Role of snow in the fate of gaseous and particulate exhaust pollutants from gasoline-powered vehicles

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Abstract

Little is known about pollution in urban snow and how aerosol and gaseous air pollutants interact with the urban snowpack. Here we investigate interactions of exhaust pollution with snow at low ambient temperature using fresh snow in a temperature-controlled chamber. A gasoline-powered engine from a modern light duty vehicle generated the exhaust and was operated in homogeneous and stratified engine regimes. We determined that, within a timescale of 30 min, snow takes up from the exhaust a large mass of organic pollutants and aerosol particles, which were observed by electron microscopy, mass spectrometry and aerosol sizers. Specifically, the concentration of total organic carbon in the exposed snow increased from 0.948 ± 0.009 to 1.828 ± 0.001 mg/L (homogeneous engine regime) and from 0.275 ± 0.005 to 0.514 ± 0.008 mg/L (stratified engine regime). The concentrations of benzene, toluene and 13 out of 16 measured polycyclic aromatic hydrocarbons (PAHs), particularly naphthalene, benz[*a*] anthracene, chrysene and benzo[*a*]pyrene in snow increased upon exposure from near the detection limit to 0.529 ±0.058, 1.840 ±0.200, 0.176 ±0.020, 0.020 ±0.005, 0.025 ±0.005 and 0.028 ±0.005 ng/kg, respectively, for the homogeneous regime. After contact with snow, 50e400 nm particles were present with higher relative abundance compared to the smaller nanoparticles (<50 nm), for the homogeneous regime. The lowering of temperature from 25 ± 1 °C to (—8) e (—10) ± 1 °C decreased the median mode diameter of the exhaust aerosol particles from 69 nm to 57 nm ($p < 0.1$) and addition of snow to 51 nm ($p < 0.1$) for the stratified regime, but increased it from 20 nm to 27 nm ($p < 0.1$) for the homogeneous regime. Future studies should focus on cycling of exhaust-derived pollutants between the atmosphere and cryosphere. The role of the effects we discovered should be evaluated as part of assessment of pollutant loads and exposures in regions with a defined winter season.

1. Introduction

The analysis in a recent report of the World Health Organization attributes 23% of the global deaths to modifiable environmental factors (Prüss-Ustün et al., 2016). Air pollution, consumption of polluted water, contamination of soils and crops, exposures to harmful chemicals, etc. contribute to over a hundred known dis- eases and injuries (Prüss-Ustün et al., 2016). Out of the estimated 12.6 million annual deaths due to environmental factors in 2012, 8.2 million can be attributed to air pollution (Prüss-Ustün et al., 2016). The substantial environmental and health toll of air pollu- tion, including the pollutants expelled into the atmosphere with vehicle exhaust, has been demonstrated in numerous studies(Brugge et al., 2007; Donaldson et al., 2005; IARC (International Agency for Research on Cancer), 2013; Lighty et al., 2000; Newby et al., 2014; WHO (World Health Organization), 2013.

Air pollution, including that from engine exhaust, consists of both particles and gases (U.S.EPA, 2006), including semivolatile organic pollutants existing in both these fractions. These fractions contain toxic, carcinogenic, mutagenic and otherwise harmful components. Concentrations and composition of air pollutants at the time of inhalation determine their immediate toxicity, as well as contribution to elevation of lifetime risks of developing different forms of cancer, pulmonary and cardiovascular diseases, and other pathological conditions (Gardner and Gardner, 1993).

An ever increasing proportion of the global population lives in cities (Grimm et al., 2008), and urban population growth is concentrated in the regions of the world with the highest air pollution and a rapidly growing number of vehicles on the roads (Coale and Hoover, 2015). Urban locations are hotspots of air pollution largely because of the high vehicle exhaust concentration in ambient air (Tsang et al., 2008). Ultrafine particles and nano- particles (nanoaerosol) overwhelmingly prevail in internal com- bustion engine exhaust, but are not currently routinely monitored or regulated (Harris and Maricq, 2001; Myung and Park, 2012). The ultrafine size fraction of particulate air pollution has been linked to significantly higher blood pressure in schoolchildren (Pieters et al., 2015) and premature infant mortality (WHO (World Health Organization), 2013, 2014). The harmful gaseous constituents of exhaust include inorganic gases, such as nitrogen and sulfur oxides, carbon monoxide, and ammonia (Faiz et al., 1996). Other gaseous constituents comprise a complex mixture of various organic com- pounds. Many are toxic and/or carcinogenic, including saturated and (poly)unsaturated long-chain hydrocarbons, cyclic hydrocar- bons, benzene and its derivatives. The four most abundant toxic/ carcinogenic volatile organic compounds (VOCs) are known as BTEX (benzene, toluene, ethylbenzene and xylenes). The list also includes aldehydes, ketones, quinones, polycyclic aromatic hydro- carbons (PAHs) and their derivatives, and so on (U.S.EPA, 2006). Many of these compounds are relatively abundant in air in both gaseous and particulate form (semivolatile organic compounds, SVOCs). Among these air pollutants, BTEX are not only toxic themselves, but are reactive in the atmosphere, contributing to formation of tropospheric ozone and nitrogen oxides. BTEX generate O_3 and NO_x partly through peroxyacyl nitrates (PANs), which are respiratory irritants themselves, and some are mutagenic and major components of photochemical smog (Derwent and Jenkin, 1991). Therefore, BTEX emissions are a concern also due to their contribution to formation of PANs, which are more stable than ozone and NO_x, so they can be transported long distances. Often far from the original pollution sources, PANs decompose generating NO_x, which then causes harmful tropospheric ozone production (Derwent and Jenkin, 1991).

Exposure to another important category of exhaust-derived organic air pollutants, PAHs, is associated with such deleterious effects as lowered intelligence quotient (IQ) in children at 5 years old (Perera et al., 2009) due to impaired neurodevelopment as a consequence of prenatal exposure to PAHs (Perera et al., 2008). Exposure to PAHs is also associated with increased risk of skin, lung, urinary bladder, and gastrointestinal cancers (Kim et al., 2013). PAHs react with ozone, nitrogen oxides and other species in the air forming derivatives, some of which are much more toxic than the original PAHs themselves (Finlayson-Pitts and Pitts, 1999). There- fore, we see an urgent need to understand and mitigate the above- mentioned classes of exhaust-derived air pollutants.

