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Rodrigo Benjamin Rangel-Alvarado and this work.

Key Points:

- The nanosized fraction of particles dominates in snow
- · Nanosized particles in fresh snow show efficient ice nucleating properties
- The nanosized fraction of particles contains both inorganic and organic matter

Supporting Information: • Figures S1 and S2

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Snow-borne nanosized particles: Abundance, distribution, composition, and significance in ice nucleation processes

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Abstract Physicochemical processes of nucleation constitute a major uncertainty in understanding aerosol-cloud interactions. To improve the knowledge of the ice nucleation process, we characterized physical, chemical, and biological properties of fresh snow using a suite of state-of-the-art techniques based on mass spectrometry, electron microscopy, chromatography, and optical particle sizing. Samples were collected at two North American Arctic sites, as part of international campaigns (2006 and 2009), and in the city of Montreal, Canada, over the last decade. Particle size distribution analyses, in the range of 3 nm to 10 µm, showed that nanosized particles are the most numerous (38–71%) in fresh snow, with a significant portion (11 to 19%) less than 100 nm in size. Particles with diameters less than 200 nm consistently exhibited relatively high ice-nucleating properties (on average ranged from -19.6 ± 2.4 to -8.1 ± 2.6 °C). Chemical analysis of the nanosized fraction suggests that they contain bioorganic materials, such as amino acids, as well as inorganic compounds with similar characteristics to mineral dust. The implication of nanoparticle ubiquity and abundance in diverse snow ecosystems are discussed in the context of their importance in understanding atmospheric nucleation processes.

1. Introduction

Aerosols are airborne, condensed matter particles present as liquids, solids, or multiphased, and are produced through anthropogenic and natural activities (Figure 1) [Andreae and Rosenfeld, 2008; Levin and Cotton, 2008; Szyrmer and Zawadzki, 1997]. Little is known about the interaction of aerosol particles with and within clouds and is highlighted as a major research uncertainty by the International Panel on Climate Change (IPCC) [Solomon et al., 2007; Stocker et al., 2013]. The health implications of aerosols are also important due to growing evidence of the adverse health effects that nanoparticle air pollution causes [Slezakova et al., 2013]. As a notable example, the World Health Organization (WHO) named airborne particulate matter and, specifically, nanoparticles, a major cause of premature infant mortality [WHO, 2013, 2014]. Nanoparticles (1 to 100 nm [Auffan et al., 2009]) are emitted into the atmosphere either directly or through gas-to-particle formation [Buseck and Adachi, 2008]. Yet there is very limited research data on nanosized compounds that are in diverse environmental matrices and on the types of physical, chemical, and biological processes, in which atmospheric nanoparticles are involved.

Snow is an important form of precipitation present near the ground surface and can provide a snapshot of atmospheric physicochemical processes [Dibb, 1996]. It is an omnipresent feature in polar and subpolar regions, as well as mountainous regions around the globe. The formation of snow in the atmosphere has been shown to drive local, regional, and global climatic effects [Seinfeld and Pandis, 2012]. It also plays a central role in hydrological cycles, radiation, and climate processes, such as precipitation [Morris et al., 2004; Simmel et al., 2007], which in turn causes removal of trace substances from the atmosphere, including select gaseous and particulate air pollutants [Flossmann et al., 1985; Flossmann and Pruppacher, 1988].

The formation of snow starts with ice nucleation. When cooled, liquid water easily enters a metastable state, called supercooled water, remaining liquid well below its melting point, to temperatures as low as approximately -38°C, or existing as a vapor at very high supersaturations [Koop et al., 2000]. In the atmosphere, such conditions are infrequent, with the exception of cirrus and other high tropospheric clouds [Finlayson-Pitts and Pitts, 1999]. More often, heterogeneous ice nuclei (IN) catalytically assist in the formation of ice or snow in the atmosphere at warmer temperatures. This heterogeneous ice nucleation process can occur by several



Figure 1. A simplified schematic of nanoparticle cycling in the atmosphere and snow-air interfaces. For simplicity, the splitting effects for clusters and the splintering effect of cloud microphysics are not shown.

mechanisms: when water vapor condenses directly onto a particle surface to form ice (deposition mode), when water vapor condenses directly onto the particle surface to form a water droplet which eventually freezes (freezing mode), when a water droplet comes into contact with an insoluble particle and freezes (contact mode), and when an insoluble particle is already immersed in a water droplet and freezes (immersion mode) [*Seinfeld and Pandis*, 2012]. It has been reported that the same aerosol particles will present different nucleation temperatures when acting in different nucleation modes. Moreover, factors, including solubility, surface tension, chemical impurities, volatility, morphology, contact angle, deliquescence, wettability, and chemical processes of aerosols are pivotal in understanding ice nucleation [*Ariya et al.*, 2009; *Hoose and Möhler*, 2012; *Keller and Li*, 2000].

