Aerosols in an urban cold climate: Physical and chemical characteristics of nanoparticles

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ABSTRACT

Atmospheric aerosols are of significant importance in climate change and health research. This study provides a 2-years meta dataset of real-time aerosol number and size distribution measurements in a model cold-climate city of Montreal (Canada). We provide selected information on the chemical composition and morphology of aerosols (~10 nm to 10 μm). We deployed a suite of complementary techniques such as aerosol particle sizers, MOUDI, S/TEM imaging, EDS, QQQ-ICP-MS/MS, IC, and TOC analyzers. The highest geometric nanoparticles (< 100 nm) number density (9260 ± 1.6 number/cm³) was observed in the winter. A broad range of metals, including emerging contaminants, was quantified in all aerosol sizes include Pb, Cd, Ni, Zn, As, Al, Mn, Co, and Se, with concentrations ranging from 0.01 to 67.64 ng/m³. Nanosize particles included Ni, Cd, Pb, Zn. Iron exhibited the highest concentrations consistently in two modes (< 180 nm and > 1 μm). S/TEM-EDS confirmed the abundance of nanoparticles, single and clusters, with multifaceted morphologies and compositions. We identified (a) emerging nanoparticles, (b) secondary organic aerosols, (c) bioaerosols, and (d) combustion particles. Diurnal, weekly, monthly, seasonal, and yearly variations of aerosols are provided. We herein discuss the implications of these results on air quality and climate modelling.

1. Introduction

Aerosols (airborne particles) are identified as key players in climate change and health by the Inter-governmental Panel for Climate Change (IPCC, 2013) and the World Health Organization (WHO, 2015). Aerosol and their interactions with clouds and radiation “continue to contribute the major uncertainty to assessments and understandings of the Earth’s changing energy budget,” thereby affecting the assessment of the Earth’s climate (IPCC, 2013; Intergovernmental Panel on Climate, 2014).

The uncertainty in the global radiation budget associated with aerosol-cloud interactions is of the same order of magnitude as the estimated radiative impact of the increase in atmospheric concentrations of major greenhouse gases associated with human activities (IPCC, 2013). Air pollution, particularly aerosols, has been directly linked to an increase in respiratory and cardiovascular diseases, as well as cancer (WHO, 2015). Air pollution is now explicitly named “the biggest cause of early childhood mortality” (WHO, 2015).

Airborne nanoparticles are aerosols with an aerodynamic diameter of less than 100 nm. There are currently no regulatory measures for nanoparticles, which are far smaller than the regulated particles with aerodynamic diameters of less than 2.5 μm (PM2.5).
and 10 μm (PM$_{10}$). The physical and chemical properties of nanoparticles, such as size, surface tension, active sites, surface properties, volatility, and photochemistry, are essential parameters in both climate and health research (Grassian et al., 2007; Rangel-Alvarado et al., 2015a).

Cities are the leading emission sources of air pollutants (e.g., PM$_{2.5}$, PM$_{10}$, CO, SO$_2$, CO$_2$ and NO$_x$) (Satterthwaite, 2008) and are the locations where most humans reside. Airborne particles are emitted into the atmosphere from various sources, both natural and anthropogenic (Kulmala et al., 2004a), and include a diverse composition of compounds such as organic, inorganic, and emerging metal contaminant species (Ariya et al., 2009; Rahim et al., 2018). The primary sources of airborne nanoparticles in urban areas have been identified as vehicle exhaust, airport, thermal plants, industries and hospital combustion process (Ahlm et al., 2012; Hitchins et al., 2000; Kulmala et al., 2004b). The combustion process is also a significant source of CO, and it can be used as a tracer for anthropogenic emissions of nanoparticles in the atmosphere (Pirjola et al., 2006; Pirjola et al., 2016). Furthermore, secondary aerosol formation, gas-to-particle conversion, and condensation of vapours on pre-existing particles lead to the formation of nanoparticles in both urban and suburban regions (Dall’Osto et al., 2011; Wegner et al., 2012; Sahu et al., 2016).

Emerging contaminants are defined as synthetic or naturally occurring chemicals or materials that have the potential to enter the environment and have adverse ecological and human health impacts, but are currently inadequately regulated because of the lack of contaminants characterization in the environment and insufficient toxicological data on their effects (Rahim et al., 2018; Sauvé and Desrosiers, 2014; Sýkorová et al., 2017). The rapid urbanization and the enlargement of the number of vehicles and industries are vital parameters of elevating the level of emerging metal contaminants in the ambient air (Gallon et al., 2011; Sanderson et al., 2014).

In the cold-climate urban regions (Järvi et al., 2014) during the winter months, the height of the planetary boundary layer is lower than during the summer months due to colder temperatures and a higher air density. This phenomenon and the additional possibility of a winter inversion layer can suppress vertical mixing, leading to entrapment of pollutants close to the Earth’s surface (Hinds, 1999). Further need for the additional heating in winter, increased emission of pollutants is also anticipated from the transport sector (i.e., idling cars and planes) to energy usage for heating buildings. Recent health studies have shown that an enhanced PM10 (< 10 μm diameter) number density causing health hazards in winter (Januszek et al., 2019), notwithstanding that many major cities in the world receive various levels of frozen precipitation (Järvi et al., 2014).

In this study, we aimed to (a) provide real-time self-consistent in-situ measurements of the number-size distribution of particles (−10 nm to 10 μm), focusing on nanoparticles (< 100 nm) in a cold-urban site, where there are limited real-time aerosol data; (b) determine complementary chemical/elemental composition of size-aggregated aerosols, (c) understand the morphology of aerosols at different sizes, and (d) the effects of selected distinct environmental conditions such as seasons, diurnal, daytime vs. nighttime and weekdays vs. weekend days aerosol number-size distribution were also evaluated. We herein focused on airborne nanoparticles and emerging nano-contaminants. We further discuss unique aerosol patterns in a model city Montreal, which receives, on average, 2.1 m of snow per year (vs. Moscow 1.2 m snow per year).

