Supplementary Information (SI) for Environmental Science: Advances.

Supplementary material

Investigation of Zn-, Pb-, and Cd-Containing Nanoparticles in Canadian urban and Arctic environments: A comprehensive study utilizing Single Particle Inductively Coupled Plasma Mass Spectrometry for Characterization

Richard Macedo de Oliveira [a,b*], Dorthe Dahl-Jensen [a,c], and Feiyue Wang [a,b]

[a] Centre for Earth Observation Science, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

[b] Department of Environment and Geography, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

[c] Niels Bohr Institute, Physics of Ice, Climate and Earth, University of Copenhagen, Copenhagen, Denmark

*Corresponding author:

Richard.Oliveira@umanitoba.ca

Figure S1: Map of the study area and sampling locations. Legends: ▲: Müller Ice Cap; ●: The Forks; ● – Assiniboine River, ● – Osborne Village, ● – Chemistry Department, ● – Recreation Area (Gym).

Table S1: ICP-MS/MS operational parameters for measuring ^{66}Zn, ^{208}Pb and ^{111}Cd NPs in snow meltwater.

Parameter	Value
RF power (W)	1400 (^{111}Cd and ^{208}Pb), 1500 (^{66}Zn)
Sampling depth (mm)	9
Carrier gas (L min^{-1})	0.8
Sample uptake rate (mL min^{-1})	0.346
Spray chamber temperature (°C)	2
Dwell time (µs)	100
Settling time (ms)	0
Acquisition time (s)	60
Acquired mass number (m/z)	^{66}Zn for Q1 and Q2 ^{208}Pb Q1 ^{111}Cd Q1
Cell gas flow rate (He, mL min^{-1})*	2

* For ^{66}Zn only

Table S2: Limits of detection in particle sizes calculated for individual particles in the snow samples from Winnipeg.

	Limits of Detection – size (nm)		
Sample ID	**Zn-NPs**	**Pb-NPs**	**Cd-NPs**
[1] Downtown Nov. 4, 2022	51.1	51.1	-
[1] Downtown Dec. 18, 2022	51.1	61.2	28.9
[1] Downtown Jan. 19, 2023	60.3	58.5	30.0
*UM April 5, 2023	51.1	45.7	-
**UM April 6, 2023	51.1	45.7	-
[2] Downtown April 7, 2023	51.1	45.6	-
[3] Downtown April 7, 2023	49.5	45.7	-
[1] Downtown April 20, 2023	51.1	48.6	28.9

1- Osborne village area (Winnipeg Downtown);
2- Assiniboine River (Winnipeg Downtown);
3- The Forks (Winnipeg Downtown);
*Gym area at the University of Manitoba;
**Chemistry Department at the University of Manitoba.

Table S3: Total concentration, mass concentration, and nanoparticle percentage for Zn, Pb, and Cd-NPs in fresh snow collected from Winnipeg, Canada.

	Snow Winnipeg - NP Zn			Snow Winnipeg - NP Pb			Snow Winnipeg - NP Cd		
Sample ID	Total concentration ($\mu g\ L^{-1}$)	Mass concentration ($ng\ L^{-1}$)	Nanoparticle, %	Total concentration ($\mu g\ L^{-1}$)	Mass concentration ($ng\ L^{-1}$)	Nanoparticle, %	Total concentration ($\mu g\ L^{-1}$)	Mass concentration ($ng\ L^{-1}$)	Nanoparticle, %
[1] Downtown Nov. 4, 2022	0.70 ± 0.04	1.3 ± 0.6	0.2	0.95 ± 0.03	90.1 ± 1.5	9.4	0.03 ± 0.01	ND	ND
[1] Downtown Dec. 18, 2022	1.0 ± 0.1	1.8 ± 0.6	0.2	0.94 ± 0.01	296.0 ± 3.3	31.5	0.07 ± 0.01	1.6 ± 0.3	2.2
[1] Downtown Jan. 19, 2023	5.9 ± 0.6	34.4 ± 6.0	0.6	1.3 ± 0.3	203.0 ± 2.3	15.7	0.50 ± 0.04	0.23 ± 0.01	0.05
*UM April 5, 2023	0.43 ± 0.02	0.7 ± 0.4	0.2	0.33 ± 0.01	1.5 ± 0.2	0.5	0.02 ± 0.01	ND	ND
**UM April 6, 2023	1.6 ± 0.2	0.7 ± 0.4	0.05	0.44 ± 0.01	1.8 ± 0.2	0.4	0.04 ± 0.01	ND	ND
[2] Downtown April 7, 2023	0.88 ± 0.01	149 ± 10	17	0.07 ± 0.01	3.0 ± 0.2	4.2	<LOD	ND	ND
[3] Downtown April 7, 2023	0.19 ± 0.04	1.8 ± 0.6	0.9	0.27 ± 0.02	1.8 ±	0.7	0.02 ± 0.001	ND	ND
[1] Downtown April 20, 2023	0.69 ± 0.03	2.7 ± 0.7	0.4	0.66 ± 0.03	29.0 ± 0.7	4.4	0.12 ± 0.02	0.8 ± 0.1	0.6