What types of engines have been the focus of pollution research? Diesels emit much higher concentrations of particulate matter compared to gasoline-powered engines. For that reason, diesel exhaust is considered a greater concern, and is easier to measure and analyze. However, when it comes to the total number of engines in use, gasoline-powered vehicles dominate in North America (U.S.EPA, 2014a) and constitute a large proportion of the automobile fleet in other parts of the world (see Supplementary Material for statistics). Therefore, we decided to focus this study on gasoline-powered engines.

The contribution of the exhaust of internal combustion engines to air pollution varies with the extent and nature of urbanization, types of engines used, traffic patterns, microenvironments and weather patterns (Elminir, 2005; Shrestha, 2009). Two types of environmental factors influence the dispersion and composition of air pollutants after emission. The first type includes ambient temperature, relative humidity, wind speed and direction, and sunlight intensity. The second factor is interaction with environmental surfaces of the ground, bodies of water, hydrometeors (rain and snow), vegetation, and anthropogenic objects (Ariya et al., 2011; Błaś et al., 2010; Brack, 2002; Dominé and Shepson, 2002; Elminir, 2005; Escobedo et al., 2011; Mayer, 1983; Radke et al., 1980; Ulrich, 1983; Ulrich and Pankrath, 1983; Yang et al., 2005).

Within the climate system, understanding the effects of low ambient temperature and snowpack interactions on exhaust pollutants will contribute to understanding the degree and mechanisms of these pollutants' influence on climate. For instance, soot particles from aircraft engine exhaust are one of the important locally produced particle types that interact with clouds (Calvo et al., 2013; Zhou and Penner, 2014). It needs to be determined if vehicle exhaust particles have a similar potential to interact with clouds upon vertical transport and aging at different conditions in the troposphere.

It is known that chemical properties and aerosol particle size distribution of pollutants exhibit seasonal variations (Becker et al., 2005; Harris and Maricq, 2001; Myung and Park, 2012), and consequently seasonal variations affect the potential of particulate air pollution to cause different health effects (Becker et al., 2005). Do therefore low temperatures and presence of snow during winters affect the fate and effects of pollutants in urbanized areas of North America, Europe, and Asia? Falling snow has been shown to scavenge air pollutant particles from the atmosphere (Radke et al., 1980), and the same was shown for ground snowpacks (Franz and Eisenreich, 1998; Leuenberger et al., 1988; McNeill et al., 2012; Vasić et al., 2012). Snow is considered a more efficient scavenger of air pollutants than rain due to its higher porosity (Franz and Eisenreich, 1998). However, when snow melts, the pollutants incorporated in it partially transfer to the soil where the snow settled down (Meyer and Wania, 2008, 2011). Another part of snow-trapped air pollutants end up in meltwater runoff (Meyer and Wania, 2008, 2011), and some are potentially released back into the air (Ariya et al., 2011). That creates an overarching question: do environmental factors and processes involving snow contribute to different environmental and health effects of exhaust-derived air pollutants? To address this question, we set the specific aims of this study, first, to investigate the absorption by the snowpack of gaseous and particulate exhaust constituents from a modern gasoline internal combustion engine, and secondly, assess the impact of subfreezing ambient temperature and interaction with snow on composition of exhaust-derived air pollution.

2. Methodology

2.1. *Chemical analysis of snow*

The total organic carbon (TOC) and ion chromatography (IC) analyses were performed by standard automated techniques with the Aurora 1030 W TOC Analyzer (O.I. Corp., College Station, TX) and the Dionex ICS-5000 system (Dionex Corp., Sunnyvale, CA, USA) according to methods described in Supplementary Material.

For gas chromatography (GC) with detection by mass spectrometry (MS), a mass of 20 ± 0.1 g of each snow sample, before and after exhaust exposure, was placed in a 20 mL headspace vial, part #5182-0839 (Agilent Technologies, Santa Clara, CA, USA), and crimp-closed with a PTFE butyl rubber septum. Each sample was then warmed up to 23 °C, and a solid-phase microextraction (SPME) fiber was inserted into the liquid phase and kept there for 30 min while the vial was gently shaken in a lab rocker. Afterwards, the SPME fiber was withdrawn from the vial and inserted into the GC-MS for analysis, which is described in detail in Supplementary Material.

2.2. *Aerosol sampling and measurements*

Aerosol size distributions were measured using a Scanning Mobility Particle Sizer (SMPS), consisting of a model 3080 electrostatic classifier (EC) and a model 3786 Condensation Particle Counter (CPC) (TSI, Inc., Shoreview, MN, USA). The SMPS operated in the aerosol size range between approximately 15 and 650 nm. The sampling flow rate of the SMPS system was 0.3 L/min. The results of the SMPS measurements were adjusted with multiple charge and diffusion corrections during data post-treatment using the associated Aerosol Instrument Manager (AIM) software. Mode diameters of size distributions registered at target CO_2 concentrations for different conditions (warm exhaust, cold exhaust, snow exhaust) were analyzed using non-parametric, multiple pair comparison SteeleDwass test (see Tables S5 and S6 in Supplementary Material).

An electrostatic precipitator ESPnano Model 100 (ESPnano, Spokane, WA, USA), operating at the standard sampling flow rate of 0.1 L/min, was used to collect aerosol particles on electron microscopy grids. The grids were Formvar Carbon Film on 200 Mesh Copper Extra Thick Option B grids, 25e50 nm Formvar & 3e4 nm Carbon (SPI Supplies/Structure Probe, Inc., West Chester, PA, USA). This type of grids was chosen based on the robustness of the formvar film, which is required to withstand the corona discharge in the electrostatic precipitator, and based on the requirement for the substrate surface to be electrically conductive (carbon film). The electrostatic precipitator aspirates the aerosol, which passes through a corona discharge that charges and collects airborne particles onto the substrate. We set the corona voltage to 5 kV and sampling time to 100 s. The instrument's internal pump was set to run for additional 15 s immediately before sampling with no corona voltage applied in order to purge the instrument.