2. Experimental section

We performed real-time in-situ particle size distribution measurements as well as sampled aerosol particles using an Impactor. The samples were analyzed to characterize the morphology and chemical compositions of aerosols. The complementary methodologies for each measurement are discussed in detail below, as well as in the supplementary information (SI).

2.1. Sampling and measurement site

Real-time measurements of airborne particle number-size distribution were performed at McGill University, downtown campus in Montreal, Canada (Fig. S1). The in-situ observations of aerosols were performed ∼ 4 m above from the ground at the intersection of University and Sherbrooke streets. A conductive tube (2 ft long) inlet was used to direct the ambient air into a NanoScan™ Scanning Mobility Particle Sizer (SMPS) model 3910 (TSI Inc.) and an Optical Particle Sizer (OPS) model 3330 (TSI Inc.).

Significant anthropogenic sources of aerosols and other pollutants are the local traffic emissions along with the nearby industrial and hospital combustion processes. Besides, Mount Royal Park is not far from the sampling site, and thus the sampling site receives biogenic aerosols.

2.2. Number-size distribution measurement

The real-time aerosols measurements were performed using an SMPS and an OPS. The SMPS measures the particle size distribution of ambient particles in the range of 10–400 nm in terms of the electrical mobility diameter. The OPS determines the particle size distribution from a size range of 0.3–10 μm in terms of optical diameter. These instruments are factory-calibrated every year with Polystyrene Latex spheres (PSL) for all the internal and external flow rates.

The particles are considered spherical, and size distribution determined by the optical counters is very close to the actual physical (or geometric) diameter (Chen et al., 2011; Hering and McMurry, 1991; Reid et al., 1994). The OPS measurements are intensely dependent on the aerosols appearances, such as the refractive index and dynamic shape factor. Based on the assumption that the aerosol particles are spherical and the particle density is 1 g/cm$^3$, the optical diameter is considered to be equivalent to the aerodynamic diameter (Hinds, 1999).

We performed routine quality assurance procedures for the SMPS and OPS to ensure the accuracy of the measured data, including the measurement of the aerosol number density, passing the air with HEPA filter, as shown in Fig. S2 (a-b). The particle number
density was observed < 1 particle/cm^3 for both SMPS and OPS.

2.3. Micro-Oorifice uniform deposit impactor (MOUDI)

MOUDI (model 100-R, MSP Corp., Shoreview, MN, USA) was used to collect size-fractionated aerosol particle samples for subsequent analysis of chemical compositions, organic carbon, and morphology of particles. The unit has eight impaction stages and is comprised of five assemblies: rotator impactor, Magnehelic gage, rotator unit, shelter, and a blower motor. The stages of MOUDI are calibrated to the following d_{50} cut-off points: 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, and 0.18 μm, equivalent to aerodynamic diameters. Further information provides in the supplementary section, Text S1.

We operated the MOUDI on the roof of the laboratory with an inlet airflow rate of 30 L/min. Aerosol samples were collected on Teflon quartz substrate (MSP Corp., Shoreview, MN, USA) during different days of sampling periods. The 24 h sampling period was from 19/07/2017 to 20/07/2017, and the longer-term sampling (i.e., 48 h) was conducted between 14/07/2017 and 16/07/2017. These aerosol samples were used for chemical analysis and determination of the morphology of particles discussed in the subsequent sections.

2.4. High-resolution S/TEM and FE-ESEM imaging with energy dispersive X-ray spectroscopy (EDS)

The airborne particles were collected onto Cu grids (SPI. Supplies, West Chester, PA USA). The TEM-grids were fixed on the filter substrate using double-sided adhesive tape and placed in the following d_{50} cut-off points: 0.18 μm and 1 μm.

The field emission gun transmission electron microscope (FEG-TEM) has an operating voltage in the range of 50 to 300 kV. The high-brightness, high-coherency gun permits large electron probe currents to focused on nanometer-sized areas of the specimen (sample). The capabilities of this gun include energy-dispersive X-ray spectroscopy (EDS), S/TEM imaging and mapping, and a CCD camera that allows magnification of thin samples (< 500 nm) up to > 1 million times (FEI, 2007). The TEM grids were analyzed using a high-resolution FEI. Tecnai G²F20 S/TEM microscope with a field emission gun (FEI, 2007).

Images were acquired using an Advanced Microscopy Technique, Corp. (AMT) XR80C CCD Camera System, which was previously used for both snow particles (Rangel-Alvarado et al., 2015b). In this study, the AMT was adapted for the collection of atmospheric aerosols directly on the grid. It allowed us to study the size, morphology, and composition (with EDS) of airborne single and aggregated nanoparticles at high resolution. The cut-off d_{50} (= 1 μm) TEM grids were subjected to the FEI Quanta 450 Environmental Scanning Electron Microscope (FE-ESEM).

2.5. Trace metal analysis

Collected samples for each fractionated size range were digested in a combination of 2% nitric acid (Omni trace ultra- nitric acid) and ultrapure Milli-Q water in a sealed microwave vessel. Digested samples were then introduced to Triple Quad Inductively Coupled Plasma Mass Spectrometry (QQQ)ICP-MS/MS) [model - Agilent technology – 8900] to determine the concentrations of the trace metals Ni, Cr, Zn, Pb, As, Se, Sr, Co, Cu, Ag, Al, V, Mn, Fe, Cd, Ba, and U.

The instrument was optimized using a standard solution containing 10 μg mL\(^{-1}\) of each metal to ensure that inherent interfering species constituted less than 2% of the signal. Calibration was achieved using a multi-element standard (SPEX, USA ISO 9001 certified) made of a 2% nitric acid solution matrix matched to the samples. Analytical drift was monitored using a 10 μg/L multi-element standard, which was repeatedly analyzed throughout the procedure, and then was subsequently used to normalize the data. The quantitative results of metals are calculated based on the sampling flow rate of 30 L/min for both the 24 h and 48 h sampling periods.