1- Osborne village area (Winnipeg Downtown);
2- Assiniboine River (Winnipeg Downtown);
3- The Forks (Winnipeg Downtown);
*Gym area at the University of Manitoba;
**Chemistry Department at the University of Manitoba.

Table S4: Limits of detection in particle sizes calculated for individual particles in the snow pit from the Müller Ice Cap.

Limits of Detection – size (nm)		
Snow pit Depth (cm)	**Zn-NPs**	**Pb-NPs**
10	74.4	14.1
20	95.3	14.1
30	167.8	14.1
40	73.9	14.1
50	74.2	13.2
60	69.5	13.2

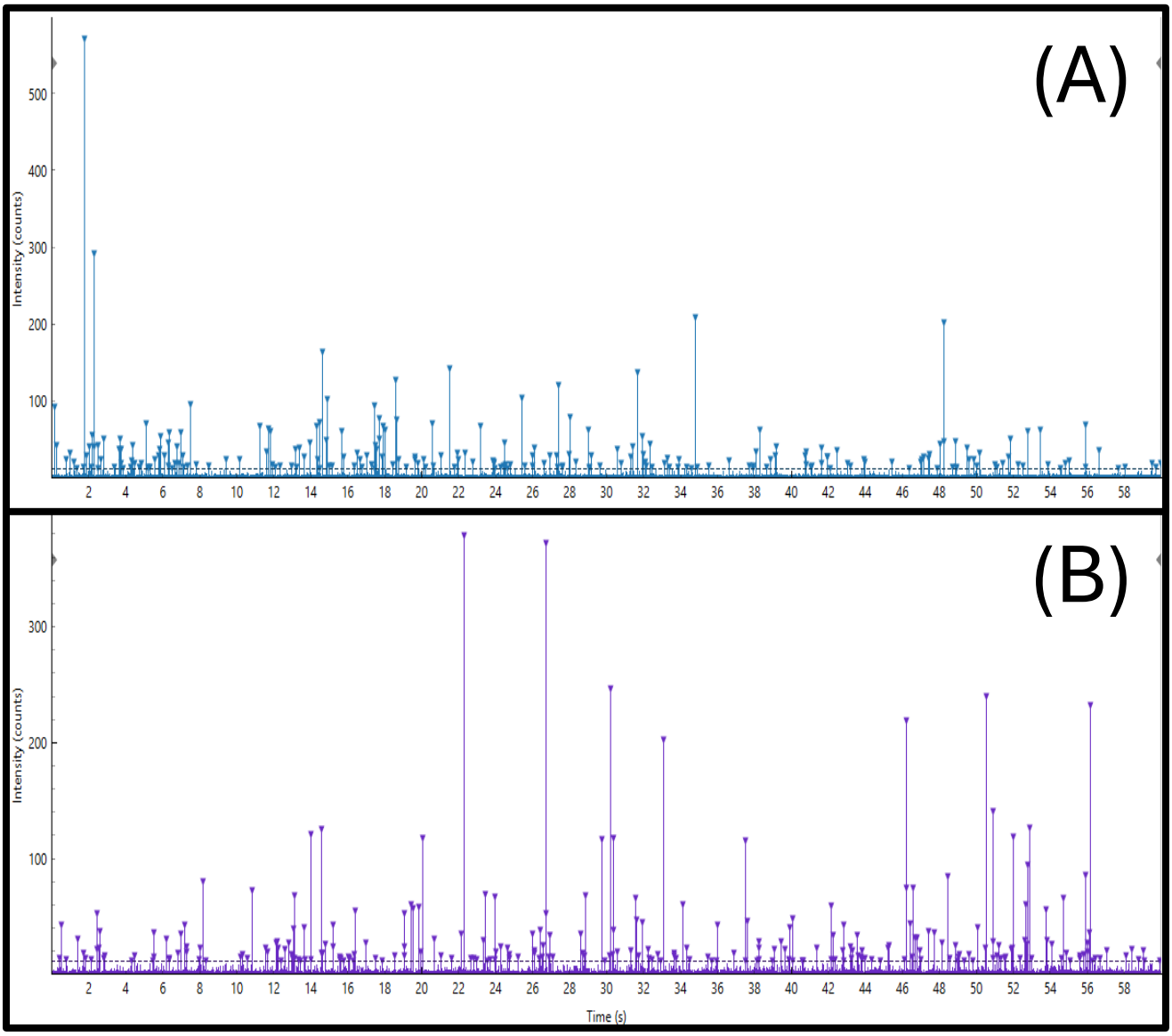

Figure S2: A representative time scan showing signals of the metal containing NPs of Zn (A) and Pb (B) in a snowpit sample at 20 cm from the Müller Ice Cap in the Canadian Arctic. Any signals above the following thresholds were considered NP pulses: 12 counts for Zn and 11 counts for Pb.

Table S5: Total concentration, mass concentration, and nanoparticle percentage for Zn, Pb, and Cd-NPs in snow pit samples collected from the Müller Ice Cap in the Canadian Arctic.

	Snow Axel Heinberg Island - NP Zn			Snow Axel Heinberg Island - NP Pb		
Snow pit Depth (cm)	Total concentration (μg L^{-1})	Mass concentration (ng L^{-1})	Nanoparticle, %	Total concentration (ng L^{-1})	Mass concentration (ng L^{-1})	Nanoparticle, %