2.3. *TEM characterization of aerosol samples*

The Transmission Electron Microscopy grids (TEM-grids) containing aerosol samples collected using electrostatic precipitation were analyzed using a Philips CM200 transmission electron microscope with a field emission gun (Koninklijke Philips N.V., Amsterdam, Netherlands), equipped with a LaB6 cathode operating at 200 kV. The images were taken with an UltraScan™ 1000 2k 2k CCD Camera System, Model 895 (Gatan, Inc., Pleasanton, CA, USA). The Energy-dispersive X-ray spectroscopy (EDS) was performed with a Genesis EDS Analysis System (EDAX, Inc., Mahwah, NJ, USA).

2.4. *Snow sampling and handling*

The snow used in the experiments was collected in Montreal, Quebec, Canada in Mont-Royal Park (45°30′38.2″N 73°35′10.6″W) between 3 and 5 p.m. on February 26, 2014 right after a heavy overnight e morning snowfall. The collection was performed away from vehicular, pedestrian or pet traffic. Sterile equipment was used to transfer snow from the top 2 cm of the snowpack into ultraclean 950 mL certified (U.S.EPA, 1992) containers (Daniels Scientific, Inc., Greenville, SC, USA), following a previously described strict sampling procedure (Franz and Eisenreich, 1998; McNeill et al., 2012; Meyer and Wania, 2008; Nazarenko et al., 2015; Vasić et al., 2012). The samples were then transferred to a 39 °C freezer for storage until the experiments were performed. For the snow exposure experiments, batches of 100 ± 5 g of snow were loaded into the chamber. For snow analyses, we took samples of snow from the original snow environmental sample storage container and from the chamber after exposure to cold dilute exhaust. Snow was transferred from the chamber with sterile HDPE sampling spatulas (Bel-Art Products, Inc., Wayne, NJ) into sterile Falcon™ 50 mL Conical Centrifuge Tubes (Corning Life Sciences, Inc., Tewksbury MA, USA), and immediately placed in a 39 °C freezer. Mass of snow samples was determined by weighing the empty and snow-filled containers.

2.5. *Snow exposure system*

Exhaust was brought in contact with snow in an environmental chamber system shown in Fig. S1. It was a modification of the setup described in detail in another publication (Nazarenko et al., 2015). Briefly, the chamber system maintains a simulated snowpack of natural snow. We refer to the snow in the chamber as simulated snowpack because snow could only be placed in the chamber following disturbance of the natural snowpack structure, as it existed in the field before sampling. In different experiments, the diluted exhaust is passed through the empty chamber at either warm or cold temperature, or passed over the simulated snowpack at the bottom of the chamber. The system maintains snow frozen under constant flow of cold air or cold dilute exhaust. A log of temperature changes during a typical experiment, monitored at different points within the system, is provided in Supplementary Material (Fig. S2).

2.6. *Production of exhaust*

The direct injection spark ignition engine used in our experiments was a 4-cylinder EP6DT class engine, from Groupe PSA (Paris, France), with a displacement of 1598 cm^3. The engine has been installed in several popular makes of light-duty vehicles since its first introduction in 2006. The engine's main parameters are described in another publication (Fournier et al., 2016). The engine ran at 2000 rotations per minute (RPM) at a break mean effective pressure of 3.5 bar (350 kPa) using homogeneous injection and stratified injection modes. Homogeneous injection is defined as fuel injection taking place during the intake stroke with the goal of generating a homogeneous fuel-air mixture. Stratified fuel injection takes place near the end of the compression stroke, so it generates a fuel-rich mixture in the vicinity of the spark plug but with an overall lean air-fuel mixture. Operation in both these modes allowed quantifying their respective impact on gaseous and particulate (aerosol) pollutant emissions and their effects at different ambient temperature and in the presence of snow. The engine, the dynamometer required to maintain engine load, and the necessary equipment to conduct the experiments were located in an engine test cell where ambient temperature was maintained at 23 ± 0.5 °C.

Maintaining a constant temperature was important to prevent the effect of engine operating temperature on composition of the raw exhaust. This approach allowed to decouple the effects of ambient temperature, at which the expelled exhaust dissipates, from the effects of engine temperature, which had been the subject of other studies (Bielaczyc and Merkisz, 1998; Mathis et al., 2005). The details of engine operation in homogeneous and stratified regimes are provided in Supplementary Material.

2.7. *Monitoring of exhaust dilution ratio and composition*

Raw exhaust gases were analyzed for CO_2, CO, NO-NO_2-NO_x, formaldehyde, ammonia, methane, and non-methane hydrocarbons in real time using an FTIR (Fourier Transform InfraRed spectroscopy) instrument model 600 from California Analytical Instruments (CAI), Inc. (Orange, CA, USA) and its associated OPUS software. The exhaust gases were transported to the FTIR at a temperature of

191 °C in a heated exhaust transport line, which allowed to prevent water condensation.

The exhaust gas sample was diluted to a ratio of 8:1 based on CO_2 emissions before being passed to the chamber system. The dilution system is made of a venturi and a secondary air supply that are both fed by pressure regulating flow controllers. A total of 10 L/ min of dilution air was split allowing the venturi to aspirate the raw exhaust achieving the initial 2:1 dilution. Then the diluted exhaust was passed into a chamber where a second dilution took place achieving a total dilution ratio of 8:1. The concentration of CO_2 and O_2 was monitored using a CO_2/O_2 analyzer, model 902P (Quantek Instruments, Inc., Grafton, MA, USA), equipped with a data logger, model HOBO U12 (Onset Computer Corp., Cape Cod, MA, USA). The sampling flow rate of the CO_2/O_2 analyzer was 0.3 L/min. The target CO_2 concentration during snow exposure was 2% and 1% for the homogeneous and stratified regimes, respectively. The difference in the target CO_2 concentration for the two modes stems from the difference in the fuel-air mixing ratio and the resulting difference of the concentration of combustion products in the exhaust. The volume of air per unit mass fuel used in the stratified engine mode was twice higher than in the homogeneous engine mode.

3. Results and discussion

3.1. *Transmission electron microscopy*

We examined the aerosol particles in the chamber outflow after electrostatic collection (Fig. 1). The purpose of the electron microscopy investigation was to determine the abundance, diameter, shape, structure, state of agglomeration, and elemental composition of exhaust-derived aerosol particles in the dilute exhaust under different temperature conditions and after dilute exhaust came in contact with snow.

