Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Electronic Supplementary Information

Role of Snow and Cold Environment in the Fate and Effects of Nanoparticles and Select Organic Pollutants from Gasoline Engine Exhaust

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This document contains supporting figures, tables, methods, and data.

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Supplementary Figures

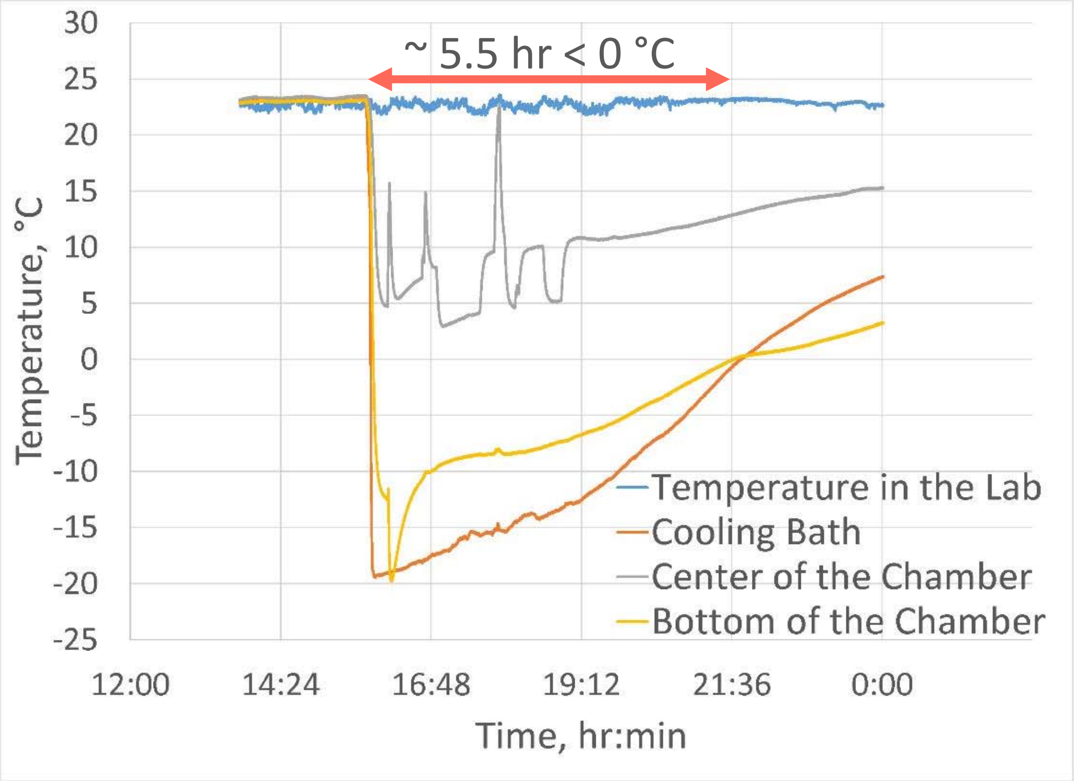
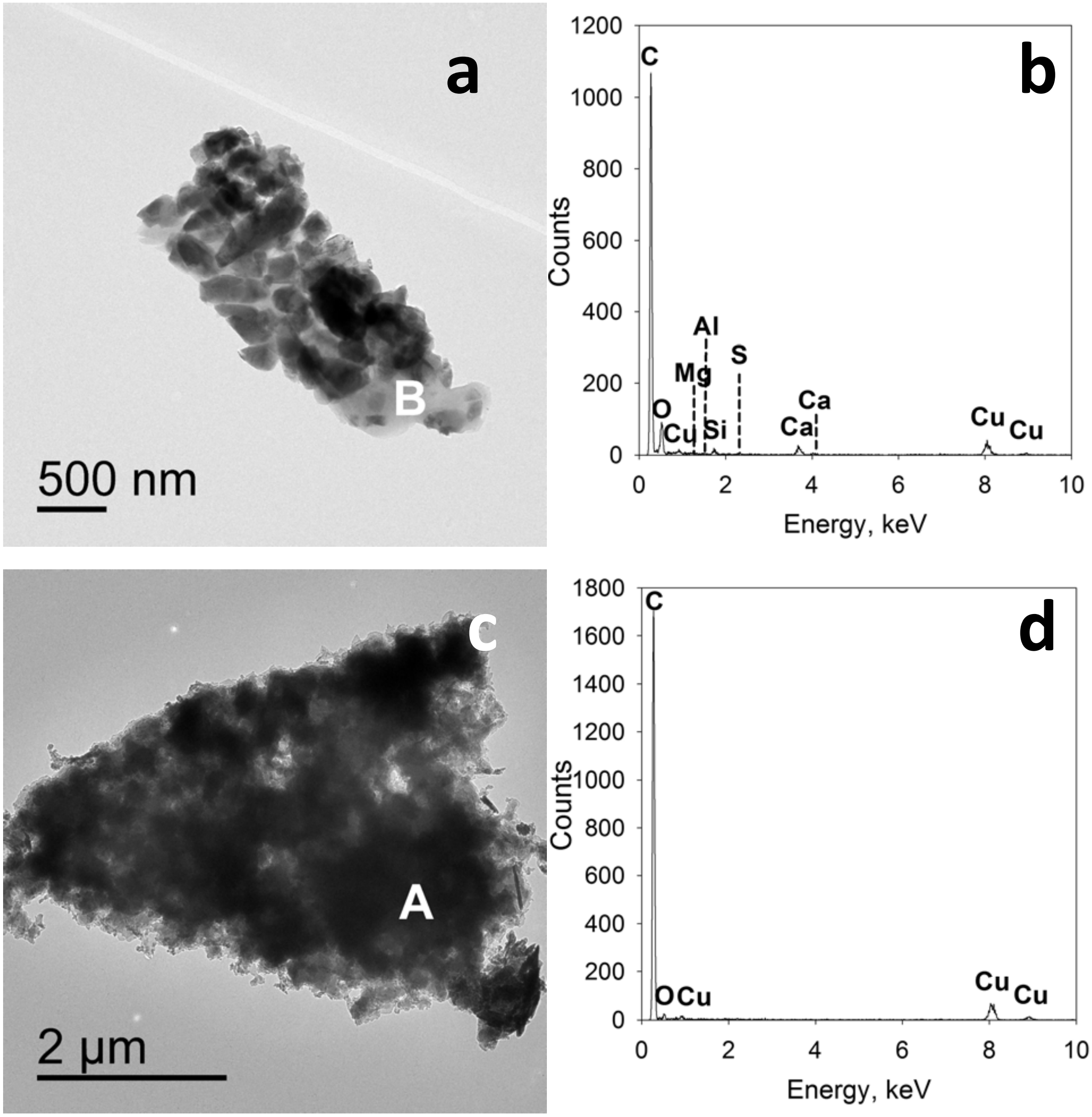