The predominant global source of IN is currently considered to be mineral dust [Archuleta et al., 2005; Szyrmer and Zawadzki, 1997]. Mineral dust exhibits size-dependent ice nucleation activity by deposition mode, which is less efficient at smaller particle sizes [Welti et al., 2009]. Although this is specific to the deposition mode, we can expect a similar trend for other modes [Hoose and Möhler, 2012]. Median freezing temperature induced by dust particles (200-800 nm in diameter) has been estimated at -33 to -35°C [Lüönd et al., 2010]. In addition to mineral dust, carbonaceous particles have also been recognized as condensation IN [Rogers et al., 2001], as have plant and soil-borne organic particles [Schnell and Vali, 1976]. Bioorganic particles, including bacteria, pollen, fungi, and spores, that are known to possess ice-nucleating abilities range in size from 500 nm to 80 µm although, recently, some fungal fragments smaller than 10 nm were found to be active in ice nucleation [Fröhlich-Nowoisky et al., 2015]. Among bioorganic ice nucleators, bacteria induce ice nucleation at the highest freezing temperatures, which can be as high as $-2^{\circ}C$ (genus Pseudomonas) [Georgakopoulos et al., 2009; Mortazavi et al., 2008]. Yet due to the presumed scarcity of bioorganic particles in the atmosphere, there has not been sufficient evidence of their importance, for instance, in cirrus cloud formation [Möhler et al., 2007]. Nevertheless, it has even been suggested that bacteria in the form of aerosols could act as condensation IN within the Arctic region [Bigg and Leck, 2001]. It is worth mentioning that bacteria are typically microscale, and, correspondingly, most ice nucleation studies involving bacterial nucleators have been limited to larger particles of that size. Although smaller bacterial particles have been found in Arctic zones, their activity, as ice nucleators, has not yet been demonstrated [*Leck and Bigg*, 2005]. Recent laboratory experiments point to size-dependent phase transitions of aerosol nanoparticles in mixed systems. Phase transitions, such as solubility and hygroscopic growth, can play an important role in the ice nucleation process, especially when considering the immersion mode [*Biskos et al.*, 2006; *Cheng et al.*, 2015]. As size plays a role in controlling these properties in nanoparticles, it is reasonable to think that size will affect nucleation by nanoparticles, along other properties such as contact angle. Currently, there is neither an atmospheric global model to explicitly include nanoparticles as relevant ice nucleating particles, nor does the IPCC consider them in major comparative modeling studies. However, of note is that nanoparticles are considered in human health impacts by both the IPCC and the WHO [*Slezakova et al.*, 2013]. On another front, experimental challenges have so far precluded researchers from evaluating various hypotheses regarding the role of nanosized materials in snow formation [*Welti et al.*, 2009]. Our group has recently developed novel methodologies overcoming some key challenges of the physicochemical and morphological characterization and quantification of snow/ice materials [*Ariya et al.*, 2009; *Kos and Ariya*, 2010; *Mortazavi et al.*, 2015].

In this study, we set out to determine whether nanosized particles (operationally defined here as \leq 200 nm in diameter) in air will affect the physical and chemical processes involved in the formation of snow and its transformations. We extensively characterized the physical, chemical, and biological properties of snow from polar sites in Canada and the U.S. collected during the international experiments in Alert, Canada, and Barrow, Alaska, and yearly over the last decade (2004–2014) at subpolar continental urban sites in Montreal and its surrounding suburbs. We provide evidence for the significant abundance of nanosized particles in snow, the importance of nanosized ice nucleators, and the potential role of biomaterials in nucleation processes.

2. Experimental and Methods

2.1. Sampling

Snow sampling sites, collection procedures, sampling, and preservation protocols are described in detail elsewhere [*Kos and Ariya*, 2006, 2010]. Snow samples were taken in 2006 and 2009 in Alert, Nunavut, Canada (82.5°N; 62.3°W; May–June 2006), and in Barrow, Alaska, USA (71.3°N; 156.8°W; March 2009), respectively, and from 2004 to 2014 in the city of Montreal and in its suburbs in Quebec, Canada. Briefly, samples were collected under sterilized conditions, using sterile equipment and clean suits, during snow precipitation events or within 1 h of snowfall from the upper 3 cm of the snowpack. All samples were kept frozen immediately after collection at $-10 \pm 2°$ C; many samples were analyzed within 24 h following sampling, and others were frozen at $-35 \pm 2°$ C and were only thawed, within their gas-tight recipient container, immediately prior to analysis under clean conditions. To ensure high-quality analysis, comparison of the blanks and dedicated frozen control samples from Alert and Barrow were performed on a monthly basis. In addition to fresh surface snow, chemical and physical analysis of aged samples was performed. As the thawing-refreezing cycle required for this analysis would disrupt particle size distribution in the samples [*Kim et al.*, 2010], only fresh samples from the series were used for all particle analyses in this study.

2.1.1. Barrow, AK, USA

Snow sampling was performed during the Ocean-Atmosphere-Sea Ice-Snowpack (OASIS) 2009 campaign in Barrow, AK, USA. Samples for microorganism analysis and volatile organic compounds analysis were taken between 4 and 20 March. A field dedicated to snow studies in the clean air sector at 71.31°N, 156.6°W, 400 m southeast of the Barrow Arctic Research Center was used for all sampling events. To limit local pollution, vehicle access to the site was restricted, and all equipment was transported on foot with a hand-pulled sled. Sampling equipment included the following: sterile single-use containers, tools and glassware, precleaned prior to departure by soaking in nutrient-free detergent, rinsing with 3% hydrochloric acid, and followed by three ultrapure water rinses. For each event, sterile amber glass sample containers with a volume of 950 mL (Daniels Scientific) were filled with snow using a fresh, sterile, high-density polyethylene spoon (Fisher Scientific). As the snow samples originated from the top 3 cm of the snow surface, they are, therefore, heavily influenced by wind conditions and photochemistry. During snow sampling, snow temperature was measured using a long-stemmed thermometer (Fisher Scientific), and meteorological conditions were recorded (air temperature, wind direction, and cloud cover). Samples were stored in a walk-in freezer set to -20°C until shipment in commercial coolers (Coleman). Once shipped out by airfreight (transit time 41 h), the maximum temperature measured upon arrival to the laboratory at McGill University in Montreal was -10° C, where storage continued in a freezer at -35° C until analysis was initiated, by melting.