A large number of TEM images and associated EDS elemental analysis spectra were acquired and analyzed, but only selected images are shown in Fig. 1. The discussion here is based on the totality of the electron microscopy observations. In both homogeneous and stratified engine regimes, and all temperature and snow presence conditions, we observed a substantial number of aggregates with a diameter around 0.5 mm, which was consistent with a corresponding peak in aerosol size distributions, discussed later (Fig. 4). These aggregates mostly consisted of two distinct types, both shown in Fig. 1a. The first type was represented by tightly packed solid aggregates of particles of various sizes, with a high content of carbon, and some with iron, copper and other elements such as aluminum, silicon and sulfur (Fig. 1i, j, k, l). The second type was represented by loosely packed aggregates resembling bundles or chains of fused 10e50 nm nanoparticles, almost exclusively composed of carbon and some oxygen (Fig. 1a, c, d, g, h). The solid aggregates dominated for the homogeneous engine regime, while the loose bundle-like carbonaceous aggregates dominated for the stratified regime. The number of *individual* (unattached) nanosized (<100 nm, also known as nucleation mode or ultrafine) particles and aggregates was comparatively low, indicating that they were either volatile and thus did not persist on the TEM-grids until analysis, or that they were comprised of low-electron-contrast substances, particularly organic compounds. These findings are consistent with previous research that showed a predominant content of organic carbon and volatile substances in the nanoparticle fraction of exhaust-derived aerosols (Kittelson, 1998). As these nucleation mode particles can form and change (evaporate, grow by condensation, agglomerate) during cooling and dilution of exhaust (Kittelson, 1998), it is mechanistically probable that temperature can substantially affect the size distribution and dynamics of exhaust aerosol in the nanosize (nucleation mode) range.

3.2. *Chemical analysis of exhaust and snow*

The concentrations of several measured ions in the exposed snow did not change significantly with the exception of the nitrate concentration, which was found to be significantly higher in snow that was exposed to exhaust generated in both homogeneous and stratified regimes (Fig. 2).

The increase of the nitrate ion content was approximately twice as large when the engine was operated in homogeneous mode rather than the stratified mode. This is consistent with the higher concentrations of NO and NO_2, measured by FTIR in the dilute exhaust from the engine operating in homogeneous mode (Fig. 3). For the homogeneous mode, the concentrations of NO were 335 ± 31, 373 ± 21 and 378 ± 16 ppm, while for the stratified mode, they were 238 ± 25, 228 ± 25 and 228 ± 23 ppm for the warm, cold and snow exhaust, respectively. The concentrations of NO_2 for the homogeneous mode were 37 ± 2.9, 52 ± 9.9 and 50 ± 8.8 ppm, and for the stratified mode: 32 ± 6.1, 33 ± 5.0 and 33 ± 4.9 ppm for the warm, cold and snow exhaust, respectively.

The engine operation mode had a substantial effect on the concentrations of non-methane hydrocarbons (NMHC) and NO in exhaust passed through the chamber. While the concentration of NO was reduced in the stratified mode, the concentration of NMHC was substantially higher compared to experiments with the homogeneous mode for engine operation. Effects of temperature and presence of snow on concentrations of the measured gaseous constituents of exhaust were minimal.

For the engine operating in both homogeneous and stratified regimes, we observed a substantial increase of the total organic carbon concentration in the snow after 30 min of passing dilute exhaust over 100 ± 5 g of snow in the chamber (Table 1). There was a variation in CO_2 concentration during snow exposure around the target 2% and 1% for the homogeneous and stratified regimes, respectively. The duration of exposure slightly deviated from 30 min due to the constraints of the experimental design. Hence, the concentrations were normalized to exactly 30 min for exposure time and to either 1.0% (stratified regime) or 2.0% (homogeneous regime) for CO_2 concentration in the dilute exhaust.

The increase of the TOC in the exhaust-exposed snow above the TOC measured in the original natural unexposed snow was approximately twice as great for the exposure to exhaust generated by the engine operating in the homogeneous mode. It is consistent with the electron microscopy data, which showed a substantially increased presence of medium-electron-contrast to low-electron-contrast carbon-rich and oxygen-rich particles (likely organic) in the exposed snow compared to the original snow. The organic substances in the snow are expected to be present in both dissolved and particulate form based on the chemical nature of pollutants in the exhaust (U.S.EPA, 2006).

Two specific classes of organic pollutants in snow were chosen to be quantified because of their known toxic and/or carcinogenic properties (Chang and Chen, 2008; Chen et al., 2008; Kim et al., 2013; Liao et al., 2011; Mazzeo et al., 2011) and their abundance in gasoline-powered engine exhaust (U.S.EPA, 2006): single- aromatic-ring BTEX and multiple-aromatic-ring PAHs. The results of the quantitative analysis of BTEX and PAHs in snow samples using SPME and GC-MS are presented in Table 2, with an additional data set for another set of repeat experiments presented in the Supplementary Material (Table S4).