Figure S1 Representative temperature dynamics in the experimental system during a typical experiment.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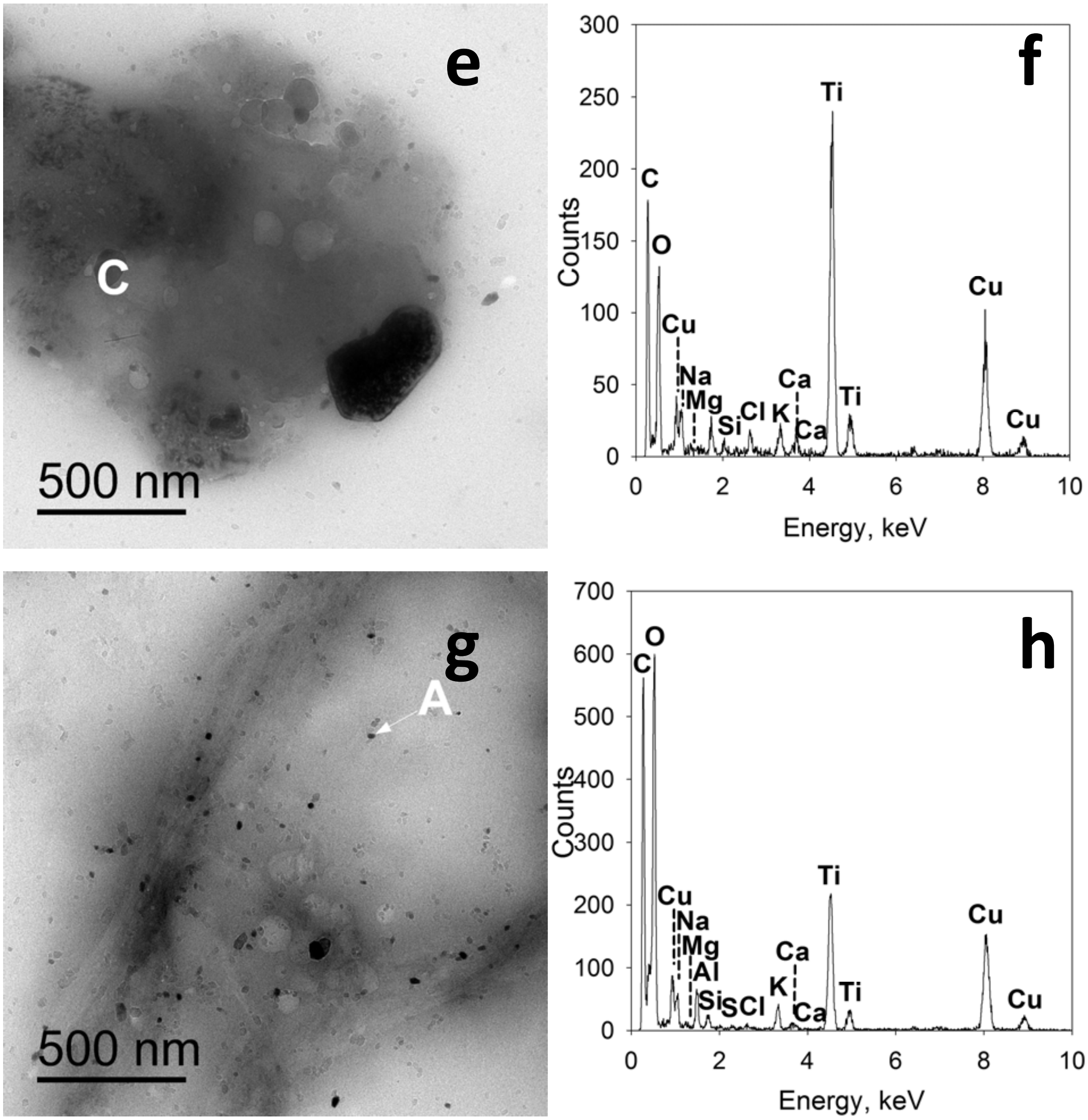

Figure S2 Supplementary transmission electron microscopy (TEM) images and energy-dispersive spectroscopy (EDS) spectra identifying the chemical elements in the particles: original snow (a, b), exhaust-exposed snow (c, d), aerosol particles captured from exhaust passed through an empty cold chamber (e, f), and from cold exhaust (gasoline with octane number 87 burned) passed over snow in the chamber (g, h). The vertical dashed lines lead to smaller peaks.

