(1–2), 153–193.

Mackay, D., and F. Wania (1995), Transport of contaminants to the arctic—Partitioning, processes and models, *Sci. Total Environ.*, *161*, 25–38.

Matykiewiczova, N., J. Klanova, and P. Klan (2007), Photochemical degradation of PCBs in snow, *Environ. Sci. Technol.*, *41*(24), 8308–8314.

McKendry, I. (1993), Ground-level ozone in Montreal, Canada, *Atmos. Environ. Part B*, *27*, 93–103.

Meyer, T., Y. Lei, I. Muradi, and F. Wania (2009), Organic contaminant release from melting snow. 2. Influence of snow pack and melt characteristics, *Environ. Sci. Technol.*, *43*(3), 663–668.

Miller, L., X. Xu, and I. Luginaah (2009), Spatial variability of volatile organic compound concentrations in Sarnia, Ontario, Canada, *J. Toxicol. Environ. Health A*, *72*(9), 610–624.

Nepotchatykh, O., and P. Ariya (2002), Degradation of dicarboxylic acids (C2–C9) upon liquid-phase reactions with O_3 and its atmospheric implications, *Environ. Sci. Technol.*, *36*(15), 3265–3269.

Nilsson, T., R. Ferrari, and S. Facchetti (1997), Inter-laboratory studies for the validation of solid-phase microextraction for the quantitative analysis of volatile organic compounds in aqueous samples, *Anal. Chim. Acta*, *356*(2–3), 113–123.

Pawliszyn, J. (1997), *Solid Phase Microextraction: Theory and Practice*, 247 pp., John Wiley, Chichester, U. K.

Pennisi, E. (2003), Microbiology—Neither cold nor snow stops tundra fungi, *Science*, *301*(5638), 1307.

Pomeroy, J., and H. Jones (1996), Wind-blown snow: Sublimation, transport and changes to polar snow, in *Chemical Exchange Between the Atmosphere and Polar Snow*, edited by E. Wolff and R. Bales, pp. 453–491, Springer, Berlin.

Preisendorfer, R. W., and C. D. Mobley (1988), *Principal Component Analysis in Meteorology and Oceanography*, 425 pp., Elsevier, New York.

Reid, N., et al. (1996), The Southern Ontario Oxidant Study (SONTOS): Overview and case studies for 1992, *Atmos. Environ.*, *30*, 2125–2132.

Satsumabayashi, H., H. Nishizawa, Y. Yokouchi, and H. Ueda (2001), Pinonaldehyde and some other organics in rain and snow in central Japan, *Chemosphere*, *45*(6–7), 887–891.

Scheppers Wercinski, S. (1999), *Solid Phase Microextraction (A Practical Guide)*, 257 pp., Marcel Dekker, New York.

Simpson, W., L. Alvarez-Aviles, T. Douglas, M. Sturm, and F. Domine (2005), Halogens in the coastal snow pack near Barrow, Alaska: Evidence for active bromine air-snow chemistry during springtime, *Geophys. Res. Lett.*, *32*, L04811, doi:10.1029/2004GL021748.

Sumner, A., and P. Shepson (1999), Snowpack production of formaldehyde and its effect on the arctic troposphere, *Nature*, *398*(6724), 230–233.

Sumner, A., et al. (2002), Atmospheric chemistry of formaldehyde in the arctic troposphere at polar sunrise, and the influence of the snowpack, *Atmos. Environ.*, *36*, 2553–2562.

Swanson, A., B. Lefer, V. Stroud, and E. Atlas (2005), Trace gas emissions through a winter snowpack in the subalpine ecosystem at Niwot Ridge, Colorado, *Geophys. Res. Lett.*, *32*, L03805, doi:10.1029/2004GL021809.

Thompson, A. (1992), The oxidizing capacity of the Earth's atmosphere—Probable past and future changes, *Science*, *256*(5060), 1157–1165.

Tuazon, E., and R. Atkinson (1993), Tropospheric transformation products of a series of hydrofluorocarbons and hydrochlorofluorocarbons, *J. Atmos. Chem.*, *17*(2), 179–199.

Valsecchi, S., C. Smiraglia, G. Tartari, and S. Polesello (1999), Chemical composition of monsoon deposition in the Everest region, *Sci. Total Environ.*, *226*, 187–199.

Viskari, E., R. Rekila, S. Roy, O. Lehto, J. Ruuskanen, and L. Karenlampi (1997), Airborne pollutants along a roadside: Assessment using snow analyses and moss bags, *Environ. Pollut.*, *97*(1–2), 153–160.

Wang, Y., J. Chen, X. Li, B. Wang, X. Cai, and L. Huang (2009), Predicting rate constants of hydroxyl radical reactions with organic pollutants: Algorithm, validation, applicability domain, and mechanistic interpretation, *Atmos. Environ.*, *43*, 1131–1135.

Wania, F., J. Hoff, C. Jia, and D. Mackay (1998), The effects of snow and ice on the environmental behaviour of hydrophobic organic chemicals, *Environ. Pollut.*, *102*(1), 25–41.

Yang, J., et al. (2002), Impacts of snowpack emissions on deduced levels of OH and peroxy radicals at Summit, Greenland, *Atmos. Environ.*, *36*, 2523–2534.

Zhang, W., P. Wu, and C. Li (2006), Study of automated mass spectral deconvolution and identification system (AMDIS) in pesticide residue analysis, *Rapid Commun. Mass Spectrom.*, *20*(10), 1563–1568.

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