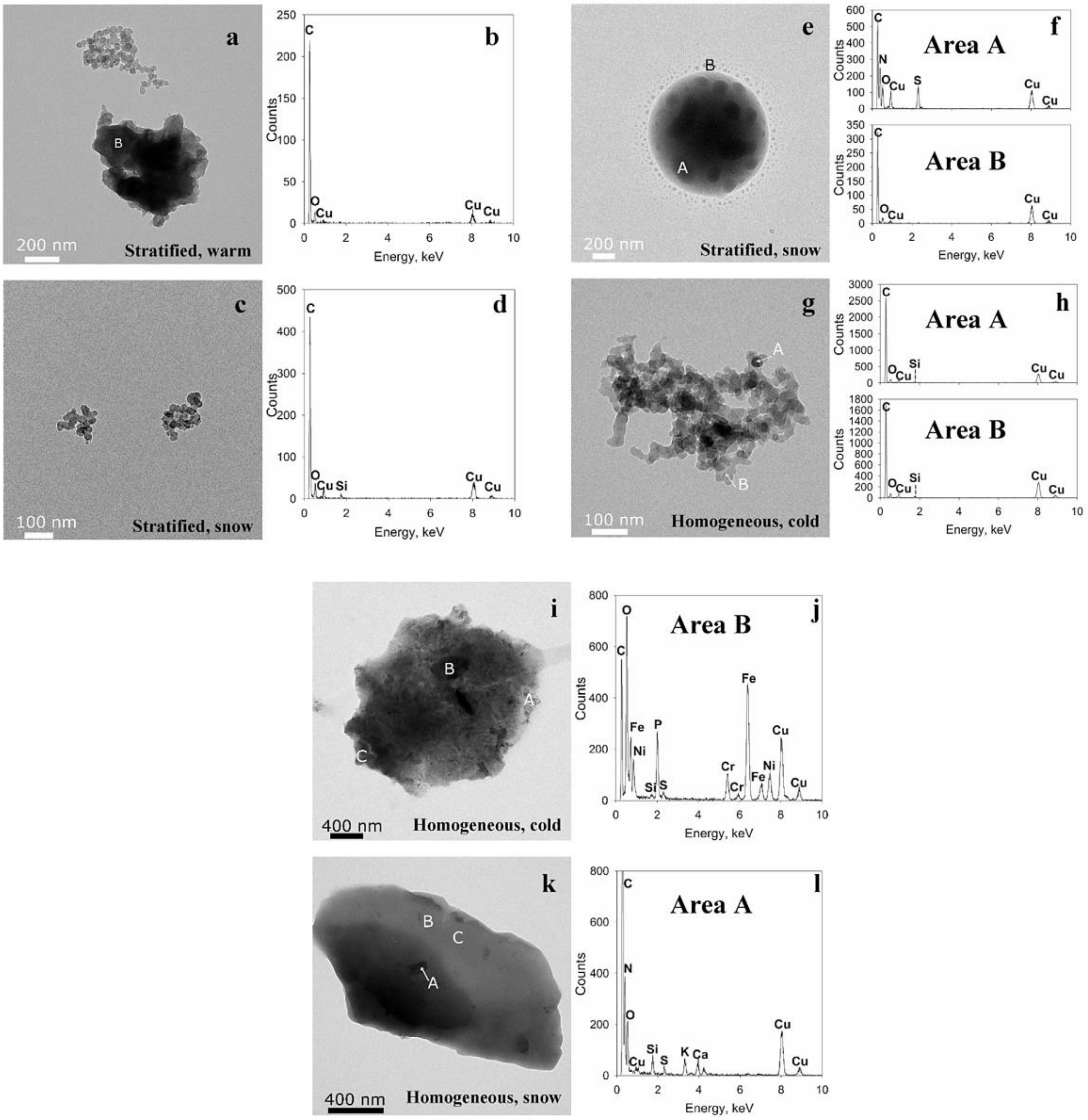

Fig. 1. Transmission electron microscopy (TEM) images and energy-dispersive spectra (EDS) identifying the chemical elements in the aerosol particles, collected from dilute exhaust passed through the chamber: in stratified engine regime at warm temperature (a, b), cold temperature over snow (c, d, e, f), and homogeneous engine regime at cold temperature (g, h, i, j) and cold temperature over snow (k, l). The vertical dashed lines in some EDS spectra lead to smaller peaks. The EDS spectra for areas A and C in image "i" and for areas B and C in image "k" are in the Supplementary Material (Figs. S3 and S4).

The concentrations of the organic pollutants in exhaust-exposed snow were normalized to exactly 2.0% CO_2 concentration for the homogeneous regime and 1.0% CO_2 for the stratified regime, and 30 min exposure time. These parameters were chosen for the same reasons and are the same as for the TOC analysis. We observed that the concentrations of all measured pollutants in the original un- exposed snow, with the exception of toluene, were close to or below the limit of detection. Upon exposure of snow to dilute exhaust, we measured marked increases of concentrations of many of the measured pollutants in snow. For most compounds, these increases of organic pollutants in exhaust-exposed snow were substantially greater for the homogeneous engine mode compared to the stratified mode. Importantly, the FTIR data showed a greater concentration of total non-methane hydrocarbons in the exhaust of the engine operating in stratified mode (Fig. 3), pointing to a likely substantial difference in the chemical nature of the organic compound composition in the exhaust from homogeneous vs. stratified engine operation regimes.

The measured single-ring aromatic hydrocarbons that had the highest concentration increases in the snow following its contact with the exhaust are benzene and toluene. Among the 16 analyzed PAHs, these four had the highest concentration increases in the snow: naphthalene, followed by benz[*a*]anthracene, benzo[*a*]pyrene, and chrysene. Increased concentrations of the following 9 analyzed PAHs were detected with some inconsistency: acenaphthylene, fluorene, phenanthrene, fluoranthene, pyrene, benzo [*b* fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-*cd*]pyrene, and benzo[ghi]perylene. The inconsistency was likely caused by the inherent variability in engine operation and by deposition in- homogeneity of pollutants into the simulated snowpack. However, it is evident that they too have a potential to accumulate in snow exposed to exhaust of gasoline-powered vehicles.

Traffic-related pollutants were previously reported in urban snowpack in field studies (Hautala et al., 1995; Kuoppamäki et al., 2014). However, the observations in the chamber, isolated from the asphalt road surface and other contaminating factors, allowed exclusion of interfering pollution sources, which are a factor in field studies. Asphalt and coal-tar-based sealcoats and road surfaces are known to contain PAHs and other harmful organic substances, including those similar to pollutants in exhaust (Takada et al., 1991). PAHs are found in water runoff from these surfaces (Mahler et al., 2014), and contribute to comparatively very high PAH exposure of road and asphalt workers through the inhalation route, with associated adverse health effects (Yilmaz et al., 2016). Conversely, the chamber-based results presented here single out and emphasize vehicle exhaust as a source of this specific type of pollution.