The lower limit of detection of the (QQQ)ICP-MS/MS) analysis was calculated as 3σ for each element measured in the ten procedural blanks. The detection limits for individual elements were: Ni - 0.0046, Cr - 0.00766, Zn - 0.08764, Pb - 0.00302, As - 0.00577, Sr - 0.00242, V - 0.0065, Mn - 0.00594, Fe - 0.02939, Cu - 0.00413, Ag - 0.00208, Cd - 0.00417, Ba - 0.00851, and U - 0.00147 μg/L.

2.6. Complementary ion analysis

The ICS-5000 AS-DP Dionex Thermo Scientific Ion Chromatography system was used to measure the ions. We analyze both the anion species (F\(^-\), Cl\(^-\), NO\(_2\)\(^-\), Br\(^-\), NO\(_3\)\(^-\), PO\(_4\)\(^3-\), and SO\(_4\)\(^2-\)) and cation species (Li\(^+\), Na\(^+\), NH\(_4\)\(^+\), K\(^+\), Mg\(^2+\), and Ca\(^2+\)) in the aerosol samples. The Dionex column AS18–4 was used to separate the anions, and the Dionex column CS16–4 was deployed for the cations. Before introducing samples into the Ion Chromatography system, we dissolved all fractionated individual aerosol samples in 5 mL of ultrapure Milli-Q water. An un-used substrate was always analyzed for blank, and concentration was observed below the instrument detection limit < 1 ppm.

2.7. Total organic carbon (TOC)

We dissolved fractionated individual aerosol samples in 40 mL of ultrapure Milli-Q water, and the resulting samples were subjected to an Aurora 1030 W TOC Analyzer. 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. Afterwards, 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.

2.8. Meteorology and auxiliary air quality data

The complementary meteorological (T, RH, wind speed) and air pollution (O₃, NOₓ, CO, SO₂, and PM₁₀) data were obtained from the City of Montreal’s Air Quality Surveillance Network (RSQA), which described in detail in the SI in Text S2.

2.9. Statistical analysis and classification

In this study, the geometric mean and geometric standard deviation were used for data interpretation to minimize outlier effects. We also performed the arithmetic average, standard deviation, median, 99th, and 1st percentile values along with geometric mean, geometric standard deviation, during the advanced data analysis, which presented in supplementary information Table S1. The details of the geomean equations were discussed in supplementary Text S3. Recent metadata analysis has justified the usage of geometric error analysis (Friedrich et al., 2012; Georgiadis et al., 2001).

This meta dataset of two years provides a one-minute temporal resolution of particle number density (numbers/cm³) with each of five sizes aggregated ranges of particles, as shown in Fig. S3. The particle number density distributions were classified for five particle sizes. Statistical analysis were carried out in each five size range i.e., < 100 nm (10–100 nm), < 200 nm (100–235 nm), < 1 μm (0.3–0.9 μm), < 2.5 μm (0.9–2.6 μm), and < 10 μm (2.6–10 μm), of airborne particles for several temporal regimes: seasonal, monthly, weekdays (Monday - Friday), weekend days (Saturday - Sunday), daytime (09:00–18:00 h), nighttime (22:00–05:00 h), weekday-daytime, weekday-nighttime, weekend-daytime, weekend-nighttime, and snow precipitation events.

In cold-climate cities such as Montreal, cold months are not confined only to winter. We followed the classification from Environment and Climate Change Canada (https://weather.gc.ca/forecast/canada/index_e.html?id=QC). Thereby, the seasons are classified as Spring (April, 21st to June, 20th), Summer (June, 21st to Sept, 20th), Fall (Sept, 21st to Nov, 30th), and Winter (Dec, 1st to April, 20th) in different days of months.

Correlations between various environmental variables (i.e., gaseous pollutants, meteorological parameters) and particle number densities were assessed by Spearman’s correlation coefficients (Spearman, 1904). The independent Student t-test was used to explore the differences between different size groups aggregated by month, weekdays, weekend days, daytime, nighttime, and snow episodes. In the correlation test, a p-value lower than 0.05 and in the independent t-test, p-values lower than 0.001 were considered to be statistically significant.

3. Results and discussion

3.1. Seasonal particle number-size distribution

The geometric mean, arithmetic means, median, 99th percentile, and 1st percentile values of aerosol number densities were provided for a comprehensive statistical representation of the data set presented in Table S1. Seasonally geometric mean, arithmetic mean, and median number densities of each of five size range particles are providing a clear depiction of the long-term variability, as shown in Fig. 1(a).

We observed a multimodel seasonal variation of each five-size range of particles over two years (Fig. 1a). Notably, nanoparticle (< 100 nm) number density revealed a periodic pattern with the high geometric mean number density (number/cm³) were observed during winter (9260.2 ± 19), followed by Spring (7562.4 ± 2.0), Summer (6278.6 ± 1.8), and in Fall (5547.6 ± 1.9) during the year 2018–2019 (Table S1). In contrast, submicron (< 200 nm) and micron (< 1 μm and < 2.5 μm) size particle geometric mean number densities were observed higher during summer. Several factors impact the seasonal distribution of nanoparticles in urban cold-climate. For instance, during winter, the combination of cold temperature and suite of meteorological conditions and anthropogenic activities in cities (e.g., heating building and vehicles, etc.), lead to lowering the mixing layer height, favour the concentration of pollutants near the surface. The peak in the summer is due to the increased photochemical processes that lead to the net production of particles, including larger particles (> 1 μm).