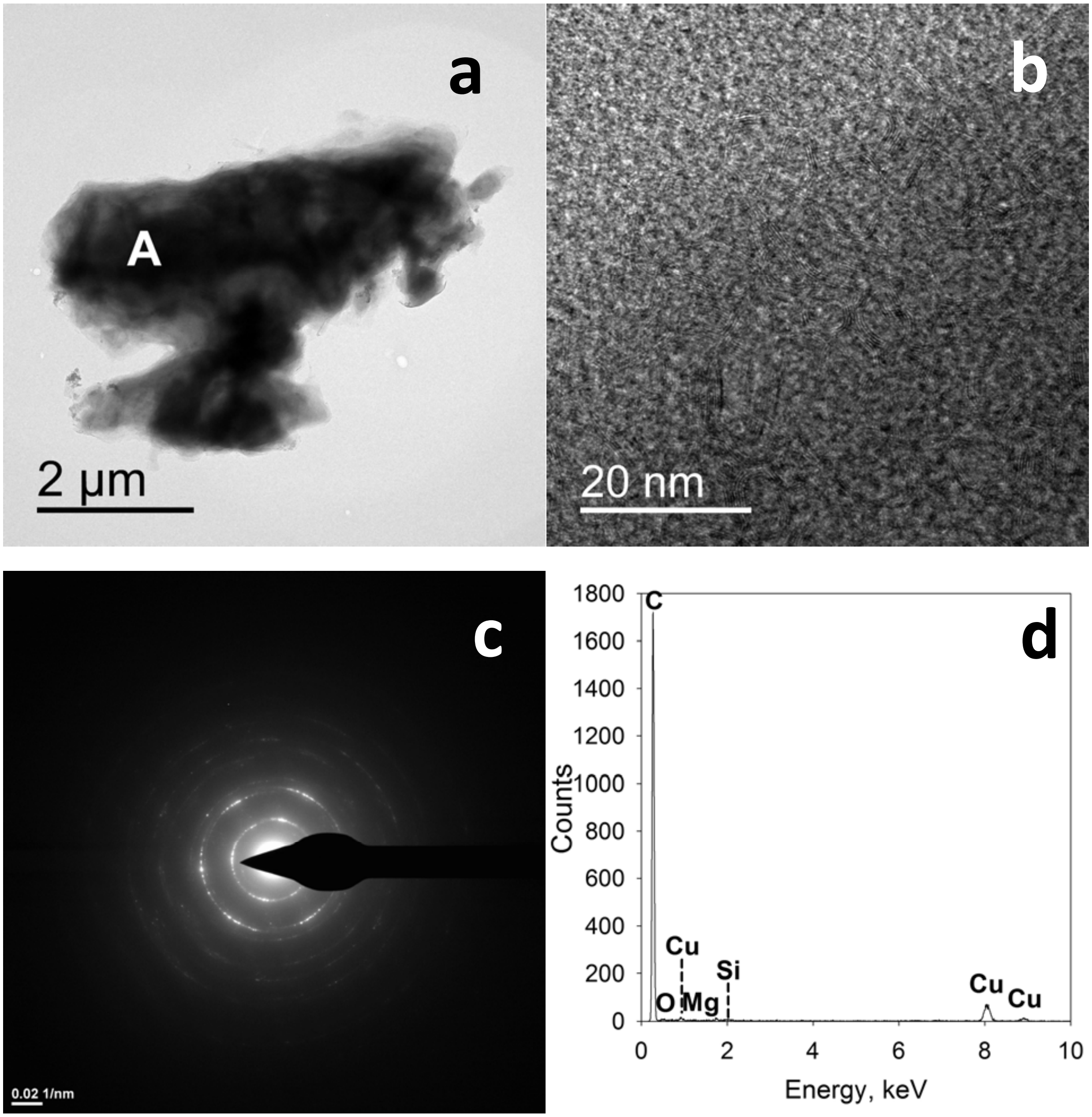

Figure S3 Representative transmission electron microscopy (TEM) images, selected area diffraction (SAED), and energy-dispersive spectroscopy (EDS) spectrum identifying presence of a crystalline phase and the chemical elements in a particle from cold exhaust (gasoline with octane number 87 burned) passed over snow in the chamber. The vertical dashed lines lead to smaller peaks to improve clarity.

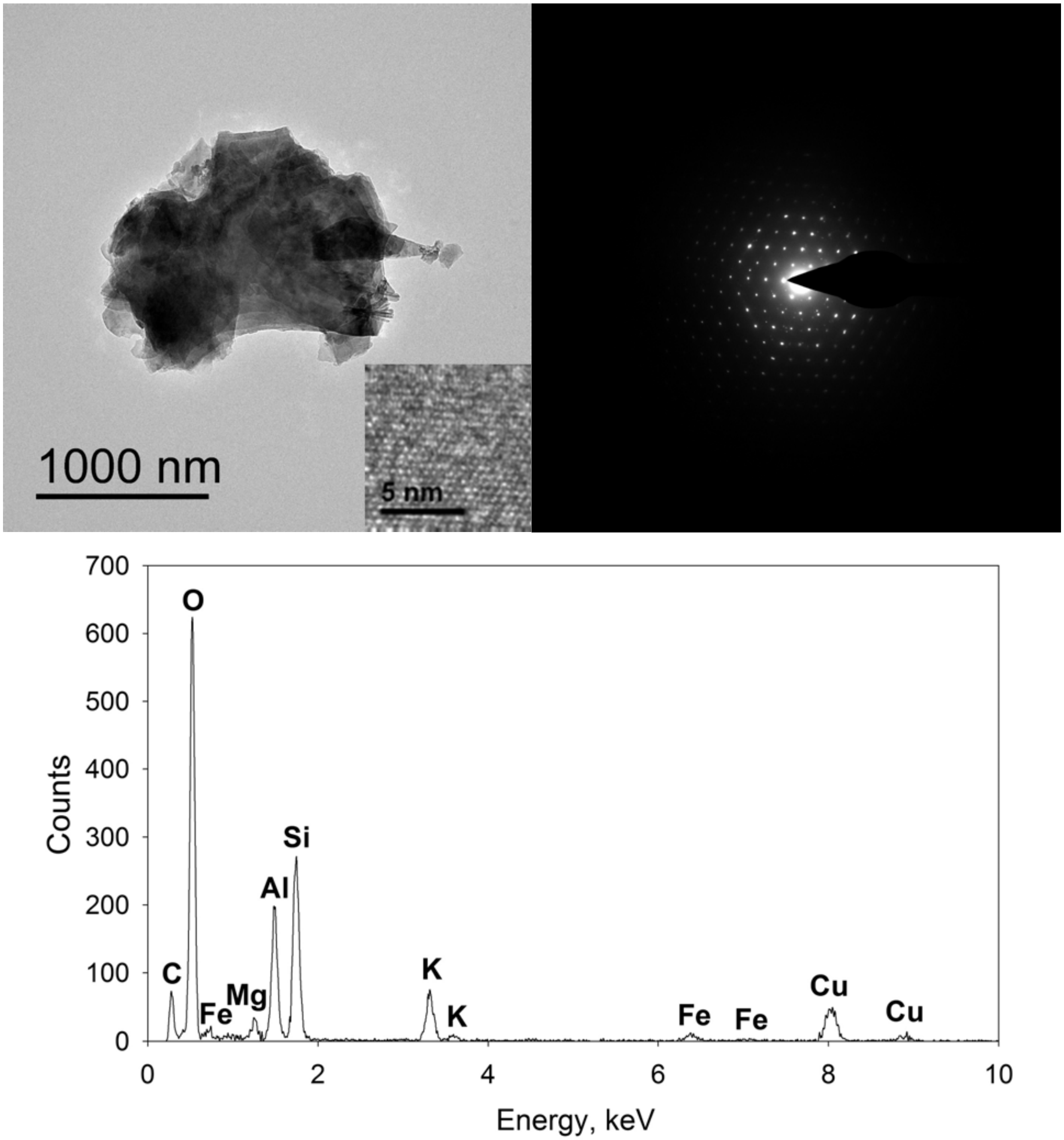

Figure S4 Transmission electron microscopy (TEM) image of a particle in a dried drop of exhaust-exposed snow with a high-magnification insert showing the atomic grid of the crystal, a selected area diffraction (SAED) pattern showing presence of a crystalline phase (dot pattern), and an energy-dispersive spectroscopy (EDS) spectrum showing a high content of minerals composed of oxygen, iron, aluminum, potassium and silicon – likely a mineral dust particle, originally present in snow before its exposure to exhaust. Gasoline with octane number 87 burned to generate the exhaust.