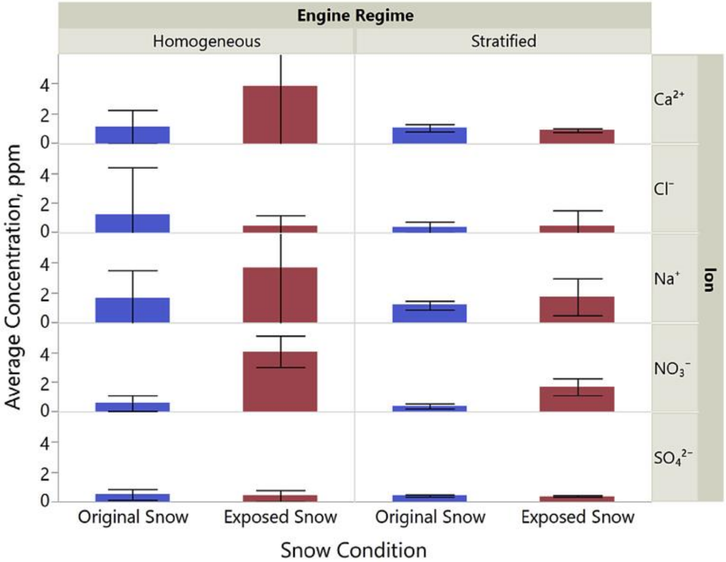

Fig. 2. Inorganic ions in snow before and after exhaust exposure. Average values ± 95% CI (confidence interval of the mean) shown. Exact values are provided in the Supplementary Material (Table S1).

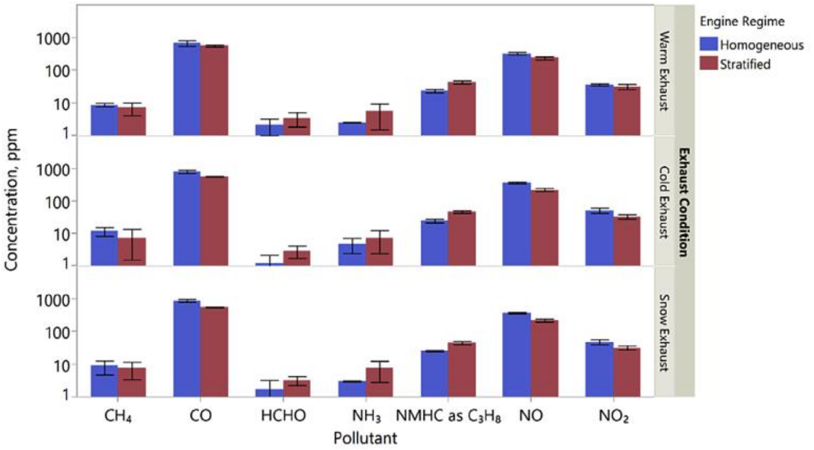

Fig. 3. Concentration of gaseous constituents of dilute exhaust. Each error bar is constructed using one standard deviation from the mean.

Exhaust-derived PAHs deposit in the snowbanks along the roadways, with a rapid decrease of concentrations in snow farther from the roads (Hautala et al., 1995; Kuoppamäki et al., 2014), which is enhanced by their lower volatility at low ambient temperatures. As the snow metamorphoses, different organic pollutants redistribute in the changing snowpack. The hydrophobic compounds are predominantly retained in the remaining snow, the lipophilic may remain associated with organic particles, others are released with early meltwater or into the air depending on their solubility and volatility (Meyer and Wania, 2008, 2011; Wania, 1997; Wania et al., 1998). The PAHs concentrate in the snow due to their low volatility and association with particulate matter. In this concentrated state within the snowpack, the accumulated PAHs find themselves in a reaction medium for photochemical transformations (Yu, 2002). The high porosity and optical transparency of snow and the availability of the pseudo-liquid aqueous phase in the snowpack above 20 °C (Grannas, 2014) create enhanced conditions for complex photochemistry involving PAHs. The number of possible photochemical reactions is high (Finlayson- Pitts and Pitts, 1999; Grannas et al., 2007), and they include photodegradation of PAHs into less toxic molecules, as well as the formation of more toxic, carcinogenic and mutagenic substances, such as quinones, aldehydes, and hydroxyl-PAHs. Amino-PAHs, common in exhaust (U.S.EPA, 2006), can be oxidized into the mutagenic nitro-PAHs (Yu, 2002). The original pollutants and products of these chemical transformations can be further released into the air (Ma et al., 2011), soil (Bengtsson, 1984; Novotny, 1988), runoff (Oberts, 1994) and groundwater (Meyer and Wania, 2008, 2011). The photoproducts of PAHs' transformations are also generally more water-soluble, and therefore more mobile and bioavailable (Yu, 2002). PAHs also persist in soils and sediments and are therefore listed as U.S. EPA priority pollutants (U.S.EPA, 2014b). In soil, photochemistry is limited. Consequently, the potential enhancement of photochemistry involving PAHs by their accumulation in the snowpack likely alters the overall environ- mental effects, as well as health effects of PAH pollution from vehicles.

Equally important for the total environmental and health effects is the issue of long-range transport of PAHs and products of their photochemical transformations, as well as other organic pollutants (Bjørseth et al., 1979; Halsall et al., 2001; Welch et al., 1991; Yang et al., 2007). Half-lives of certain PAHs in snowpack are relatively short when it is illuminated with sunlight (Ram and Anastasio, 2009). Therefore, when PAHs and certain other pollutants accumulate in the snowpack, compared to the environmental situation when there is no snow, we can expect alteration of these pollutants' concentrations and chemical composition as they are transported long distances from sources. Therefore, snowpack effects are not just local, but regional and global.

The engine injection strategy had a profound effect on the rate of accumulation of organic pollutants in the exhaust-exposed snow in part because there is a difference in equivalence ratio between each injection strategy (Table 1, Table 2, Table S4). Thus, it is suggested that studies should be pursued to quantify the influence of the injection strategy, equivalence ratio, exhaust after treatment, and other engine parameters on pollutant emissions, as to identify pollutants with the highest potential to contaminate snow.

It is important to note that besides the 16 priority PAHs quantified in this study, other toxic and carcinogenic polycyclic aromatic compounds (PACs) exist. These other PACs may be involved in the exhaust-snow interactions and snowpack processes and have an equal or even higher potential to cause damage to public health and the environment (Andersson and Achten, 2015). Examples of these compounds include higher molecular weight PAHs, alkylated PACs, hetero-PACs, oxy- and nitro-PAHs, some substantially more toxic than the 16 priority PAHs (Andersson and Achten, 2015). Andersson and Achten recently proposed expanded lists of several categories of PACs highly relevant for evaluation of toxicity in the environment (Andersson and Achten, 2015). These PACs could be part of future research and monitoring of the fate and effects of exhaust-derived air pollutants, including photochemistry in the snowpack.