2.1.2. Alert, NU, Canada

Samples presented here were collected in Alert, NU, on Ellesmere Island from May to June 2006. The study location was near the Alert meteorological station, chosen to avoid local contamination from a nearby military base. Sampling was performed on a flat plateau, upwind approximately 6.5 km away from the base. The site was accessed by truck parked downwind, with the final leg of approximately 500 m reached on foot in accordance with on-site regulations. All equipment was transported with a hand-pulled sled. For select sites in Alert, depth-profile samples were collected from a snow pit dug with a precleaned and sterilized shovel. Depth profiling was completed over the course of not more than 3 h.

2.1.3. Montreal, QC, Canada and Its Suburbs

Sterile snow sampling equipment was employed, using procedures as described above, and samples were kept frozen upon collection. Sampling was undertaken on a biweekly basis, during the winter months of December to April over a decade (2004–2014). Fresh snow samples were regularly analyzed within the same day. In addition to fresh surface snow, the depth profiles and analysis of aged samples were performed for physical, biological, and chemical characterization.

2.2. Aerosol Size Distributions

We used a NanoScan[™] Scanning Mobility Particle Sizer (SMPS) model 3910 (TSI Inc.) to measure particle size distributions from aerosolized melted snow samples in terms of electrical mobility diameter and an Optical Particle Sizer (OPS) model 3330 (TSI Inc.) to obtain particle size distributions as aerodynamic diameter. Melted snow was aerosolized using a C-Flow 700d PFA Nebulizer (Savillex Corporation) for a total aerosol flow rate of 0.9 SL/min (SL stands for liters at standard temperature and pressure, 273.15 K, 100 kPa). The aerosol stream was dried using an in-house-built double diffusion dryer and diluted to 1 L/min with particle-free air to match the combined sampling flow rates of the NanoScan[™] SMPS and the OPS. These instruments are factory-calibrated on a yearly basis with Polystyrene Latex spheres and for all the internal and external flow rates.

It is important to note that electrical mobility and aerodynamic diameters, measured by the two above mentioned aerosol instruments, are different metrics based on different physicochemical particle properties. Two different particle size regions are measured using the two techniques. The NanoScanTM SMPS system effectively measures in the range 10 nm to ~350 nm, whereas the OPS system measures larger particle sizes—confidently within the size range of ~350 nm to 10 μ m. The aerodynamic diameter measured by the OPS is similar to the electrical mobility diameter, under the assumption that particles are spherical with densities of 1.0 g/cm³ [*Hinds*, 1999]. We only make this assumption when discussing the SMPS and OPS aerosol particle size measurements, and not for any other results. When operated simultaneously, the two aerosol instruments perform particle size measurements from 10 nm to 10 μ m.

The approach of melted snow aerosolization and subsequent sizing of the resulting airborne particles has a number of advantages over other techniques used to characterize particulate matter in snow. Nebulization with compressed air generates aqueous droplets containing particulate matter originally present in snow. When these droplets are dried by a diffusion dryer, only the core particles remain [*Tuch et al.*, 2009]. Desalination of the snow samples by dialysis prior to aerosolization minimizes salt particle formation and crystallization on aerosol particles in the drying process. Note that potential modifications of the original size distribution of soluble salts may have occurred as snow was melted. Aerosol size distributions were the average of five runs for each sample.

2.3. Hydrodynamic Diameter Distribution

The hydrodynamic size distributions of unprocessed snow were measured by Nanoparticle Tracking Analysis (NTA) using a Malvern NanoSight NS500 with a laser wavelength of 532 nm and an Electron Multiplying Charge Coupled Device camera. The capture settings were set to a 29.0099 ms shutter speed, 309 camera gain, a 17.8 fps frame rate, and a temperature of 26.6°C. The hydrodynamic diameter, also called Stokes diameter, is by definition the diameter of a hypothetical rigid sphere that diffuses in a liquid at the same speed as the sample particle [*Hinds*, 1999]. The diameter includes the electric double layer around the particle. This technique is based on the visualization of particles in a liquid medium and tracking their Brownian motion to determine the size of individual particles allowing analysis directly of the original unprocessed, as well as processed (filtration and dialysis) melted snow samples. Hydrodynamic diameter distributions were obtained by averaging 10 runs per sample. Weighed standard deviations were plotted.