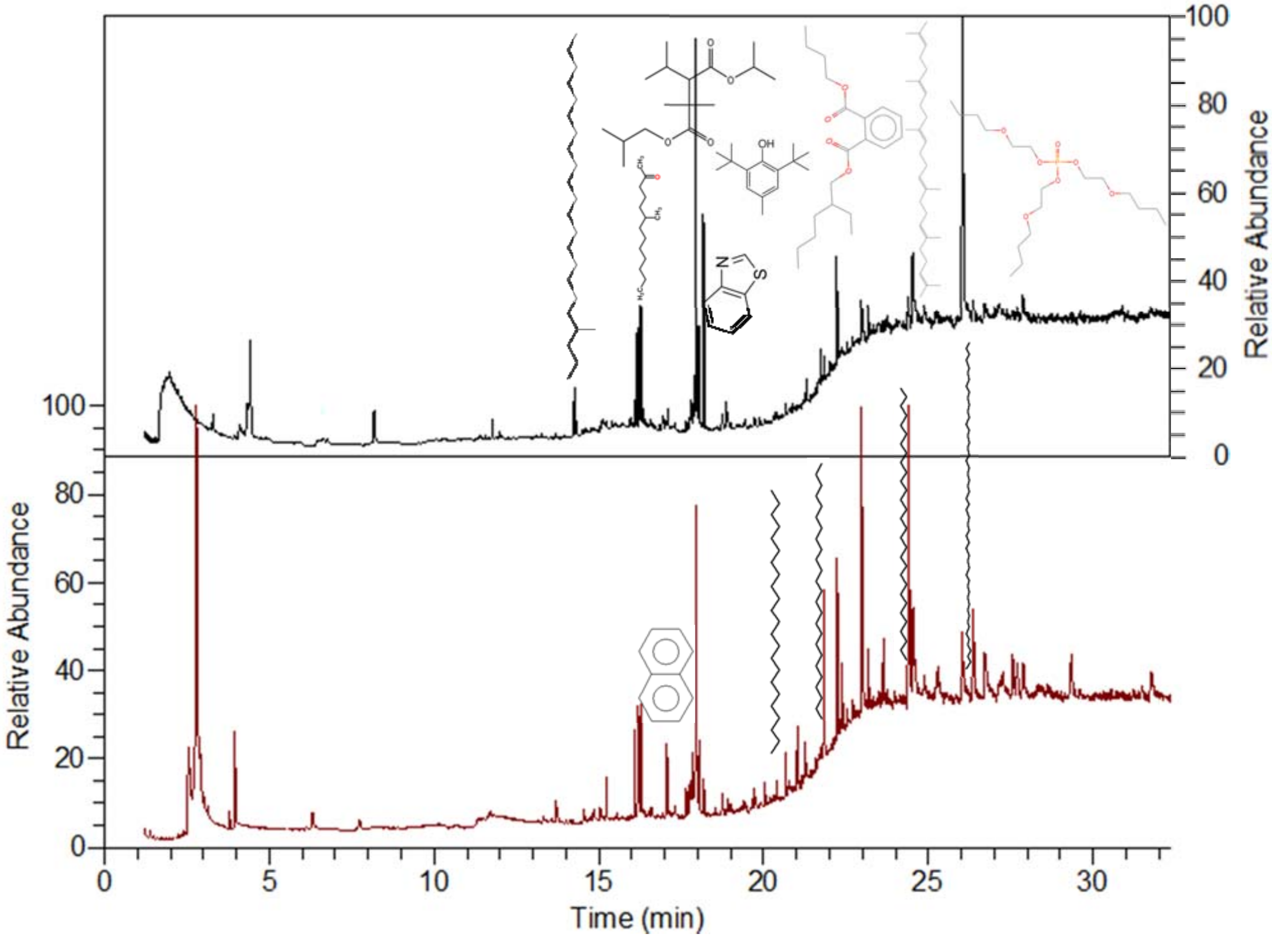

Figure S5. Gas chromatograms of the original (top) and exhaust-exposed (bottom) snow samples (100 μm polydimethylsiloxane (PDMS) fiber). Gasoline with octane number 87 burned to generate the exhaust for this analysis.

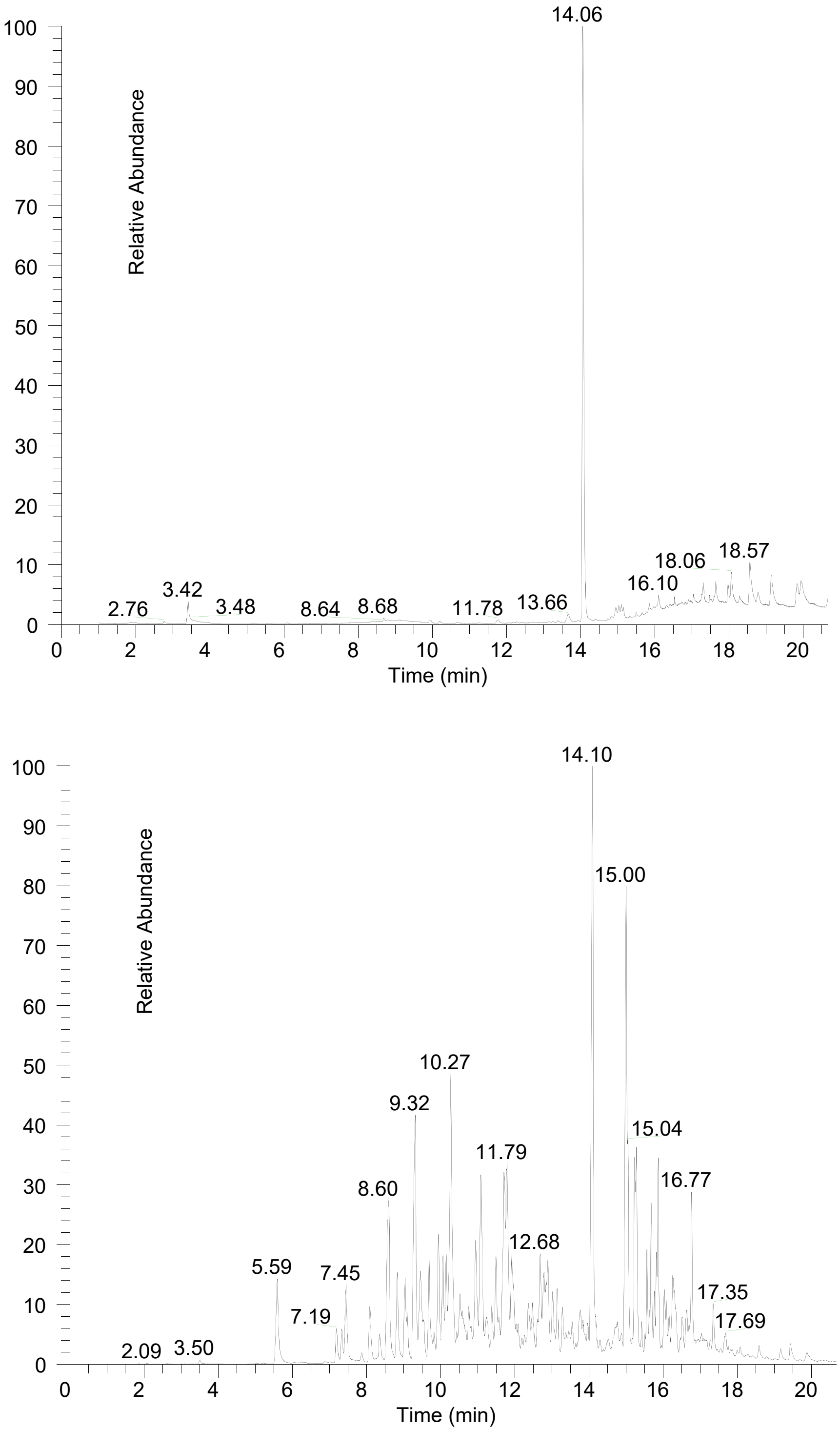

Figure S6. Gas chromatograms of the original (top) and exhaust-exposed (bottom) snow samples (65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber). The peak at RT 14.1 (14.06 - 14.10) min is the internal standard.

Supplementary Tables

Table S1 Descriptive Statistics of Aerosol Size Distributions and carbon dioxide (CO_2) / oxygen (O_2) Mixing Ratios in Measured Dilute Exhaust. “T” stands for “temperature”.