In this study, we observed the highest nanoparticle number density during the winter season. This observation is in contrast to previous studies (Wu et al., 2008; Hussein et al., 2004; Andronache et al., 2006), rather than the cold-urban climate such as Montreal. These researchers have observed higher aerosol number density during spring (Wu et al., 2008; Hussein et al., 2004; Andronache et al., 2006) and summer (Venzac et al., 2009). Other studies have confirmed that the seasonal differences in aerosol number densities differ in the northern hemisphere to the southern hemispheres (Morawska et al., 2008; Mejia et al., 2007). They had concluded that the observed seasonal trends in the northern hemisphere (Pirjola et al., 2006; Morawska et al., 2008; Aalto et al., 2005; Virtanen et al., 2006), contrary to the southern hemisphere (Mejia et al., 2007; Mejia and Morawska, 2009).

The northern hemisphere contains approximately 90% of the global population and about 68% of earth landmass, while the southern hemisphere is mainly occupied by oceans (Dominick et al., 2019). This means that the northern hemisphere required more energy and resources, which elevated the anthropogenic deeds. Besides that, the differences in vegetation/agriculture between the northern hemisphere and the Southern Hemisphere (Box, 2002), along with significant meteorological differences (Mejia et al., 2007), are likely to result in different aerosol properties in the southern hemisphere (Mitchell et al., 2017). This study is one of the
very few studies in cold-urban regions with specific characteristics of aerosols. Thus the observed systematic winter maximum of aerosols is likely a specific characteristic of this climatic region. Hence, more studies are required to understand the characteristics of aerosols in various hemispherical, topographical, and climatic regions.

### 3.1.1. Winter seasons: the highest observed nanoparticle number density

During the peak winter months (Dec, Jan, and Feb), as shown in Fig. 1(b), the highest nanoparticle number density was observed throughout the years (2017–2019). The geometric mean number density of nanoparticle during Dec 2017 and Feb 2018 was observed 8447.6 ± 1.9 and 7463.3 ± 2.3 number/cm³, respectively. Along with nanoparticle number density, the CO mixing ratio also observed higher during winter seasons (Dec, Jan and Feb) compared to other seasons (See Fig. S4). The monthly averages of CO mixing ratios (ppbv) during Dec 2017, Jan and Feb 2018 were observed 235.8, 271.4 and 262.9 ppbv, respectively. While CO mixing ratios during Dec 2018, Jan and Feb 2019 were observed 257.6, 247.6 and 239.5 ppbv, respectively. The higher concentration of both nanoparticles and CO in the winter is associated with an increase in anthropogenic activity, higher traffic density, along with lower traffic circulation due to the snow removal operation in Montreal.

Additionally, lower atmospheric boundary layers in winter allow more accumulation of pollutants, particularly nanoparticles, where the deposition rate is much lower than larger particles (Hussein et al., 2006; Kumar et al., 2015). Besides the lower boundary layer, the cold-temperature (Monthly average temperature: Dec 2017 (−8.1 °C), Jan 2018 (−8.7 °C), Feb 2018 (−3.2 °C), Dec 2018 (−4.4 °C), Jan 2019 (−9.8 °C), and Feb 2019 (−7.5 °C), respectively (Fig. S5)) induced inversion or kind of inversion (leaking inversion) which again allow to pre-concentration of particles. Thus it increases in the emission of particles due to idling in cold-climate.

Higher number densities of submicron and micron-size particles were found during summer. Such a phenomenon has been attributed to enhanced photochemistry in the summer and elevated biological activities (Ariya et al., 2009; Ahlm et al., 2012), which release directly micron-sized particles (e.g., bio-aerosols like bacteria) or produce precursors for coagulations processes resulting in the high concentrations of submicron and micro-aerosols (Wu et al., 2008; Ren et al., 2017).

The nanoparticle’s geometrical yearly mean, geometric standard deviation, and median values (given in parenthesis) were observed to be 5516.2 ± 2.1 (5822.6) number/cm³ from May 2017 to May 2018 and 6979.3 ± 1.84 (7514.8) number/cm³ in May 2018 to May 2019. These observations concluded that the nanoparticle’s geometric mean number density elevated up to ~25% from the year 2017 to 2019 in the cold urban setting of Montreal.

Several factors can affect the aerosols observations as herein report, such as (a) meteorological impact of the lower height of boundary layer, suppression of vertical mixing, and cold temperature in Montreal, and (b) potential increase in anthropogenic emission.

### 3.2. Comparison with previous research on airborne particle distribution

We compared the measured particle number densities in this study to previous studies, which have been conducted worldwide. These results are given in Table S2. In this study, the total geometric mean number density (10 nm - 10 μm) during the two years of observation was 6776 ± 1.8 cm⁻³. This value is the second-lowest number density compared to other worldwide studies, shown in Table S2. The contribution from the number densities of larger particles (1 μm to 10 μm) was small relative to the total particle number density. The number density of particles within the range of 10 nm to 1 μm in downtown Montreal was comparable to the particle number densities from Santiago (Chile), Helsinki (Finland), and Prague (Czech Republic). Number densities in other regions were 2 to 4 times higher than this study.

### 3.3. Chemical analysis of airborne particles

#### 3.3.1. Trace metal concentration

The trace metal concentration (ng/m³) determined by the triple quad ICP-MS/MS shown in Table 1. In this study, different groups of airborne metals were observed, namely; alkaline earth metals (Mg, Ca, Sr, and Ba), transition metals (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, and Cd), post-transition metals (Al and Pb), metalloids (As, Sb) and other nonmetals (Se) (Table 1).

The observations revealed that the emerging metal contaminants, namely: Ni, Cr, Zn, Pb, As, Co and Cd were abundant in the 180 nm size particles (nanosized particles) and then in 320 nm and 560 nm size particles, respectively. Whereas, the concentrations of elements such as Cr (2.8 ng/m³), Ni (1.48 ng/m³), and V (0.05 ng/m³) were found to be maximum in the 0.18–0.32 μm fraction size range. Al and Fe showed the highest concentrations in each fraction size range particles. Since these data can be of interest to urban biogeochemical researchers, we have also provided in the supplementary data, per unit of aqueous volume.