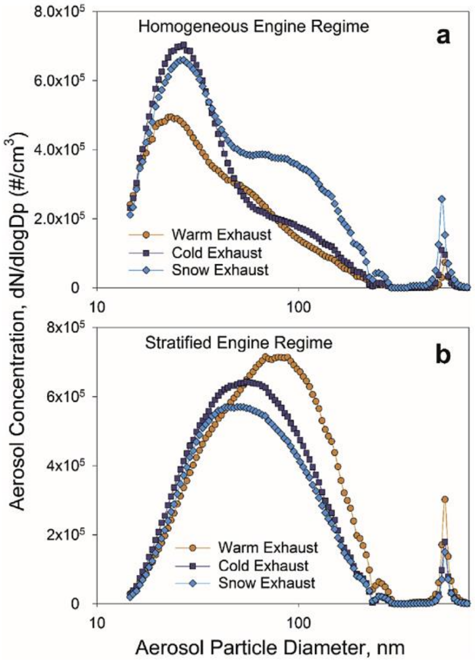

Fig. 4. SMPS Aerosol size distributions of dilute exhaust passed through the chamber at warm and cold temperature and in the presence of snow, as defined in Methods.

Table 1
Total Organic Carbon (TOC) in snow before and after exposure to exhaust. Average TOC concentrations in mg per 1 L of melted snow ± *s* (one standard deviation based on replicate analyses of the snow samples) shown.

Engine operation mode and snow condition		Average TOC ± *s*, mg/L
Homogeneous Engine Mode	Original Snow	0.948 ± 0.009
	Exhaust-Exposed Snow	1.509 ± 0.004
Stratified Engine Mode	Original Snow	0.275 ± 0.005
	Exhaust-Exposed Snow	0.537 ± 0.005

Table 2
Concentrations of organic pollutants in snow.

Pollutant	Unexposed snow	Exposed snow, Stratified engine mode	Exposed snow, Homogeneous engine mode
Benzene	<0.001	0.223 ± 0.025	1.488 ± 0.160
Toluene	0.310 ± 0.030	0.776 ± 0.085	2.182 ± 0.240
Ethylbenzene	0.030 ± 0.005	<0.001	<0.001
m-Xylene	0.030 ± 0.005	<0.001	<0.001
Naphthalene	0.090 ± 0.010	0.074 ± 0.008	0.485 ± 0.050
Acenaphthylene	0.004 ± 0.005	<0.001	0.223 ± 0.025
Acenaphthene	0.010 ± 0.005	<0.001	<0.001
Fluorene	<0.001	<0.001	<0.001
Phenanthrene	0.017 ± 0.005	<0.001	0.208 ± 0.023
Anthracene	<0.001	<0.001	<0.001
Fluoranthene	0.004 ± 0.005	<0.001	0.417 ± 0.046
Pyrene	0.002 ± 0.005	<0.001	0.097 ± 0.011
Benz [*a*]anthracene	0.001 ± 0.005	0.009 ± 0.005	0.089 ± 0.010
Chrysene	0.001 ± 0.005	0.011 ± 0.005	0.029 ± 0.005
Benzo [*b*]fluoranthene	<0.001	<0.001	0.074 ± 0.008
Benzo [k]fluoranthene	<0.001	<0.001	0.338 ± 0.037
Benzo [*a*]pyrene	0.001 ± 0.005	0.012 ± 0.005	0.058 ± 0.006
Dibenz [a,h]anthracene	<0.001	<0.001	<0.001
Indeno [1,2,3-*cd*]pyrene	<0.001	<0.001	0.043 ± 0.005
Benzo [ghi]perylene	0.001 ± 0.005	<0.001	0.074 ± 0.005

3.3. *Aerosol size distribution analysis*

The results of the real-time aerosol monitoring of dilute exhaust that passed through the chamber under various experimental conditions are presented in Fig. 4.

Only the aerosol size distributions measured when CO_2 con- centration in the exhaust was 2.0 ± 0.05% in the homogeneous engine mode and 1.0 ± 0.05% in the stratified engine mode were considered. It is evident from the shape of particle size distributions that smaller particles dominated in homogeneous mode while larger particles prevailed in stratified mode at similar number concentrations, so total particle mass was higher in stratified mode, consistent with previous research (Sementa et al., 2012). The aerosol measurements showed that certain particle size fractions (50e400 nm) in exhaust from the engine operating in homogeneous mode have a higher relative abundance in dilute exhaust after contact with snow, as compared to freezing, (—8) e (10) ± 1 °C, and warm, 25 ± 1 °C ambient temperature measurements. At the same time, presence of snow diminished the total number density of nanoparticles <50 nm, consistent with our earlier study with a different type of gasoline-powered engine (Nazarenko et al., 2015). Qualitatively, the substantial differences of shapes of the aerosol size distributions for exhaust at warm, cold temperature, and cold exhaust that came in contact with snow reflect different relative abundances of aerosol particles of different sizes. When the vehicle engine was operated in the stratified regime, freezing ambient temperature ~~(~~(-8) e (10) ± 1 °C) shifted the most abundant (mode) aerosol size in dilute exhaust to a smaller 57 nm mode, compared to the most abundant aerosol size at warm ambient temperature (69 nm), p 0.0014. The presence of snow decreased the mode size even more (51 nm) compared to exhaust at warm temperature, p 0.0001. The mode particle diameters in the ultrafine aerosol size range <100 nm in dilute exhaust produced by the engine running in homogeneous regime (~20e30 nm) were much smaller than the mode aerosol diameters for the stratified engine regime (~45e70 nm). For the homogeneous engine regime, lowering of temperature and addition of snow increased mode particle size in the ultrafine particle size range from 20 nm to 27 nm ($p < 0.1$). In the second (typical) particle concentration peak around 450e600 nm, for the homogeneous mode only, we observed a shift of the mode particle diameter with the decrease in ambient temperature and introduction of snow from ~530 nm (warm temperature) to ~ 520 nm (freezing temperature) and ~515 nm (snow). The large concentration of carbonaceous and organic-like particles observed in exhaust-exposed snow using electron microscopy also supports a substantial capacity of snow to take up exhaust-derived pollution particles.