2.4. Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry

Samples were filtered with a Millex syringe filter with a 0.22 µm pore size hydrophilic PVDF membrane, concentrated using a Thermo ModulyoD-115 freeze dryer for 1 d and desalted with a ZipTip C18 reversed phase column in order to lower matrix cluster formation that can generate background interference in the analysis of peptides [*Caprioli et al.*, 1997]. A 50:50 acetonitrile to water solution and 0.1% trifluoroacetic acid (TFA) aqueous solution were used to wet and equilibrate the ZipTip column. Passing a sample through the column binds the peptides in the sample onto the ZipTip column. The ZipTip was washed with a 0.1% aqueous TFA solution to remove excess salts. Elution of peptides into the matrix was performed with the same 50:50 acetonitrile to water solution. Concentrated and desalted samples were deposited on a prespotted AnchorChip PAC II 384/96 α -cyano-4-hydroxycinnamic acid by spotting two to three 0.5 µL drops of the solution. Matrix-Assisted Laser Desorption/lonization (MALDI) spectra were collected using a Bruker AUTOFLEX III time-of-flight mass spectrometer (TOF-MS/MS) operating in linear positive ion mode. The MALDI/LDI ionization source was a 355 nm frequency tripled Nd:YAG SmartBeam[™] laser (Bruker). The resolution of the instrument in linear mode is \geq 5, 000 with a mass accuracy of \leq 20 ppm for protein samples.

2.5. Electrospray Ionization Mass Spectrometry

Snow samples were analyzed without further processing other than melting at room temperature. Mass spectra were collected using an Agilent Technologies 6130 Series Quadrupole LC/MS System with an electrospray ionization (ESI) source. The ESI-MS instrument has an isotopic resolution at 10,000 μ s and a mass accuracy within the calibrated mass range of $\pm 0.13 \,\mu$ in scan mode. The mass range used was from 1000 to 2000 amu, positive scan, N₂ as drying gas at 350°C flowing at 11 L/min. The fragmentation voltage was set to 70 V, capillary voltage to 3000 V, with the flow rate of melted snow at 150 μ L/min, and a total run time of 5 min.

2.6. Total Organic Carbon

Unprocessed samples of freshly melted snow were analyzed with an Aurora 1030°W total organic carbon (TOC) analyzer using a persulfate oxidation method. A 5 ml aliquot of water was used from each sample. To detect total inorganic carbon, 0.5 ml of 5% phosphoric acid was added to the subsample and combusted at 700°C. Afterward, to detect organic carbon, 2 ml of 10% sodium persulfate was added and combusted at 980°C. The resulting CO₂ gas from these two reactions was detected separately by a nondispersive infrared sensor. Each sample was processed in duplicate or triplicate. External standards (0 and 5 ppm) were included in each batch of samples to ensure consistency of results between analyses.

2.7. High-Resolution Transmission Electron Microscopy With Energy Dispersive X-Ray Spectroscopy

Snow samples were stored in 50 mL sterile plastic conical tubes at -20° C until processed. The samples were melted and filtered, as mentioned above, and preconcentrated and freeze dried using a Thermo ModulyoD-115 freeze dryer for 1 day prior to high-resolution transmission electron microscopy (TEM). Aliquots of 5 μ L concentrated samples were deposited on glow-discharged carbon film coated copper electron microscopy grids. The droplets were kept on the grids for 1 min, followed by blotting off the excess liquid with an edge of a piece of filter paper. The samples were stained with 2% uranyl acetate (SPI-Chem) and air dried before being imaged using a FEI Tecnai 12 Biotwin TEM microscope (FEI Electron Optics) equipped with a tungsten filament at 120 kV. Alternatively, uranyl formate (Electron Microscopy Sciences) was used to stain replicate samples. Images were acquired using an Advanced Microscopy Techniques, Corp. (AMT) XR80C CCD Camera System.

2.8. Drop-Freezing Assays

Microphysics experiments were performed on snow from each of the three sampled sites. All snow samples were left to melt at room temperature $(23 \pm 0.5^{\circ}C)$ in their gas-tight containers. Drop-freezing assays were performed, as described by *Vali* [1971], with several samples from each site, using both filtered and unfiltered samples, as well as centrifuged. Samples were centrifuged using a Hermle Z200M/H bench-top centrifuge at 4000 rpm for 15 min (about 1000 g). For each sample, 240 droplets were placed on a cooling plate (in-house-made copper plate) and the temperature of the plate (starting at ~0°C) cooled at a rate of 1°C/min. The temperature, at which each droplet froze, was recorded [*Mortazavi et al.*, 2008]. All experiments were run with filtered versions of the same samples. Filtration was performed as described above. The copper

plate was evenly coated with Vaseline petroleum jelly. The samples were loaded as 10 µL droplets. Ultrapure water droplets from a Simplicity 185 Ultrapure Water System (Millipore Corporation) and tap water were used as blank controls.

2.8.1. Ice Nucleation Data Analysis

For comparison of drop-freezing assay populations, we performed the analysis using the MATLAB function t test 2, which tests the null hypothesis that data in two different populations are independent random samples from normal distributions with equal means and equal but unknown variances at a 95% confidence level.

2.9. Ion Chromatography

For ion analysis of snow samples, a Dionex ICS-500 Ion Chromatography system was used along with a separation column Dionex AS14 with $3.5 \text{ mM} \text{ Na}_2\text{CO}_3/1.0 \text{ mM} \text{ Na}\text{HCO}_3$, as mobile phase for anions, and a separation column Dionex CS12 with 20 nM methanesulfonic acid, as mobile phase for cations. Ions analyzed included the following: sulfate, phosphate, nitrate, chloride, sodium, potassium, magnesium, calcium, and a ammonium. The mobile phase flow rate for analysis of anions was 0.30 mL/min and for analysis of cations 0.25 mL/min. Detection was performed by suppressed conductivity using an Anion Self-Regenerating ASRS 300 2 mm and a Cation Self-Regenerating CSRS Ultra II 2 mm suppressor. The detection limit for all ions was 0.1 ppm. Analysis was performed in triplicate using 10 μ L samples of melted snow.