	Exhaust, Warm T, After Chamber	Exhaust, Cold T, After Chamber	Exhaust, Snow	Exhaust, Warm T, Before Chamber	Exhaust, Cold T, Before Chamber
Gasoline with octane number 87					
Mode, µm	43	51	54	82	36
Geometric Mean (dg), µm	48	51	56	83	38
Geometric Standard Deviation (σg)	1.66	1.54	1.63	1.62	1.60
CO_2 Mixing Ratio, %	2.23	1.22	-	1.20	-
O_2 Mixing Ratio, %	18.1	19.8	-	18.9	-
Gasoline with octane number 89					
Mode, µm	50	49	46	68	44
Geometric Mean (dg), µm	49	45	46	67	46
Geometric Standard Deviation (σg)	1.55	1.53	1.59	1.68	1.62
CO_2 Mixing Ratio, %	1.39	-	0.57	1.01	-
O_2 Mixing Ratio, %	18.8	-	20.9	19.4	-
Gasoline with octane number 91					
Mode, µm	49	49	56	57	47
Geometric Mean (dg), µm	46	49	54	59	50
Geometric Standard Deviation (σg)	1.54	1.54	1.52	1.64	1.65
CO_2 Mixing Ratio, %	1.12	-	0.62	1.25	-
O_2 Mixing Ratio, %	19.4	-	21.0	19.04	-

Table S2 Solid-phase microextraction-gas chromatography-mass spectrometry (SPME-GC-MS) identification[a] of organic compounds in the original snow.

Retention Time	Compound	Formula	Description[b,c]
14.22	4-Methyldocosane	$C_{23}H_{48}$	Long-chain hydrocarbon
14.29	3-Methyldocosane	$C_{23}H_{48}$	Long-chain hydrocarbon
16.12	10-Methyl-Z-11-tridecen-1-ol acetate	$C_{16}H_{30}O_2$	Oxidized hydrocarbon
16.23	6-Methyl-2-tridecanone	$C_{14}H_{28}O$	Oxidized hydrocarbon
16.30	6-Octenal, 3,7-dimethyl-	$C_{10}H_{18}O$	Oxidized hydrocarbon
17.95	Pentanoic acid, 2,2,4-trimethyl-3-carboxyisopropyl, isobutyl ester	$C_{16}H_{30}O_4$	Plant-derived compound
18.03	Propanoic acid, 2-methyl-, 2,2-dimethyl-1-(2-hydroxy-1-methylethyl)propyl ester	$C_{12}H_{24}O_3$	Plant-derived compound
18.18	Butylated Hydroxytoluene	$C_{15}H_{24}O$	Common antioxidant in plastics
18.73	Benzothiazole	C_7H_5NS	Common industrial chemical, used as vulcanization accelerator, in paper industry etc.
19.72	Cinnamic acid, 4-hydroxy-3-methoxy-, {5-hydroxy-2-hydroxymethyl-6-[2-(4-hydroxy-3-methoxyphenyl)ethoxy]-4-(6-methyl-3,4,5-trihydroxytetrahydropyran-2-yloxy)tetrahydropyran-3-yl} ester	$C_{31}H_{40}O_{15}$	Plant-derived compound
21.30	2,4,6-Trimethylmandelic acid	$C_{11}H_{14}O_3$	Plant-derived compound
21.74	10,13-Octadecadiynoic acid, methyl ester	$C_{19}H_{30}O_2$	Plant-derived compound
21.82	CAMP	$C_{10}H_{11}N_5O_6P$	Very common plant-derived compound
22.23	1,2-Benzenedicarboxylic acid, butyl 2-ethylhexyl ester	$C_{20}H_{30}O_4$	Common alkyl phthalate, used as a plasticizer
22.98	Pregn-4-ene-3,20-dione, 16,17-epoxy-, (16a)-	$C_{21}H_{28}O_3$	Used in synthesis of certain pharmaceuticals
24.39	Heptadecane, 9-hexyl-	$C_{23}H_{48}$	Plant-derived compound
24.53	l-(+)-Ascorbic acid 2,6-dihexadecanoate	$C_{38}H_{68}O_8$	Plant-derived compound
26.06	Squalene	$C_{30}H_{50}$	Common natural triterpene

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[a] Manual peak identification, only compounds with match factors > 90 % accepted.

[b] AroKor Holdings Inc. Chemicalland21. http://chemicalland21.com/ (accessed April 5, 2015).

[c] LookChem Look for Chemicals. http://www.lookchem.com/ (accessed April 5, 2015).

Table S3 Solid-phase microextraction-gas chromatography-mass spectrometry (SPME-GC-MS) identification of additional organic compounds in the exhaust-exposed snow. "U.S. EPA" stands for the United States Environmental Protection Agency.

Retention Time	**Compound**	**Match Factors, (N-net, W-weighted, S-simple, R-reverse)**	**Description *or* Presence in the U.S. EPA Master List[a] of Compounds Emitted by Mobile Sources**
2.77	Cyclohexane	N=91; W=91; S=84; R=91	**U.S. EPA List**
14.54	Acetic acid	N=87; W=92; S=86; R=91	**U.S. EPA List**
14.68	Furfural	N=76; W=91; S=57; R=90	Biogenic compound[b,c]
14.74	1-Hexanol, 2-ethyl-	N=64; W=74; S=49; R=71	**U.S. EPA List**
16.35	Acetophenone	N=84; W=94; S=69; R=92	**U.S. EPA List**
17.06	Naphthalene	N=99; W=99; S=94; R=99	**U.S. EPA List**
18.23	Naphthalene, 2-methyl-	N=72; W=84; S=57; R=83	**U.S. EPA List**
18.54	1-Undecanol	N=71; W=88; S=56; R=84	Biogenic compound[b,c], Chemically similar to compounds in the **U.S. EPA List**
18.70	Naphthalene, 2-ethyl-	N=78; W=91; S=60; R=88	**U.S. EPA List**
18.76	Naphthalene, 1,8-dimethyl-	N=69; W=95; S=51; R=90	**U.S. EPA List**
18.90	Biphenyl	N=65; W=80; S=37; R=89	**U.S. EPA List**
18.93	Phenol	N=90; W=94; S=73; R=93	**U.S. EPA List**
19.02	Naphthalene, 1,2-dimethyl-	N=67; W=84; S=44; R=80	**U.S. EPA List**
19.41	Hexadecane	N=60; W=82; S=66; R=78	**U.S. EPA List**
19.41	Eicosane or Icosane	N=63; W=79; S=54; R=74	**U.S. EPA List**
19.61	N-Nitrosodiphenylamine	N=82; W=92; S=58; R=91	Industry[b,c], cooking emissions[d]
19.73	Tributyl phosphate	N=68; W=77; S=48; R=81	Plasticizer[b,c]
19.77	Benzene, 1,1'-ethylidenebis-	N=72; W=89; S=49; R=86	**U.S. EPA List**
20.48	9H-Carbazol-3-amine, 9-ethyl-	N=65; W=72; S=51; R=71	Industrial chemical used in production of dyes, pigments, pharmaceuticals[b,c]
20.67	Tricosane	N=69; W=77; S=71; R=74	**U.S. EPA List**

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[a] U.S.EPA, The Master List of Compounds Emitted by Mobile Sources. In National Service Center for Environmental Publications (NSCEP): 2006.