The observations have shown that the metals are not only abundant in micron-sized particles but are also ubiquitous in airborne nanoparticles, which are considered as emerging contaminants (Table 1). Notwithstanding, even in one nanosized particle, showed several metal elements (e.g., Fe, Al, Ni, Cr, and Ti), as confirmed by HR-S/TEM analysis, presented in section 3.4.

#### 3.3.2. Ions in aerosols

The concentrations of the anions, Cl⁻ (1637 ng/m³), and SO₄²⁻ (1520 ng/m³), and the cations, Mg²⁺ (414 ng/m³), and Ca²⁺ (2062 ng/m³), were observed maximum in 0.18–0.32 μm size particles (Table 1). While, the concentrations of NO₃⁻, NO₂⁻ and K⁺ were observed higher in the 1.8–3.2 μm particle size range, as shown in Table 1. The concentrations of nitrate (88 ng/m³) and
(caption on next page)
ammonium ions (10 ng/m³) in the size fraction 0.18–0.32 μm were observed considerably lower than in size fractions 0.56–1.0 μm, (264 and 278 ng/m³, respectively) and 1.8–3.2 μm, (847 and 35 ng/m³, respectively) respectively. The previous study has also confirmed that the concentrations of nitrate and ammonium ions were at a maximum in the submicron to micron size range 0.45–1.09 μm of aerosols (Rogula-Kozłowska, 2016). The concentrations of ions, F⁻, Br⁻, PO₄³⁻, and Li⁺, were observed to be below the detection limit (< 0.1 ppm).

The conversions of gaseous pollutants such as SO₂, NOₓ, and NH₃ into ions, namely; SO₄²⁻, NO₃⁻, and NH₄⁺ are vital for increasing secondary aerosol formation. The abundance of SO₄²⁻ and NO₃⁻ in nanosized particles may indicate the contribution of secondary aerosols (Samara et al., 2016).

Fig. 1. Size aggregated particle number densities (#/cm³), (a) Seasonal variation of geometric mean, arithmetic mean, and median particle number densities, and (b) Monthly box plots of size aggregated particle number densities data from May 2017 to May 2019. The horizontal line through each whisker box represents that month’s median value, and the lower and upper edges of the whisker boxes present the 25th and 75th percentiles values, respectively. Whiskers above and below the boxes are maximum and minimum values, respectively. The outliers are not shown. The rectangular shapes inside the box present monthly mean number density.
In this study, TOC concentration is dominant in the nanosized and sub-micron size aerosols. The TOC concentration in nanosized particles, submicron and micron-sized particles were 240 ng/m³, 836 ng/m³, and 57 ng/m³, respectively (Table 1). The existence/presence of TOC in the nanosized particles indicates that carbon-containing compounds are constituents of nanoparticles. These observations were further validated by the morphology and elemental analysis of particles using S/TEM coupled with EDS (section 3.4), which provided the evidence for organic and inorganic carbonaceous compounds as well as mixed organic-inorganic carbon-containing particles.

More than half of the total organic carbon in atmospheric aerosols has been estimated to be secondary (Yang and Fleming, 2019; Chu et al., 2017). However, the mechanisms of secondary organic aerosol (SOA) formation are not fully understood, leading to difficulties in the modelling of SOA in air quality models (Volkamer et al., 2006). Pre-existing metal-containing aerosol particles in urban air have been found to either suppress or enhance SOA formation via metal-mediated pathways for aerosol-phase oxidation of organics (Chu et al., 2017; Chu et al., 2012; Chu et al., 2013). These studies have suggested that the effects of transition metals in aerosol particles on SOA formation must be considered in modelling urban air quality (Volkamer et al., 2006; Stevens and Dastoor, 2019). The concurrent physical and chemical data on different sizes of the particle can be parameterized in air quality models, particularly those focusing on cold-climate regions.

### Table 1

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<th>14–16 July 2018 (48 h)</th>
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<tr>
<td>NH₄⁺</td>
<td>10.42</td>
<td>277.78</td>
</tr>
<tr>
<td>K⁺</td>
<td>160.42</td>
<td>222.22</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>413.89</td>
<td>69.44</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>2062.5</td>
<td>Nd</td>
</tr>
</tbody>
</table>

- Nd represents the below filter blank
- Blank space represents no data (No measurements) on that particular day

3.3.3. TOC observations

In this study, TOC concentration is dominant in the nanosized and sub-micron size aerosols. The TOC concentration in nanosized particles, submicron and micron-sized particles were 240 ng/m³, 836 ng/m³, and 57 ng/m³, respectively (Table 1). The existence/presence of TOC in the nanosized particles indicates that carbon-containing compounds are constituents of nanoparticles. These observations were further validated by the morphology and elemental analysis of particles using S/TEM coupled with EDS (section 3.4), which provided the evidence for organic and inorganic carbonaceous compounds as well as mixed organic-inorganic carbon-containing particles.
3.4. HR-S/TEM and FE-ESEM observation of airborne particles: Focus on nanoparticles

Analysis of particle morphology is essential for determining the impacts and possible sources of airborne particles. In this study, the insights on particle size, morphology, and surface crystallinity, along with concurrent elemental analysis, are discussed below in four groups:

(a) Emerging contaminants (TiO$_2$)

Fig. 2(a, a1) are the nanostructures related to titanium-containing complexes, and EDS analysis confirmed that the particle is emerging metal or metal oxide nano-contaminants. Selected area electron diffraction (SAED) of particles in Fig. 2a confirmed a crystalline nature of titanium oxide nanoparticles. As previously shown in the literature (Banerjee et al., 2017), such morphologies are likely related to synthetic nanoparticles of titanium compounds or nanocrystals of TiO$_2$. Since the reactivity of various titanium oxides in the presence of light and various atmospheric compounds have been previously studied (Snider and Ariya, 2010), further research on the atmospheric chemistry of these emerging anthropogenic nanoparticles and their potential impacts on health is recommended.