2.10. Materials and Supplies

Chemical reagents were purchased from Sigma-Aldrich and gaseous compounds were obtained from Praxair. TraceClean wide mouth packers, amber glass for sampling, and storage of snow samples were obtained from VWR International. DNA extraction and purification kits were obtained from Qiagen and Epicentre Technologies. Millex syringe filters with a 0.22 μ m pore size hydrophilic PVDF membrane, as well as ZipTip C18 reversed phase columns, were obtained from EMD Millipore Corporation. The prespotted AnchorChip used for MALDI-TOF was obtained from Bruker Biosciences Corporation. Along with the 0.22 μ m pore size filter, we utilized 0.1 μ m pore size filters, but as there was a lack of statistically significantly difference under our experimental conditions, we only discuss the results obtained with the 0.22 μ m pore size filter in this publication.

3. Results and Discussion

3.1. Nanosized Particle Size Distributions

Size distributions of particles in aerosolized fresh snow samples as a function of the electrical mobility diameter as well as aerodynamic diameter are depicted in Figure 2a (red bars). We observed that in all studied snow samples from all three sites, there is a substantial fraction of particles that have electrical mobility diameters smaller than 200 nm (about 2 orders of magnitude higher in abundance than at larger sizes). It is worth mentioning that in Montreal, there are several sources of local pollution from the hospitals, motor vehicles, waste processing and other industry, water and wastewater treatment, and so forth [Gagnon et al., 2007]. This local pollution may have an effect on the snow particle size distribution. At electrical mobility diameters greater than 200 nm, we observe a decline in the concentration of particles. Furthermore, a decrease in particle concentration becomes more noticeable at aerodynamic diameters greater than 300 nm. Although we cannot correlate electrical mobility diameter with aerodynamic diameter directly, both provide a good approximation of the impact of size on the concentration of particles in snow. Conversion of electrical mobility into aerodynamic diameter is theoretically possible, though parameters, such as the shape of particles and their density, need to be known. These properties differ substantially depending on particle structure and composition. For simple aerosols or standard suspensions and colloid solutions, these parameters are available, however for environmental samples, the number of types of particles is so large that it becomes virtually impossible to perform an accurate conversion, and thus, as done by other researchers [Nazarenko et al., 2011, 2014; Pant et al., 2009], in order to prevent introduction of error of unknown scale, we report the original metrics without conversion. We also note that although the dialysis of samples reduced potential formation of particles from soluble nonvolatile constituents of melted snow during aerosol drying, the effect cannot be fully eliminated. As a result, a certain portion of smallest particles measured by the aerosol instruments are likely from substances dissolved in melted snow that persisted after dialysis.

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Figure 2. Size distributions of snow-borne particles. (a) Measured concentrations of particles as a function of particle size (logarithmic scale) using both nanoparticle tracking analysis (NTA) and aerosolization techniques in Montreal, Alert, and Barrow. (b–d) Particle abundance as a function of hydrodynamic diameter for several snow samples from Montreal, Alert, and Barrow sites; different colors represent different samples.

To compliment the aerosolization process and to directly investigate particles in the liquid melted snow, we measured hydrodynamic diameter by NTA, as shown in Figure 2. The number density of particles measured by NTA (Figure 2a, blue bars) was consistently higher than when measured in aerosol phase as electrical mobility and aerodynamic diameter in the ranges of 101–200 and 201–500 nm, correspondingly, with a number density peak at approximately 200 nm (Figures 2b–2d). Moreover, particles less than 500 nm in hydrodynamic diameter represented an absolute majority of the total observed particles in snow matrices, under the experimental conditions used. We note that the particle hydrodynamic diameter distributions

Repeats; Detection Limit: 0.1 ppm)										
Sample (ppm)	TOC	SO_4^{2-}	PO_4^{3-}	CI^-	NO_3^-	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	${\rm NH_4}^+$
Alert site 1	1.30	0.39	<0.1	12.76	<0.1	7.12	0.23	0.87	1.01	<0.1
σ	0.02	0.06	<0.1	0.26	<0.1	0.22	0.02	0.04	0.07	<0.1
Alert site 2	1.50	0.43	<0.1	16.78	<0.1	7.13	0.26	0.98	0.74	<0.1
σ	0.05	0.06	<0.1	0.14	<0.1	0.31	0.02	0.06	0.08	<0.1
Barrow site 1	2.53	0.68	<0.1	13.59	<0.1	5.24	0.21	0.66	1.06	<0.1
σ	0.07	0.02	<0.1	11.05	<0.1	4.13	0.03	0.50	0.35	<0.1
Barrow site 2	2.16	0.53	<0.1	7.91	<0.1	3.70	0.19	0.51	0.58	<0.1
σ	0.05	0.04	<0.1	0.07	<0.1	0.14	0.02	0.02	0.05	<0.1
Montreal site 1	4.01	0.82	<0.1	0.29	<0.1	0.48	0.09	<0.1	0.86	<0.1
σ	0.02	0.02	<0.1	0.01	<0.1	0.10	0.02	<0.1	0.04	<0.1
Montreal site 2	1.46	1.47	<0.1	11.40	<0.1	4.74	<0.1	0.59	5.16	<0.1
σ	0.04	0.01	<0.1	0.05	<0.1	0.16	<0.1	0.02	0.06	<0.1

Table 1. Total Organic Carbon (TOC) and Ion Concentrations (ppm) in Two Snow Samples From the Three Sampling Sites (σ : Standard Deviation of at Least Three Repeats; Detection Limit: 0.1 ppm)^a

^aData for different snow samples from Barrow, Alaska, USA; Alert, Nunavut and Montreal, Quebec, Canada.