[b] AroKor Holdings Inc. Chemicalland21. http://chemicalland21.com/ (accessed April 5, 2015).

[c] LookChem Look for Chemicals. http://www.lookchem.com/ (accessed April 5, 2015).

[d] Fine, D. H.; Ross, R.; Rounbehler, D. P.; Silvergleid, A.; Song, L., Formation in vivo of volatile N-nitrosamines in man after ingestion of cooked bacon and spinach. *Nature* 1977, *265*, 753 - 755.

20.72	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- or Acetosyringone	N=71; W=87; S=53; R=86	Biogenic compound[h,i], chemically similar to compounds in the **U.S. EPA List**
20.77	Phenol, 2,4-bis(1,1-dimethylethyl)-	N=80; W=92; S=54; R=90	Chemically similar to compounds in the **U.S. EPA List**
21.02	Menthol	N=69; W=72; S=66; R=76	Biogenic compound[h,i]
21.26	Tetracosane	N=66; W=77; S=54; R=78	**U.S. EPA List**
21.30	Diethyl Phthalate	N=81; W=90; S=56; R=88	Plasticizer[h,i]
21.67	Benzoic Acid	N=80; W=90; S=64; R=89	Biogenic compound[h,i]
21.83	Pentacosane	N=84; W=90; S=80; R=87	**U.S. EPA List**
22.05	Benzophenone	N=79; W=92; S=75; R=90	UV-blocker in plastics, industrial chemical[h]
22.24	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester or Diizobutyl-phthalate	N=91; W=94; S=80; R=94	Plasticizer[i]
22.34	Cyclohexane, ethyl-	N=63; W=70; S=55; R=69	**U.S. EPA List**
23.18	Dibutyl phthalate	N=91; W=96; S=68; R=95	Plasticizer[h,i]
23.34	Acetophenone, 2-chloro-	N=64; W=93; S=53; R=90	Chemically similar to compounds in the **U.S. EPA List**
23.75	Anthracene	N=78; W=91; S=56; R=90	**U.S. EPA List**
24.40	Triacontane	N=89; W=92; S=82; R=90	Chemically similar to compounds in the **U.S. EPA List**
24.40, 26.38	Tetrapentacontane (two peaks at two different RT)	Peak 1: W=83; R=84 Peak 2: W=83; R=83	Chemically similar to compounds in the **U.S. EPA List**
24.41	Hexacosane	N=88; W=92; S=79; R=89	**U.S. EPA List**
24.53	n-Hexadecanoic acid	N=61; W=68; S=43; R=66	**U.S. EPA List**
26.72	Octadecanoic acid or Stearic acid	N=68; W=74; S=57; R=78	In plant-derived fats and oils, used as a lubricant[h]
27.56	Di-n-octyl phthalate	N=62; W=60; S=54; R=88	Plasticizer, acaricide[h,i]
27.57	Bis(2-ethylhexyl) phthalate	N=84; W=90; S=41; R=88	Plasticizer, acaricide[h,i]

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[h] AroKor Holdings Inc. Chemicalland21. http://chemicalland21.com/ (accessed April 5, 2015).

[i] LookChem Look for Chemicals. http://www.lookchem.com/ (accessed April 5, 2015).

Supplementary Methods

Chamber

An access port on the top of the chamber was available for the loading and unloading of snow, in addition to cleaning the interior of the chamber. The cover of this access port contained a glass well with a T-type thermocouple inside that reached the x-y-z center of the chamber. A second T-type thermocouple-containing glass well was perpendicular to the first well extending to the x-z center of the chamber, 5 cm from its bottom. When there was snow in the chamber, the tip of this second well was covered with snow allowing for the continuous measurements of the snow temperature. The chamber was also equipped with a relative humidity/temperature (RH/T) probe, installed in a port immediately to the side of the top chamber-access port, fitted through a polytetrafluoroethylene (PTFE)-covered septum. The probe was model PROBE-SHT2X (Aginova, Inc., Freehold, NJ, USA) and had a 5 mm diameter cylindrical stainless steel housing with a slit for the sensor. The RH/T probe was used with a data logger, model iCelsius Wireless IPROBE-3000-0001 (Aginova, Inc.), capable of recording temperature and RH data with 1 sec time resolution. The same RH/T probe and data logger were used for all other RH measurements.

The experimental chamber was placed in a double-walled polypropylene tray that, for controlled cold temperature experiments, was filled with a cooling bath. The manifold of the sampling train was built using stainless steel wyes and electrically conductive silicone tubing to minimize electrostatic aerosol losses. This configuration allowed for the simultaneous connection of several sampling instruments. The exhaust ports of all the instruments were connected to adjacent fume hoods to prevent release of exhaust-derived air pollutants into the laboratory atmosphere. The combined aspiration flow rate of all the sampling instruments was approximately 2 L/min, which was below the total outflow rate from the chamber.

After each experiment, the snow-exposure chamber and the glass wells inside it were washed using 75 % ethanol and deionized, Milli-Q water (18.2 MΩ·cm at 25 °C), at least twice, followed by dry clean air flushing to evaporate residual water. A vacuum glass tube, inserted into the chamber, facilitated the removal of washing liquids

Generator

The model of the generator used was equipped with a 4-stroke, vertical shaft, air-cooled, overhead-valve (OHV) gasoline engine with an electronic ignition system, model XG-139F. The volume of the engine was 31 cm^3, the compression ratio 7.4:1, and maximum rotational speed of 5500 revolutions per minute (RPM).

The engine was used with the recommended type of lubricant oil SAE 15W40 and unmodified ethanol-spiked gasoline, purchased at a regular gas station in Montreal, QC, Canada in February-July 2014.

The generator was set up in a fume hood and electrically loaded with a 100 W incandescent light bulb. The unit operated in the economy mode, so the speed of the engine was set automatically at a lower than maximum level. Operating the generator at a reduced power output was required to decrease noise, vibration and exhaust generation to match the capacity of the fume hood to evacuate it.

Dilution Air Module

In the dilution air module, the dry air (RH < 2 %) from the laboratory mainline supply was passed through an in-house-made activated carbon-filled capsule of ~ 1 L volume and a high efficiency particulate air (HEPA) filter, model Whatman™ 6702-9500 HEPA-Cap 150 (GE Healthcare Life Sciences, Little Chalfront, Buckinghamshire, UK) to clean it from gaseous and particulate pollutants. The clean air then passed through another HEPA filter (TSI, Inc.) and a mass flow meter, model 4040 (TSI, Inc.). That second HEPA filter was a standard unlabeled unit, supplied with the mass flow meter, which we tested to remove all particles present in ambient air, detectable by the aerosol measurement instruments used in this study, at the experimental flow rates. After the mass flow meter, the air passed into a custom-built stainless steel heat exchanger. This unit was an open rectangular stainless steel chamber with dimensions 8×11×6 in. Inside the chamber was a stainless steel coil (3/16 in. outside diameter (o.d.), 0.1 in. inside diameter (i.d.)). During the cold stages of the experiments, the chamber was filled with a salt (NaCl)/ice mixture, which allowed cooling the dilution air to between -16 ± 0.6 and -19 ± 0.6 °C. The dilution air module was continuously operated during and between the experiments to prevent moisture accumulation and maintain ultralow RH.