(b) Secondary organic aerosols

Fig. 2 (b, c) depicts likely secondary organic particles with multiple phases. The EDS revealed that the particles in Fig. 2(b, c) contained a significant carbon and oxygen peaks followed by elements S, K, Ca along with other metals. SAED analysis confirmed that the particle in Fig. 2(b) has an amorphous nature. Particles in Fig. 2(c) represents the multiphase dendrite structures with diverse elemental compositions (EDS spots A, B and C). Although the morphologies of particles A, B, and C are similar, their elemental compositions were found to be quite distinct, suggested that the complexity of emission sources in an urban environment.

(c) Bio-aerosols

Bioaerosols are referred to as airborne living organisms (such as bacteria, viruses, algae) and remnants of biological activities such as natural polymers or semi-volatile organic compounds. The morphology of the particle in Fig. 2(e) depicts a likely biological particle. The elemental composition of particles are contained an abundance of C, O, and minor traces of K, Mg, and P. Previous studies have shown that the similar elemental composition of biological particles (Ariya et al., 2009; Coz et al., 2010; Després et al., 2012).

(d) Combustions particles

Fig. 2(d) displays the nearly spherical or non-regular shape particle of organic, inorganic, and mixed-phase organic-inorganic components, containing the peak amount of carbon and oxygen followed by metals Si, Fe, Ni, and Cr, which indicate industrial and combustion sources.

As shown in Table 1, the highest carbon content (TOC) was not observed only in nanosized particles, but also observed in micron-sized particles (SEM images in Fig. S6 (a-f)), indicate the existence of soot particles and carbonaceous materials. EDS analysis confirmed that these carbonaceous particles could be soot, black carbon, or related carbon nanotubes and graphitic matter (Buseck et al., 2012; Rangel-Alvarado et al., 2019; Shi et al., 2000).

Based on the morphology and elemental composition analysis of airborne particles, we identified multiphase organic, inorganic, and biological particles in the atmosphere with different shapes and sizes, namely single and clusters, spherical and non-spherical, and chain-like aggregated particles as shown in Fig. 2(a-e), and Fig. S6(a-f). The elemental composition analysis of these particles by EDS was consistent with the chemical analysis of the same samples by using (QQQ)ICP-MS/MS, IC and TOC analyzers (Table 1).

3.5. Distinct trend of weekday and weekends of nanoparticles distribution in summer and winter

The geometrical mean and median number densities of nanoparticles were observed consistently higher during weekdays compared to weekends in both winter and summer seasons (Table 2).

For instance, the geometric mean number density of nanoparticles was observed 7384.9 and 10,466.5 number/cm$^3$ during winter weekdays in 2017–2018 and 2018–2019, respectively. Whereas the geometric mean nanoparticle number densities during the summer weekdays 2017 and 2018 were observed to be 5427.7 and 6518 number/cm$^3$, respectively. The observation indicates the ~40% higher values in winter weekdays in comparison to the summer weekdays. However, nanoparticle number density was up to ~30% higher in winter weekends than in summer weekends. This observation reveals that the colder meteorological conditions (average monthly temperature in winter months < −9 °C, Fig. S5) in combination with higher emission of nanoparticles (heating, car operation, etc.) likely leads to an enhancement nanoparticle's number density during winter.

3.6. Day-night variation of aerosols

The statistical summary of each of the five-size ranges particle number densities during weekdays, weekends, daytime and
nighttime, are presented in Table 3. The 25th, median, and 75th percentile values of number densities of nanoparticles (<100 nm), <200 nm, <2.5 μm, and <10 μm particle sizes were observed consistently higher during the weekday-daytime to weekday-nighttime (independent t-test, \( p < 0.001 \)) except the <1 μm size particles (\( p = 0.009 \)).

In contrast, the number densities of particle sizes <1 μm, <2.5 μm, and <10 μm, did not exhibit significant statistical differences (\( p = 0.81 \), \( p = 0.31 \) and \( p = 0.43 \) respectively) during weekend-daytime to weekend-nighttime. It could be due to the coagulation and condensational growth of particles emitted or formed during the daytime (Rodríguez et al., 2007; Wang et al., 2010).

Fig. 2. High-resolution transmission electron microscopy images (a-d) with EDS of airborne particles (a) Represents the crystalline structure of TiO₂ and close-up (a1) represents titanium nanostructure, (b) and (c) represents the secondary organic particles with multiphase morphological structures, (d) represents spherical shaped organic-inorganic particles mixed with emerging metals. (e) Scanning electron microscopy with EDS represents biological particles.
Fig. 2. (continued)
The number densities for particles in other size ranges, < 1 μm, < 2.5 μm and < 10 μm, did not change significantly from weekdays to weekends; this suggests a vehicle exhaust emissions consist of predominantly smaller particles (Hama et al., 2017; Putaud et al., 2010; von Bismarck-Osten et al., 2013).

3.7. Seasonal and diurnal variations: Rush hours effect

The diurnal pattern of particle number densities during weekdays and weekends shown in Fig. 3(a-d). On weekdays, the first peak of nanoparticle’s number density is observed between 6:00 to 9:00 a.m. linked with the morning rush hour (Fig. 3(a)). The second peak of nanoparticle number density is observed around noon from 11:00 a.m. to 1:00 p.m., suggesting aerosols formation from photochemical pathways (Kulmala et al., 2004a; Stanier et al., 2004).

On weekends, the nanoparticle number density increased later in the morning from 08:00 to 10:00 a.m. due to late vehicle circulation. The second peak was likely to correspond to the photochemical production of nanoparticles was observed at the same time as weekdays (11:00 a.m. to 1:00 p.m.). Nevertheless, we observed higher nanoparticle density at the weekend during the late night to early morning period from 10:00 p.m. to 05:00 a.m. in contrast to the same hours during weekdays, as shown in Fig. 3(a, d). This could be associated due to the late-night activities in downtown Montreal.