Figure 3. Examples of (a) MALDI-TOF MS mass spectra depicting patterns related to bioorganic materials with suggested structures; (b) ESI/MS spectra showing relatively high molecular mass with suggested structures in case the analyzed molecules are in fact 707 peptides; (c) EDS showing elements such as silicon and iron, which are usually found in 708 ice nucleating mineral dust particles.

(Figures 2b-2d) are fitted to the total concentration measurement, so that the areas underneath the curves match the total particle concentrations in the samples. We cannot directly correlate the diameter measured by NTA to the electrical mobility diameter, nor with the aerodynamic diameter. We also could not assess whether the total concentration of aerosols correlates with the concentration of particles in snow meltwater; hence, normalization of aerosol concentrations by volume of melted snow was not possible. Therefore, the value of aerosol measurements lies in determining most abundant particle sizes. However, we can confidently confirm that nanosized particles (<200 nm) dominate the total aerosol distribution (Figure 2a).

3.2. Chemical Composition of the Observed Nanosized Materials and Particles

We identified a significant amount of total (dissolved and suspended) organic (TOC) compounds in snow samples, as listed in Table 1. In an earlier study, we had already confirmed presence of certain volatile and semivolatile organic compounds in snow samples from the sampling sites during the same period [Kos and Ariya, 2006]. With two samples analyzed per site for three locations, the total number of samples analyzed is guite limited and indeed should not represent typical TOC values in the Arctic. These measurements merely represent the total carbon content of samples taken under experimental conditions, described herein. We expect much more variability with more samples over a wider range of Arctic regions were performed [Grannas et al., 2004; Hagler et al.,

2007; Voisin et al., 2012]. We therefore encourage additional research to provide a broader range of TOC content across a wider range of Arctic regions and different seasons.

To characterize the chemical composition of the nanosized fraction specifically, we performed MALDI-TOF analysis on preconcentrated samples. We discarded the possibility of matrix interferences, as the observed peaks did not systematically correspond to known matrix cluster signatures (Figure S2 in the supporting information). The measured MALDI-TOF spectra are inconsistent with inorganic materials but are similar to those for bioorganic materials, such as macromolecules with mass-to-charge ratios from 1100 to 1350 amu [*Caprioli et al.*, 1997], consisting of compounds such as amino acids or monomers. We certainly cannot suggest that HUmic Llke Substances (HULIS) were absent in the sample, or that they were not isolated by



Figure 4. Electron microscopy images of filtered snow samples depicting filaments and vesicles likely of organic origin and the probable presence of some inorganic compounds.

the column along with peptides. However, it must be noted that the molecular weights of most simple HULIS are relatively smaller in comparison with the molecular weights found in this study by MALDI. Furthermore, the repetition of specific mass units, as illustrated in the MALDI-TOF spectrum in Figure 3, suggests a possible polymeric structure. The patterns of monomer loss upon ionization are also indicative of mac0072omolecules of polymeric nature [*Wesdemiotis et al.*, 2011; *Yol et al.*, 2013]. We suggest specific amino acids, molecular weights of which match the above mentioned mass decreases, so the potential polymers are likely peptides and are shown in Figure 3a. Moreover, proteins and macromolecules have previously been observed in atmospheric aerosols [*Gelencsér*, 2004; *Jaenicke*, 2005], as well as ice and snow [*Antony et al.*, 2011]. Using the soft ionization technique of electrospray mass spectrometry, shown in Figure 3b, we obtained an almost identical spectrum to MALDI-TOF mass/charge ratio range, supporting the existence of bioorganic materials such as various amino acids.

TEM images provided evidence for the existence of numerous submicron particles in snow samples with sizes of ~500 nm and smaller, as illustrated in Figure 4. It is important to mention that sizes of these particles, identified by electron microscopy, do not match hydrodynamic diameter, as only the electron-contrast cores of particles, excluding any electron-transparent coatings, are visible in TEM and also because the hydrodynamic diameter includes the double electric layer. Nevertheless, we can observe that these particles are still nanosized and dominate the electron microscopy images. Furthermore, the shape of these particles resembles globular structures (Figures 4a and 4b), as well as fibrous structures (Figures 4c and 4d) typically adopted by polymers and peptides/proteins [*Jones*, 1984]. High-electron-contrast particles are likely inorganic in nature, whereas low-electron-contrast particles are probably bioorganic in nature [*Watson*, 1958], which is consistent with our mass spectrometry analysis shown in Figure 3. Note that the uranium-based negative stains we used do not bind to most organic matter leaving it low contrast [*Hayat and Miller*, 1990].

