

Supporting Information for

Size-fractionation of trace elements in dusty snow from open pit bitumen mines and upgraders: collection, handling, preparation and analysis of samples from the Athabasca Bituminous Sands region of Alberta, Canada

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SWAMP laboratory cleaning procedure for polypropylene bottles

Based on experience to date in the SWAMP laboratory, the recommended procedure for cleaning PP bottles is summarized as follows:

- 1) soak for minimum 1 day in soapy water (2-5% v/v Fisher Versa Clean)
- 2) rinse thoroughly with ASTM Type II water
- 3) soak for minimum 1 day in 5% w/w HCl (Trace grade)
- 4) rinse with ASTM Type II water
- 5) soak for minimum 7 days in 10% w/w HNO₃ (Trace grade)
- 6) rinse with ASTM Type II water
- 7) leach for 6-8 hours at 80 °C with fresh 10% w/w HNO₃ (Trace grade)
- 8) rinse 3 times with ASTM Type II water
- 9) rinse 3 times with ASTM Type I water

The bottles are then allowed to air dry in a metal-free (PP), Class 100, laminar flow clean air cabinet. Once the bottles are dry, the lids are put on and then the bottles are packed in PE ziplock bags in preparation for work in the field.

Sample collection from the Athabasca Bituminous Sands region

All the snow samples were collected in acid cleaned 1L PP bottles, double packed in polyethylene (PE) ZipLock bags and kept frozen during transportation to the laboratory. Four samples were collected from every site: surface, top (15 cm below the surface), middle (30 cm below the surface), and bottom (45 cm below the surface). The surface snow samples were collected to determine dissolved/filterable TE concentrations ($< 0.45 \mu\text{m}$), and therefore, to avoid reaction of dust particles during storage, the samples were not acidified. Snow samples were also collected from subsurface layers, namely ca. 15 cm below the surface (top, Fig. 2A), 30 cm below the surface (middle) and 45 cm below the surface (bottom); these bottles contained nitric acid (4 mL/L) that had been purified twice, by sub-boiling in a quartz still: these samples were used to determine acid soluble TEs.

Laboratory experiments for snow sample handling and processing

a) Losses of particulate TEs by entrapment in the pores of container walls

A second experiment was conducted to mimic bulk snow having particulate matter (~20 mg in 50 mL). Filtered unacidified snowmelt ($< 0.45 \mu\text{m}$) was spiked with a range of solid certified reference materials (CRMs: coal fly ash, NIST 1633a; Montana soil, NIST 2711; sediment, BCR 320 and road dust) and incubated for 24 hrs at room conditions in a clean air cabinet (Class 100). The same experiment was conducted using MQW spiked with the same amount of solid CRMs. After 24 hrs, the samples were decanted, filtered through acid cleaned PTFE filters ($0.45 \mu\text{m}$), acidified, and analyzed for TEs. The empty bottles used for the experiments were cut open and examined for particulate matter adsorption using SEM-EDX.

b) Proton-promoted dissolution of particulate matter during sample acidification

A third experiment was conducted to determine the proton promoted dissolution of particulate matter in bulk snow (~20 mg in 50 mL). Filtered snowmelt (<0.45 μm) was spiked with solid CRMs (coal fly ash, NIST 1633a; Montana soil, NIST 2711; sediment, BCR 320 and road dust), acidified using HNO_3 ($\text{pH} < 2$) and incubated for 24 hrs at room conditions in a clean air cabinet. The same experiment was conducted using MQW spiked with the same amount of solid CRMs. After 24 hrs, the samples were filtered through acid cleaned PTFE filters (0.45 μm) and analyzed for TEs. The empty bottles used for the experiments were cut open and examined for particulate matter adsorption using SEM-EDX.

Table caption

Table S1. Location of the snow samples collected in 2015, GPS coordinates and distance from the midpoint between two upgraders.

Table S2. Accuracy and precision of trace metal concentrations in NIST 1640a (National Institute of Standards and Technology) and SPS-SW2 (LGC standards) along with the LODs and LOQs measured using ICP-QMS (iCAP Qc).