Sampling Flow Heater

The heating tape was controlled with a proportional-integral-derivative controller (PID controller), model CN2110-T10-AL (Omega Engineering, Inc., Stamford, CT, USA). The controller operated with a K-Type thermocouple, placed in a glass tee in the excess flow stream, which was one of the sampling train branches of the manifold.

Exhaust Dilution Ratio

The dilution ratio for the exhaust was calculated based on the concentration of oxygen in the dilute exhaust. We assumed a zero concentration of oxygen in pure exhaust corresponding to lean fuel/air mixture burning regime because we did not have an instrument that would be capable of measuring oxygen in pure exhaust without being damaged. With this assumption, the following equation was used to calculate the dilution ratio:

$$d = \frac{C_{O_2}^{d.e.} - C_{O_2}^{e}}{C_{O_2}^{a} - C_{O_2}^{d.e.}}$$

Eq. S1

Where $C_{O_2}^{d.e.}$ is concentration of oxygen in dilute exhaust, $C_{O_2}^{e}$ is the assumed concentration of oxygen in pure exhaust, and $C_{O_2}^{a}$ is concentration of oxygen in pure air.

Exhaust Diversion System

The exhaust from the generator was passed through a 24 in. long flexible high-temperature-resistant PTFE-lined stainless steel-braided hose, model SS-FL8TA8TA8-24 (Vannes et Raccords Laurentian, Ltd., St-Laurent, QC, Canada). The i.d. of the hose and all other stainless steel tubes in the exhaust module was 0.5 in. The temperature of exhaust as measured by a thermocouple did not exceed 80 °C at the exit from the generator, which was substantially below the upper limit of thermal resistance of the hose. The exhaust from the hose entered a custom-built stainless steel valve that we used to regulate the amount of exhaust diverted to the chamber system. The diverted exhaust passed to the chamber system through a silicone electrically conductive tube. The tube was pinched closed when no exhaust introduction was needed. To start flow of exhaust into the chamber system, this tube was opened after the generator warmed up for ~ 2 min. The excess exhaust was allowed to exit into the fume hood. Two condensate collection vessels were fitted under the excess exhaust expulsion pipe.

Details of Environmental Snow Collection and Storage

We used sterile HDPE sampling spatulas (Bel-Art Products, Inc., Wayne, NJ, USA) and pre-cleaned certified 950 mL amber glass environmental sample containers (Thermo Fisher Scientific, Waltham, MA, USA) with PTFE-lined lids to collect and store the snow samples. The sampling team were equipped with special clean hydrophobic suits with booties, facemasks and nitrile gloves fitted over their insulated gloves. We only collected freshly fallen snow from the top 3 cm layer. Immediately after sampling, the samples were transported to the laboratory in a cooler, approximately 2 km from the sampling site, and placed in a freezer for storage at approximately -39 °C for two – four months before the experiments were performed.

Exposure of Snow to Exhaust

We exposed snow to dilute exhaust in its original frozen condition by placing it at the bottom of the cooled glass chamber and passing cold dilute exhaust over it. Fresh snow was exposed to dilute exhaust for 1 hr. The snow remained frozen throughout the experiments. The mass of snow used in the aerosol experiments was 160 ± 10 g. The mass of all snow samples was determined by means of pre-weighing the empty and then snow-filled containers using a Sartorius TE2101 balance (Sartorius AG, Göttingen, Germany).

When snow was exposed to generate samples for the above snow analyses, the temperature at the top of the snowpack started at around -17 °C and within one hour increased to around -9 °C, before prompt sampling from the chamber. During this one-hour period of exhaust passing through the chamber, the RH in the outflow ranged between ~ 6 and 7.5 %. When the dilute exhaust was passed into the chamber, the concentration of exhaust in the chamber was controlled by adjusting the dilution airflow rate to maintain an approximate concentration of oxygen (O_2) and carbon dioxide (CO_2) in the outflow, of 18.5 – 19.5 % O_2 and 1.5 – 2 % CO_2. Maintaining a very stable concentration of exhaust is always a challenge in exhaust studies, so we calculated the average concentration of O_2 and CO_2 as a quantitative descriptor of the exposure level of snow to dilute exhaust. The average concentration of O_2 in the dilute exhaust during the period of exposure was 18.27 % and that of CO_2 1.67 %. This corresponds to an average exhaust dilution ratio of 7.7.

Operation of the Aerosol Measurement and Sampling Instruments

The NanoScan™ charges and separates aerosol particles (10 nm to 420 nm) according to their mobility in an electric field, and scans this entire aerosol particle size range in 60 sec. The OPS uses single-particle optical counting in 16 particle size channels and measures 0.3 – 10 µm sized particles.

The upper part of the NanoScan™ range overlaps with the lower part of the OPS range, where the two instruments provide complementary information. Correspondingly, we observed matching higher number concentrations of the smallest particles (0.3 µm) in the OPS size distributions of the snow-affected runs and cold temperature runs.

The ESPnano™ instrument generates a high-voltage corona discharge that charges and drives aerosol particles to the collecting substrate (transmission electron microscopy (TEM) grids). The precipitator was at 5 kV, 100 sec sampling duration and a 30 sec purge before sampling. The TEM-grids used as substrate were mechanically strong FCF200-Cu-EB grids (Formvar Carbon Film on 200 Mesh Copper Extra Thick Option B grids, 25 – 50 nm Formvar & 3 – 4 nm Carbon), manufactured by SPI Supplies / Structure Probe, Inc., West Chester, PA, USA.

Analysis of Total Organic Carbon (TOC) in Melted Snow Samples

The snow was melted at ambient temperature in the same certified sample storage containers, in which it had previously been collected. 40 mL aliquots of melted snow were then prepared in sterile Falcon™ 50 mL Conical Centrifuge Tubes (Corning Life Sciences, Inc., Tewksbury MA, USA). The TOC was analyzed with an Aurora 1030W TOC Analyzer (O.I. Corp., College Station, TX) using the persulfate oxidation method. The method uses a 5 mL subsample from each original aqueous sample. A volume of 0.5 mL of 5 % phosphoric acid is added to the subsample followed by combustion at 700 °C, allowing detection of total inorganic carbon (TIC).

Next, the detection of organic carbon is facilitated by addition of 2 mL of 10 % sodium persulfate, followed by combustion at 980 °C. The CO_2 from these two reactions is detected separately by a nondispersive infrared sensor (NDIR). The samples were analyzed in triplicate. The quality of analyses was controlled through addition of external standards (0 and 5 mg/L) to each sample series. The instrument was calibrated using 0.0, 1.1, 2.0, 5.0, and 10 mg/L standards. The sensitivity of the method with this calibration curve was near concentrations in the 0.1 – 0.2 mg/L range.