Energy dispersive X-ray spectroscopy (EDS) analysis also revealed presence of inorganic components in the snow samples containing elements common to inorganic particles, such as iron and silicon (Figure 3c),



Figure 5. Comparison of the cumulative nucleus spectra (Log10, Ice Nuclei/Liter) of the top layers (3 cm) of surface snow samples. (a) All sampled sites; (b) Alert, Nunavut; (c) Barrow, Alaska; and (d) Montreal, Quebec. Same symbol shapes represent the same sample types in all regions. The mean freezing temperatures of unprocessed snow are for Barrow $-12.52^{\circ}C$ (standard deviation (σ): 8.58); Alert $-11.48^{\circ}C$ (σ : 2.94); and Montreal $-12.82^{\circ}C$ (σ : 2.60). The mean freezing temperatures of filtered snow are for Barrow $-17.3^{\circ}C$ (σ : 7.8); Alert $-17.1^{\circ}C$ (σ : 6.3); and Montreal $-15.0^{\circ}C$ (σ : 1.7).

reported in literature [*Archuleta et al.*, 2005; *Baustian et al.*, 2012; *Krueger et al.*, 2004]. The electron micrographs, shown in Figure 4, suggest an abundance of particles that are likely organic in nature, as the negative stain did not bind to them revealing sharp boundaries between the particles and the background [*Domine et al.*, 2011; *Kos et al.*, 2014].

3.3. Nanosized Ice Nuclei

Figure 5 illustrates the cumulative nucleus distribution of over 20 000 data points in all three sampling locations, obtained by drop-freezing experiments. We had two distinct sampling sites at each location. The number of active nuclei at or above a certain temperature is $[\ln N_0 - \ln N(\theta)]V - 1$, where N_0 is the total number of drops in the experiment, $N(\theta)$ is the number of unfrozen drops at a certain temperature θ , and V is the volume of the drop. Note that the cumulative nuclei concentration is not a direct measure of the number concentration of particles in a solution or suspension. The shape of a logarithmically scaled spectrum offers insight into nonuniformities among nuclei since the various nuclei differ in their nucleating activities independently from one another [*Vali*, 1971].

We observed that the drop-freezing assay data points of freshly melted snow, with particles already immersed in water, vary within and across the sites (Figures 5–7) ranging from (-17.0 ± 2.5) to (-4.4 ± 0.7) °C (red curves). Interestingly, we also observed that the filtered snow samples (green curves) showed distinctly different ice nucleation patterns to their respective unfiltered counterparts $(-19.6 \pm 2.4 \text{ to } -8.1 \pm 2.6$ °C). The mean freezing temperature of all data points (all locations) corresponding to unprocessed snow samples was -12.0 ± 6.4 °C, whereas the mean freezing temperature of all data points corresponding to filtered snow samples was -17.2 ± 7.1 °C. With these two mean temperature values, we performed a *t* test with a significance level of 5%. The *p* values obtained suggest these two types of samples are two different populations.



Figure 6. Cumulative nucleus spectrum of centrifuged snow samples. From Alert, Nunavut (solid circle); Barrow, Alaska (solid triangle); and Montreal, Quebec (solid square). Green curves represent samples from the top 1 cm layer of centrifuged samples, and red curves represent samples from the bottom 1 cm layer of a 1.5 mL conical vial. The blue line is the average of samples from the top layer, whereas the black line is the average of samples from the bottom layer.

Ice nucleation study results suggest two different populations for unprocessed and filtered snow. However, there is a possibility that the filtering process leads to an alteration of select physical characteristics and/or the chemical composition of the particles [Hudson et al., 2011], which could in turn affect their nucleating ability. We therefore also centrifuged our snow samples to separate different particles without potential alterations from particle-filter interactions (Figure 6). The centrifugation process separates particles as a function of density. Since bacteria have been identified as the most efficient IN. we centrifuged our samples with an acceleration of about 1000 g (g force or relative centrifugal force) forcing bacteria and any other high-density particles to settle to the bottom layer [Peterson et al., 2012]. We performed drop-freezing experiments on droplets isolated from

the top and bottom layers of the centrifuged samples (Figure 7). The statistical analysis indicated that the freezing temperatures of the top layer were lower than the ones at the bottom layer by ~4.4°C, similar to the difference between filtered and unprocessed snow, shown in Figure 5. Statistical analyses on data sets from all sites indicated that both filtered and centrifuged populations of samples, representing snow without particles larger than 200 nm, exhibit significant differences from unperturbed snow samples (-13.2 ± 0.6 to -4.3 ± 0.8 °C) yet seem to be excellent IN (-17.6 ± 3.4 to -6.1 ± 1.2 °C). Conversely, it has been reported that the presence of soluble material coating inorganic particles can enhance their nucleating properties, one of the best known examples of this phenomenon being mineral dust particles coated by (NH₄)SO₄ [*Baustian et al.*, 2010; *Wise et al.*, 2010]. To



Figure 7. Cumulative nucleus spectrum of snow samples from Montreal, Quebec, collected at different depths. Lower layer (solid square), 5 cm close to the ground, intermediate layer (solid triangle), and top 3 cm of snow (solid circle). Green curves represent samples containing particles with sizes smaller than 0.22 μ m, and red curves represent unfiltered samples. Grey circles represent Milli-Q water for comparison.

eliminate the possible influence of dissolved ions on ice nucleation temperatures, we explored the ionic diversity in the studied snow matrices with the mean ion concentrations and standard deviations given in Table 1. We considered this especially important to check because salts such as $(NH_4)_2SO_4$ have been found in Arctic samples [Bigg and Leck, 2001]. We determined it to be unlikely that compounds such as (NH₄)₂SO₄ would have a considerable effect on ice nucleation temperatures because, in most cases, the concentration of ammonium found in snow samples taken at different sites was below the detection limit.