The fact that aerosol size distribution is affected by the operating mode of the engine and by the ambient temperature and interaction with snow is important for the following reasons. First, certain semi-volatile organic pollutants, including PAHs, exist in both the particulate and gaseous fractions (Kim et al., 2013), with ambient temperature influencing gas-to-particle partitioning. Second, the deposition efficiency of differently sized aerosols in the head airways, tracheobronchial and alveolar regions of the human respiratory system depends on particle size (Mayer, 1983). Third, gaseous constituents interact with aerosol particles (Lighty et al., 2000; Yu, 2002). There is increasing evidence that ultrafine par- ticulate air pollution may be more harmful per unit mass concen- tration than larger pollutant particles (Grannas, 2014; Tsang et al., 2008). Therefore, it is important that snowpack seems to reduce the concentration of the small (<50 nm) nanoparticulate fraction of exhaust pollution, yet increase larger ultrafine particles (50e100 nm) and fine particles up to 400 nm (100e400 nm). The substantial differences in effects for smaller (<50 nm) and larger (50e100 nm) ultrafine particles suggest that there is a need to study these two fractions of ultrafine particles separately rather than measure and evaluate the health and environmental effects of the combined 1e100 nm ultrafine particle fraction.

Snowpacks are dynamic and have various structure depending on the nature of snow that formed them initially and the envi- ronmental conditions during and after snowpack formation. It would be expected that the effects of snow on the exhaust-derived air pollutants change over time as the snow metamorphoses and pollutants from different sources continue accumulating at the air- snow interface and in different phases within the snowpack. Future studies should therefore explore evolution of snowpack and how it impacts the physical and chemical processing of the interacting pollutants.

The chamber measurement approach we employed in this study eliminated interference from the background atmospheric aerosol and background organic pollutants such as PAHs e a factor in field measurements. Normally, ambient concentrations of ultrafine aerosols are higher in wintertime (Ariya et al., 2011), so in a field study it could mask the decrease of the nanoparticulate fraction at low temperatures and in the presence of snow that we observed. Therefore, chamber-based experiments are of high value to complement field observations in future research.

Further physical chemistry and biogeochemistry research is required to narrow the gap in the knowledge of snow-atmosphere-soil/water feedbacks in urban and other polluted regions. Additional studies of snow processes affecting the albedo, snow-borne particle size, distribution, configuration, chemical composition, heterogeneous reactions, surface properties, and photochemistry are essential (Ariya et al., 2009, 2015). It has become increasingly clear that both the climate and toxicity-health impact of aerosols are significantly affected by physical and chemical characteristics and processes such as size, gas-particle partitioning, liquid-liquid phase separation, kinetics, surface tension, viscosity, molecular configuration, surface properties, and chemical composition (Buzea et al., 2007; Grassian, 2008). There is evidence that reactions of halogens with organic and trace metals take place in the gas phase and at environmental interfaces with snow and ice (Ariya et al., 1999; Coquet and Ariya, 2000). We therefore urge further field, laboratory and modeling studies of the complex chemical trans- formations involving both metals and organic compounds in snow, ice, and air-snow/ice interfaces.

The present work can contribute to the assessment of pollution emission and transformation from transport industries in northern locations, particularly in light of the current and proposed regulations focusing on pollution reduction in the transportation sector (U.S.EPA, 2016), including ground-based fossil-fuel-powered vehicles (Government of Canada (2016); Litman, 2013) and aircraft ICAO (International Civil Aviation Organization), 2016.

4. Conclusions

Further studies and environmental monitoring could help identify the most harmful pollutants in the context of the total fate and effects of exhaust-derived pollutants in the air, snowpack, meltwater, and soil within the complex environment. These iden- tified organic pollutants should be targets for reduction in formulations of gasoline and in optimization of engines and catalysts.

The differences between aerosol size distributions in dilute exhaust depending on ambient temperature and presence of snow distinctively manifested in the following specific size ranges: < 50 nm, 50e100 nm, 100e400 nm, and 515e530 nm. The size distribution of inhaled aerosol particles is known to influence the degree and nature of adverse health effects caused by exposure to air pollution (Hetland et al., 2004; Scott et al., 2012), as well as the environmental effects (Elias et al., 2009; Levin and Cotton, 2008; Olszyk et al., 1989). Therefore, this finding points to potential differences in health and environmental effects of exhaust-derived air pollution depending on the ambient temperature and presence, amount and condition of the snowpack. The effects also substan- tially depended on the operating regime of the engine (homogeneous vs. stratified modes) and manifested to a different extent for different pollutants. Consequently, ambient temperature and the presence of snow should be considered in future exposure, health and environmental studies of vehicle-exhaust-derived air pollution, and the fate and effects of pollutants should be correlated based on the above aerosol size ranges, with consideration of specific engine operation mode.

We trust that this study will encourage future studies, especially in government research laboratories. The government environmental protection agencies need to start routine monitoring of traffic-derived pollutants in urban snow and ice, as well as the meltwater from it. The results of this monitoring will help deter- mine the extent of ongoing harm to the environment, as well as to the public and occupational health, particularly for the road workers and other heavily exposed workers, such as policemen and professional drivers. Likewise, the monitored air pollution levels and composition should be correlated with the weather and snowpack presence and condition to determine corresponding human inhalation exposure levels. The findings of such monitoring programs and occupational/public health studies should be communicated to the regulators, so appropriate action can be taken and standards can be set to adequately protect people and the environment.

This research is expected to trigger further efforts to understand air pollution in northern winter and incentivize developers of regulations for air quality and vehicle emissions to focus on the specifics of air pollution in regions of the world with a defined winter season. The findings should motivate environmental protection agencies and regulators to improve the understanding of the interaction between harmful emissions and various atmospheric conditions. Finally, the obtained results suggest that sub- zero temperature behavior and interactions with snow of exhaust- derived aerosols and gases should become an important topic of climate research and modeling.

Competing interest statement

The authors declare no conflict of interest.

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