We also explored the diurnal pattern based on the seasons. Nanoparticle number densities exhibited the three-peak pattern in all seasons, as shown in Fig. 4(a-d). These three peaks were observed corresponding to morning, midday, and evening hours, respectively. The first peak of nanoparticles was observed consistently with morning rush hours in all seasons, which reflects a higher traffic density.

The highest number density of nanoparticles was observed in winter morning rush hours compared to the other seasons, partly due to the idling of cars, more energy to heat the cars at subzero temperatures, and more extended circulation period due to snow/ice coverage on the roads. The midday peak of nanoparticles was observed from 12:00–01:00 p.m. in all seasons, suggesting that the formation of new particles by the photochemical process (Stanier et al., 2004; Kulmala et al., 2005). The night peak was observed around 08:00 p.m. in winter, while the peaks shifted around 09:00 p.m. to 10:00 p.m. during summer seasons. This is attributed to longer daytime hours in the summer. Besides, the late-night activity starts in the summer bit later than the winter months shift the local traffic later in the night.
3.8. Anthropogenic sources of nanoparticles

The spearman correlation coefficient values (Table S4) and closely correlated diurnal time series of particle number densities with CO during weekdays and weekends, as shown in Fig. 3(a-d). The monthly time series of co-pollutants such as CO, O3, NOx, SO2, and PM2.5 are shown in Fig. S4.

On weekdays, the mixing ratios of CO and nanoparticle concentrations are increasing simultaneously during morning rush hours and evening rush hours, as shown in Fig. 3(a), hinting at the similar emission sources and the predominance of anthropogenic activities. Whereas during the afternoon from 12:00 to 02:00 p.m., the nanoparticle number density increases, but CO concentration decreases. The nanoparticles peak at noon comes due to the photochemical pathways, while the lower mixing ratios of CO are associated with less traffic in the afternoon.

The positive correlation ($r = 0.74$) was observed between the nanoparticle number density and CO during weekdays morning rush hours (Fig. 3a). It suggested that nanoparticle number densities are likely associated with a strong influence of traffic emissions in urban environments (Hitchins et al., 2000; Wang et al., 2010). CO and nanoparticles also showed a positive correlation on weekends during early evenings to late-night, as shown in Fig. 3d, which indicates the combined effect of traffic along with late-night outings/activities in the downtown area.

3.9. Snow impact on nanoparticles

Table 3 illustrates the statistical analysis of snow impact on nanoparticle distributions.

We observed that the snowfall decreased the nanoparticle number densities. The impact of snow on nanoparticles is dependent on
several factors, such as the wind speed, frequency, duration and intensity of precipitation, humidity, etc. For instance, in events 1 and 2, the mean number densities of nanoparticles during snowfall were observed to be 5627.8 cm$^{-3}$ and 21,397.7 cm$^{-3}$, respectively. While, the next day to a snowfall, nanoparticles number densities were observed 5075.5 cm$^{-3}$, 15,685.8 cm$^{-3}$, respectively. These observations suggested that the snowfall enhanced the nanoparticle number densities. It could be due to the deposition of exhaust vapour on the snowflakes. In contrast, during event 3, the average nanoparticle number densities were observed a slightly higher day after snowfall than during snowfall, as shown in Table 4. The behavioural differences of the snow event 3 in comparison to the snow events 1 and 2, might be due to the colder day temperature (average temperature − 15.7 °C), associated with the increase in the vehicle density and the higher requirement of local heating. In addition, the clear sky on that particular day may have elevated the photochemical production of nanoparticles. Snowmelt contains various organic and inorganic contaminants. Thereby, it is vital for future study to consider the concurrent physicochemical measurements of snow/ice/air interfaces, as well as understanding the snow photochemistry during and after snowfall/snowmelt process, are essential parameters to model and assess their impacts on cold-climate urban air quality (Ariya et al., 2018; Ariya et al., 2011; Schwarz et al., 2013).

4. Importance of emerging metal contaminants observations in the atmosphere

4.1. Potential environmental implications of airborne metal-containing nanoparticles

The extensive usage of anthropogenic nanoparticles/nanomaterials in diverse domains such as construction, pharmaceutical, cosmetic, health, and electronics industries can add to the complexity of urban atmospheric chemistry (Snider and Ariya, 2010). The production and the usage of nanomaterials have been suggested to increase metallic-nanoparticles into the Earth’s environment, including in the atmosphere (Sýkorová et al., 2017; Darlington et al., 2009). Once the nanoparticles enter the environment, they can undergo complex processes. These particles can interact with other particles or gases compounds and alter the aerosol numbers. Size distribution, and their chemical composition, and optical properties are influencing urban air quality (Chouvelon et al., 2017). Examples of other chemical reactions, including the interactions, include reactions with halogens in cities (Coquet and Ariya, 2000;
Fig. 4. Seasonal, diurnal plot for nanoparticle number density (#/cm$^3$). (a) Summer months from 2017 and winter from 2017 to 2018, (b) Summer months from 2018 and winter from 2018 to 2019, (c) Spring and fall months from 2017 and (d) Spring and fall month from 2018.
Table 4
Snow impact on nanoparticles. Three snow events were analyzed. Mean, median number densities of nanoparticles were calculated the day before, during and the day after a snowfall in each event. The averages temperatures, relative humidity, total precipitation and snow on the ground data are also given.