Since there is no reference technique for measuring the number of nanosized ice nucleating particles in snow, to make an estimation, we use the assumption [*Archuleta et al.*, 2005; *Möhler et al.*, 2006; *Steinke et al.*, 2011] that approximately 0.1% of these nanosized particles can



Figure 8. Electron microscopy images of snow samples. (a and b) Scanning electron microscopy images of some microorganisms in different types of snow. (c-h) Transmission electron microscopy (TEM) images of filtered snow samples using a filter with a pore diameter of 0.22 µm.

exhibit ice nucleation abilities in the immersion mode. If this assumption is correct, our results suggest that snow nanosized particles' contributions to nucleation are significant, in comparison to microscale ice nucleating particles (Figure 2). Particles with diameters less than 200 nm amount to 38–71% of all snow-borne particles, whereas nanoparticles account for ~11% to 19% of the total nuclei across a wide range of studied distinct snow types.

In order to relate the particles in snow samples to their likely points of origin, we verified back trajectory data published in previous studies for the same dates in Barrow and Alert [*Domine et al.*, 2011; *Kos et al.*, 2014]. Data from Barrow showed that most of the trajectories come from northern locations, that is, directly from the Arctic Ocean. This may explain the sea-salt content within the samples. Similarly, data from Alert showed that the air masses affecting the sampling area came primarily from northwest and southwest locations, again the Arctic Ocean, as well as some terrestrial locations, where organic particles could have originated from local vegetation.

3.4. Microbiological Diversity in Snow

Since bacterial species are considered to be among the most efficient identified IN, in a parallel study, we focused our research on the identity, population, and ice nucleation ability of the bacterial and fungal communities in the different types of snow examined [*Mortazavi et al.*, 2015]. Complementary morphology of the identified taxa was obtained using TEM (Figure 8). Freezing-point temperatures of bacterial isolates ranged from approximately -20° C to -5° C. These identified bacteria were generally larger than 1 μ m. Therefore, the systematically elevated ice nucleation temperatures for nanosized particles observed in sampled snow at all snow collection sites cannot be explained. Microbial cellular materials, which are smaller in size, could, however, be a source of the observed nanoparticles, which are in agreement with the TEM observation of the

vesicular and filament structures (Figure 4) in filtered snow samples, similar to some organic matter [Pummer et al., 2014; Wilkinson et al., 1999].

It has been speculated that viruses could serve as potential nanosized IN [Junge and Swanson, 2008]. We used several microscopy techniques and stains, routine for virus analysis [Leberman, 1965; Markham et al., 1963], for several samples taken during this study but found no conclusive evidence of the presence of viruses within the samples. Nevertheless, this negative result does not entirely preclude the role of viruses in ice nucleation processes or lack thereof.

3.5. Why Do Nanosized Compounds Act as Efficient Ice Nuclei?

Both bioorganic compounds and inorganic nanoparticles were observed within our snow samples (Figure 4). Although inorganic compounds, containing elements such as iron are similar to nano dust particles, we cannot overrule iron containing biological remnants, which should be further studied. Our results support that some nanosized particles may exhibit similar ice nucleating temperatures as microscale mineral dust particles, under our experimental conditions. Since contact angle is a key parameter in determining the nucleation capability of particles [Chen et al., 2008], further studies not only of size but also of contact angle calculations under different environmental conditions are recommended. Select theoretical studies have proposed that possible ice nucleation mechanisms are likely due to nanosized effects [Marcolli, 2013; Matsumoto et al., 2002]. Considering the high abundance of the larger nanosized particles observed, ice nucleation may be altered due to possible additional active corner and edge sites for water uptake, larger total surface area, and complex surface curvatures. It is also conceivable that pores and cracks in these nanoparticles are inducing the formation of different phases of ice that is more stable at warmer temperatures [Algara-Siller et al., 2015]. Adsorbed water molecules can be subjected to ideal pressures, which, at a nanosized level, form the first ice embryo from which ice can start growing [Algara-Siller et al., 2015]. We do not overrule the existence of other nanosized effects that have yet to be considered. Further research should be focused on understanding the nature of nanosized ice nucleators, namely, their composition, phase, configuration, and surface properties and evaluate whether these nanosized ice nucleators are mostly bioorganic in origin or not.

4. Concluding Remarks and Future Work

This work provides the snow-borne size-aggregated particle number density, distribution, and chemical composition of snow, as well as microphysical data on ice nucleation of snow at various conditions at two Arctic sites during field campaigns and data, collected in Montreal over a decade (2004–2014). We showed for the first time that nanosized particles are the most abundant particle size in snow and that nanoparticles are abundant over a wide range of ecosystems studied. This study expands our previous understanding of the ubiquity of nanosized nuclei in precipitation [*Vali*, 1966, 1978]. As the phenomenon of ice-nucleating nanoparticles seems to be widespread in North American snow, these particles may have potential implications in cloud formation and consequently influence precipitation, biogeochemistry, ecosystem health, and climate change. Further research should focus on understanding the nature of nanosized particles as ice nucleators. Specifically, their composition, configuration, surface properties, including active sites, size distribution, and mechanism(s) of initiation of ice nucleation should be investigated. In a changing climate with increases in the incidence of extreme weather, the transport of nonnative chemicals to the polar regions is intensifying, and this in turn will potentially affect the diversity and distribution of chemicals in the polar regions, resulting in melting and refreezing of snow and ice. Lastly, since some snow-borne nanoparticles can have health effects [*WHO*, 2013, 2014], further research on environmental and human toxicology is also recommended.

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