Ion Chromatography (IC) Analysis of Melted Snow Samples

For the IC analysis, we used the same samples as for the TOC analysis. Similar to the TOC analysis, samples of undiluted melted snow were prepared in sterile Falcon™ 50mL Conical Centrifuge Tubes (Corning Life Sciences, Inc., Tewksbury MA, USA), but in 20 mL aliquots. The Dionex ICS-5000 system (Dionex Corp., Sunnyvale, CA, USA) was used for analysis. An IonPac AS 14 separation column with 3.5 mM Na_2CO_3/1.0 mM $NaHCO_3$ mobile phase, held at ambient temperature, was used to analyze the anions. A 10 µL injection volume and 0.30 mL/min flow rate were used. The Anion Self-Regenerating ASRS 300 2-mm suppressor was used for detection by suppressed conductivity. For cations, an IonPac CS 12 separation column with 20 mM methanesulfonic acid mobile phase, held at ambient temperature, was used. The analysis was performed using the 10 µL injection volume and 0.25 mL/min flow rate. The Cation Self-Regenerating CSRS Ultra II 2-mm suppressor was used for detection by suppressed conductivity. The limit of detection for both anions and cations was 0.1 ppm with this method.

Transmission Electron Microscopy and Energy Dispersive Spectrometry

The samples on the TEM-grids were analyzed on an HR-TEM Tecnai G2F20 S/TEM with a field emission gun (FEI Comp, Hillsboro, OR, USA), operated at 200 kV. The UltraScan™ 1000 2k×2k CCD Camera System, Model 895 (Gatan, Inc., Pleasanton, CA, USA) was used to acquire the images and the Genesis EDS Analysis System (EDAX, Inc., Mahwah, NJ, USA) was used for EDS.

Gas Chromatography – Mass Spectrometry (GC-MS)

The unexposed and exhaust-exposed snow samples were probed with solid-phase microextraction (SPME) and analyzed by a GC-MS system consisting of a Thermo Fisher Scientific, Inc. (Waltham, MA, USA) Trace GC Ultra with a Polaris-Q ion trap mass spectrometer. A 100 µm polydimethylsiloxane (PDMS) SPME fiber (Supelco, Inc., Bellefonte, PA, USA) was used for the chemical identification analysis, and a 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber (Supelco, Inc.) for the quantitative analysis. The GC was performed following the same procedure for both qualitative and quantitative analysis using a nitroterephthalic-acid-modified polyethylene glycol (PEG) column DB-FFAP 0.25 mm × 15 µm × 30 m (Agilent Technologies, Santa Clara, CA, USA). Immediately after the inlet was a cryofocusing zone: 5 cm segment of the column cooled to -40 °C at the injection moment for 1 min. The carrier gas was ultra-high-purity helium at 25 m/min velocity. The GC was operated in split mode (1:5). Column temperature was held at 35 °C for 8 min, followed by a 15 °C/min ramp to 250 °C held for 10 min.

The inlet temperature was 260 °C, the inlet liner was a capillary 0.8 mm i.d. of deactivated glass (Supelco, Inc., part number 2876605-U), and the transfer line to the MS was deactivated fused silica, 0.1 mm i.d., at 260 °C. The MS was run in positive mode, with the ion source held at 150 °C ranged (backed), with a scan range from 50-450 m/z, dwell time 25 ms, and damping gas flowrate of 0.3 mL/min. The qualitative analysis of the GC-MS data was carried out using the NIST 11 MS database. During the qualitative data analysis, the large number of compounds and overlapping peaks in the chromatograms of exhaust-exposed snow required peak deconvolution using AMDIS 2.70 in tandem with the above-mentioned NIST database.

Preparation of Standards for Quantitation by Gas Chromatography – Mass Spectrometry (GC-MS)

The internal standard was prepared by dissolving isotope-labeled, fully deuterated Naphthalene-d8, 99%, ISOTEC® in 2-propanol (both from Sigma-Aldrich, St. Louis, MO, USA) to the final concentration of 0.1 mg/mL. As a solvent for the internal standard and the stock solutions of benzene, toluene, ethylbenzene and xylenes (BTEX), we used HPLC-grade 99.9 % 2-propanol (Fisher Scientific). The deionized water was of Milli-Q grade (18.2 MΩ·cm at 25 °C).

BTEX stock standards were prepared by dissolving 0.2 ± 0.0001 g each of benzene (99.9 %), toluene (99.8 %), ethylbenzene (99 %) and m-xylene (99 %) from Sigma-Aldrich in 2-propanol to the 10 mL volume in Kimax® 10 ± 0.02 mL volumetric flasks (Kimble Chase, Vineland, NJ, USA). Stock solutions of BTEX (100 µg/mL and 1 µg/mL in 2-propanol) were obtained by precise volumetric dilution. Final calibration standards were prepared as follows: 10 mL of Milli-Q water, measured using a Fisherbrand® 10 ± 0.02 mL volumetric pipette, part #13-650-2L (Thermo Fisher Scientific, Inc., Waltham, MA, USA), in 20 mL headspace vials, part #5182-0839 (Agilent Technologies, Santa Clara, CA, USA), were spiked with a required amount of either 1 µg/mL or 100 µg/mL BTEX stock solution to get a final concentration in the range 0.01 – 1000 ppb (ng/mL) of BTEX. After addition of 10 µL of the internal standard, each vial was crimp-closed with a PTFE-butyl rubber septum. Sets of a minimum of 12 standards were prepared to cover the ranges of required concentrations. The method has a lower detection limit of

0.01 ppb (ng/mL) with a quadratic calibration curve in full range with a very good fit ($R^2 > 0.9995$) for each of BTEX.

Supplementary Data

System Characterization

The RH, measured with the probe in the outflow from the chamber, ranged from < 2.0 to ~ 6.5 % and only spiked as high as ~ 30 % when the chamber was opened for loading or sampling of snow. The temperature of the heated outflow was very stable around 23 ± 0.6 °C.

During the warm temperature experiments, the temperature in the center of the chamber (T_{cc}) and its bottom (T_{bc}) was 23 ± 0.6 °C. When the cooling baths were loaded with the salt/ice mixture, as cold clean air passed through the system, T_{cc} ranged from 10.0 ± 0.6 °C to 6.0 ± 0.6 °C and T_{bc} ranged from -11.0 ± 0.6 °C to -10.0 ± 0.6 °C. When cold dilute exhaust passed through the chamber without snow, T_{cc} ranged between 4.0 ± 0.6 °C and 8.0 ± 0.6 °C and T_{bc} between -11.0 ± 0.6 °C to -10.0 ± 0.6 °C. When cold clean air passed over snow in the chamber, T_{cc} was 7.0 ± 0.6 °C and T_{bc} was -11.0 ± 0.6 °C to -10.0 ± 0.6 °C. Finally, when cold dilute exhaust passed over snow in the chamber, T_{cc} ranged between 4.5 ± 0.6 °C to 7.0 ± 0.6 °C and T_{bc} ranged between -11.0 ± 0.6 °C to -7.0 ± 0.6 °C.