<table>
<thead>
<tr>
<th>Snowfall events (MM/DD/YYYY)</th>
<th>Days</th>
<th>Total prec.</th>
<th>Snow on the ground</th>
<th>Number density (number/cm³)</th>
<th>CO</th>
<th>Ave. Temp</th>
<th>Ave. RH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(mm)</td>
<td>(cm)</td>
<td>Mean</td>
<td>Median</td>
<td>(ppb)</td>
<td>(°C)</td>
</tr>
<tr>
<td>Event 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before</td>
<td>12/2/2018</td>
<td>17.6</td>
<td>9</td>
<td>9604.2</td>
<td>7606.3</td>
<td>268.2</td>
<td>1.8</td>
</tr>
<tr>
<td>During</td>
<td>12/3/2018</td>
<td>8.9</td>
<td>6</td>
<td>5627.8</td>
<td>4510.1</td>
<td>294.7</td>
<td>1.4</td>
</tr>
<tr>
<td>after</td>
<td>12/4/2018</td>
<td>–</td>
<td>7</td>
<td>5075.5</td>
<td>4702</td>
<td>177</td>
<td>–4.5</td>
</tr>
<tr>
<td>Event 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before</td>
<td>1/28/2019</td>
<td>–</td>
<td>61</td>
<td>18,558.1</td>
<td>16,600.1</td>
<td>210.8</td>
<td>–17.4</td>
</tr>
<tr>
<td>During</td>
<td>1/29/2019</td>
<td>8</td>
<td>60</td>
<td>21,397.7</td>
<td>21,285.6</td>
<td>269.5</td>
<td>–12.5</td>
</tr>
<tr>
<td>after</td>
<td>1/30/2019</td>
<td>0.2</td>
<td>71</td>
<td>15,685.8</td>
<td>13,610.2</td>
<td>210.1</td>
<td>–10.9</td>
</tr>
<tr>
<td>Event 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before</td>
<td>2/25/2019</td>
<td>0.2</td>
<td>84</td>
<td>5508.8</td>
<td>4187.5</td>
<td>182.7</td>
<td>–4.5</td>
</tr>
<tr>
<td>During</td>
<td>2/26/2019</td>
<td>0.2</td>
<td>82</td>
<td>16,371</td>
<td>16,476.2</td>
<td>203.5</td>
<td>–14.5</td>
</tr>
<tr>
<td>after</td>
<td>2/27/2019</td>
<td>–</td>
<td>82</td>
<td>19,856.4</td>
<td>18,107</td>
<td>260.8</td>
<td>–15.7</td>
</tr>
</tbody>
</table>

Sherwen et al., 2017). There is now increasing evidence that halogen oxidation is not only crucial in polar or marine environments but also coastal cities (Sherwen et al., 2017; Ariya et al., 1999). Additional reactions include the transformation of organic compounds (Ryzhkov and Ariya, 2003), interactions with trace metals such as mercury (Snider and Ariya, 2010; Ariya et al., 1999; Ariya et al., 2015), and composite reactions with ozone. Several of these processes can furthermore be influenced by surfaces, such as snow/ice (Ariya et al., 2011; Nazarenko et al., 2016).

It is noteworthy that urban chemistry is closely linked with meteorology and urban built, and thus increasingly complex. There are also feedbacks between biogeochemical processes and atmospheric chemistry (Côté et al., 2008). We recommend future integrative studies to understand these emerging aspects of urban chemistry in an evolving chemical environment.

4.2. The importance of this metadata to improve cold-climate air quality modelling

An inherent assumption in most air quality and climate models is that within a specific size range, the aerosols are internally mixed concerning composition and morphology. However, observations in this study demonstrate various compositional and morphological mixing states within a single size range. The assumption of complete internal mixing can lead to the inaccurate prediction of gas-particle partitioning and climate-relevant aerosol properties such as cloud condensation nuclei concentrations and optical properties in models (Zaveri et al., 2010). The findings in this study will motivate improved representation of mixing state in models, and the measurement data will facilitate the detailed evaluation of modelled aerosols in simulations of urban air quality.

5. Conclusions and future directions

- We herein provided self-consistent 2-years real-time metadata on number density, distribution and selected physical and chemical characterization of airborne particles for a model cold climate urban site of Montreal.
- We observed distinct seasonal variations of aerosols in this cold-climate city, namely the highest nanoparticle density in winter.
- We demonstrate that in the cold-climate urban regions, the combination of winter meteorology (lowering of the boundary layer and suppression of vertical mixing) and higher pollution emission due to the enhanced usage of energy (transport sector and heating building) enhance nanoparticle density in the lower troposphere, which is currently not considered. Nevertheless, it is of potential significance in human health and air quality.
- We provided evidence that nanoparticle formation is of anthropogenic origin during the rush hours. The high-resolution S/TEM confirmed that airborne nanoparticles are not ubiquitously spherical; the nanoparticles exhibited varied structures - single/cluster, chain-like, regular, and irregular. We observed a suite of emerging contaminants such as Ni, Cd, Zn, Pb, and As in particles of all sizes, including in nanosize particles. Diverse anthropogenic sources of precursors, ever-increasing emission of emerging contaminants further complicating the urban atmospheres.
- Cold temperature, snow/ice surfaces, in addition to Urban built, are likely factors that can alter the atmospheric chemistry of cold-climate. Various salts are being used for the deicing of urban surfaces in cold-climate cities. These salts have been recently shown to produce tropospheric oxidants such as photolabile chlorine (Ryan Hall et al., 2020). We recommend that air quality and climate models adapt to the unique features of cold-climate urban regions.
- Further physical, chemical, biogeochemical, and health studies are required for better understanding and modelling of urban air quality in a changing climate and increasingly complex chemical emissions.
Author contribution

DP provided most data, data analysis and wrote the draft of the paper. AD provided insights and wrote a section. PAA wrote to the proposal which is the basis of this work, conceptualization, supervision, review, and editing of all drafts. The authors have declared that this is an original paper which is not submitted elsewhere, and all authors have read and agreed with the content.

Declaration of Competing Interest

The authors have declared that they have no known competing for financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References