10	0.68 ± 0.02	16.9 ± 1.2	2.5	60.0 ± 2.0	0.5 ± 0.1	0.9
20	0.9 ± 0.1	72.6 ± 4.2	7.6	140 ± 8.0	2.9 ± 0.2	2.1
30	1.0 ± 0.1	296.7 ± 21.1	28.8	90.0 ± 2.0	2.7 ± 0.2	3.0
40	0.50 ± 0.03	23.1 ± 1.4	4.6	52.1 ± 5.0	2.0 ± 0.2	3.8
50	0.59 ± 0.03	14.1 ± 0.8	2.4	30.0 ± 3.0	0.9 ± 0.1	3.0
60	0.31 ± 0.01	10.0 ± 0.8	3.2	50.0 ± 4.0	1.9 ± 0.2	3.9

Table S6: Concentration of ^{66}Zn, ^{208}Pb and ^{111}Cd in certified reference materials TM-27.4 (trace elements in water, ECCC) and 1643f (trace elements in water, NIST) by ICP-MS.

	Ionic concentration (μg L^{-1})		
Sample	^{111}Cd	^{208}Pb	^{66}Zn
1643f – Certified:	5.89 ± 0.13	18.488 ± 0.084	74.4 ± 1.7
1643f – Measured:	5.8 ± 0.2	18.5 ± 0.6	75.2 ± 0.1
TM-27.4 – Certified:	1.07 ± 0.1	2.81 ± 0.22	16.6 ± 1.9
TM-27.4 – Measured:	1.1 ± 0.1	2.9 ± 0.1	16.6 ± 1.3

Table S7: Pb isotopic ratios of the certified reference material NIST SRM981 determined by ICP-MS/MS.

Isotope Ratio	Measured values (Mean ± SD) (N=22)	Certified values (Mean ± SD)	δ, ‰
Pb^{204}/Pb^{206}	0.05904 ± 0.0004	0.059042 ± 0.000037	-0.03
Pb^{207}/Pb^{206}	0.9146 ± 0.003	0.91464 ± 0.00033	-0.04
Pb^{208}/Pb^{206}	2.1683 ± 0.007	2.1681 ± 0.0008	0.009