Table S3. Concentrations of trace elements in the acidified (A) and not acidified (NA) snow and Milli Q water (MQW) spiked with 10, 20 and 30 ng/L multielemental standards (CLMS-1 and CLMS-2AN) as well as Mo, Re, Sb, Te, Ti, W and Zr to determine sorption to PP bottle walls over time: immediately after spiking (T0), after one hour (1), after 1 day (24), after 1 week (168) and after one month (720).

Table S4. Release of trace elements from solids to dissolved fraction of TEs ($< 0.45 \mu\text{m}$). Acidified (A) and not acidified (NA) snow and Milli Q water (MQW) spiked with solid CRMs (coal fly ash, NIST 1633a; Montana soil, NIST 2711; sediment, BCR 320 and road dust) and incubated at 24 hrs at room conditions in the clean air cabinets in the SWAMP lab.

Table S5. Concentrations of “dissolved” (filterable through $0.45 \mu\text{m}$), acid soluble, particulate, total trace elements (TE), and TE in dust extracted from snow samples collected in 2015 from different peat bogs: MIL, JPH4, McK, McM and ANZ. The results shown in the table are average concentration of triplicate samples ± 1 std. dev. For particulate TE, the percentage of particulate TE is given in parenthesis.

Table S6. Enrichment Factor (EF) of TE in dust in snow samples collected in 2015. The EF was calculated using Th as a conservative lithophile element. The elemental crustal abundance was obtained from Rudnick and Gao, (2014).

Table S7. Concentration of acid soluble elements (TEs) in snow samples collected in 2015 from different peat bogs: MIL, JPH 4, McK, McM and ANZ. The results shown in the table are average concentration of triplicate samples ± 1 std. dev.

Table S8. Comparison of TE ratios in snow from ABS versus TE ratios in bulk ABS and its bitumen and mineral fractions. The TE concentrations in ABS, bitumen and mineral fractions are taken from Bicalho et al., (2017).

Table S1.

Site ID	Latitude	Longitude	Distance from midpoint (km)
MIL	56° 55'50.4" N	111° 28'30.3" W	11.0
JPH4	57° 6'44.10" N	111° 25'24.42" W	12.4
McK	57° 13'42.4" N	111° 42'00.8" W	24.9
McM	56° 37'40.4" N	111° 11'39.1" W	48.7
ANZ	56° 28'19.08" N	111° 2'33.66" W	68.4

Table S2.

	LOD	LOQ	NIST 1640a		SPS SW2		Accuracy	Precision
			Certified value	Measured value	Certified value	Measured value		
	ng L ⁻¹	ng L ⁻¹	µg L ⁻¹	µg L ⁻¹	µg L ⁻¹	µg L ⁻¹	%	%
V	0.7	3.4	15.1±0.3	15.8±0.2	50.0±0.3	53.5±0.9	105-107	1-2
Ni	2.9	23.4	25.3±0.1	23.3±0.2	50.0±0.3	50.2±2.7	92-100	1-5
Mo	0.4	1.8	45.6±0.6	43.7±0.9	50.0±0.3	52.3±1.4	96-105	2-3
Cd	0.2	0.7	4.0±0.1	3.6±0.3	2.5±0.0	2.6±0.2	90-106	8-9
Pb	0.1	0.8	12.0±0.0	10.9±0.4	25.0±0.1	23.5±1.7	91-94	4-7
Sb	0.3	1.8	5.1±0.0	4.6±0.1	NA		91	3
Tl	0.2	0.8	1.6±0.0	1.5±0.1	2.5±0.0	2.5±0.1	93-102	5-6
La	0.1	0.2	NA		2.5±0.0	2.4±0.1	98	4
Th	0.1	0.2	NA		2.5±0.0	2.4±0.1	98	5

* Bold values: informational purposes only

Table S6.

	V	Ni	Mo	Cd	Pb	Sb	Tl	La
McK	2	3	12	4	1	3	1	1
JPH4	1	1	7	3	1	2	1	1
MIL	3	3	16	5	1	4	1	1
McM	2	2	14	5	1	4	1	1
ANZ	2	5	19	7	2	7	1	1
Average	2	3	14	5	1	4	1	1