## Supporting Information for

# Accumulating mercury and methylmercury burdens in watersheds impacted by oil sands pollution

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The Supporting Information contains additional information on the methods and materials, Figure S1, and Tables S1–S4.

## Additional methods and materials

## Snowpack sampling

Sampling sites were accessed by helicopter with samples collected 50 to 100 m upwind of the landing sites as in Kirk et al.<sup>1</sup> and Manzano et al.<sup>2</sup> Snowpits were dug to the bottom of the snowpack using a stainless-steel shovel, and the sampling face smoothed using a Teflon scraper. Samples for THg and MeHg analyses were collected using the two-person Hg "clean hand, dirty hands" protocol into 1 L IChem© glass trace-level grade quality assured containers guaranteed to be contaminant free following the OSWER Directive 9240.0-05A (referred to hereafter as 'precleaned'). In HY2012, composite snowpack samples were collected by pressing the precleaned glass jars directly into the sampling face.<sup>1</sup> Methods were revised for HY2013 and HY2014 with full snowpack depth samples collected using custom made 10-cm diameter stainless-steel corers. At each site, the weight and depth of 10 cores were recorded for determination of surface water equivalent (SWE; using a fiberglass Adirondack corer in HY2012 and HY2014). Samples for water chemistry and trace metals were collected into 13 L pre-cleaned high-density polypropylene pails in all years. After collection, samples were frozen until processed at the Canada Centre for Inland Waters (CCIW), in Burlington, Ontario, Canada.

River water samples were obtained by wading into the river, rinsing bottles three times with sample water, then collecting a sample at approximately 50 cm below the water surface. THg and MeHg samples were collected into precleaned glass bottles using the standard "clean-hands-dirty-hands" protocol. All Hg samples were preserved with concentrated trace metal grade HCl equal to 0.2% of the sample volume. Samples for water quality parameters and trace element analyses were collected into acid-washed polypropylene bottles following standard protocols.

## Snowpack and water sample analyses

Snow samples were returned frozen to the clean laboratory at the Canada Centre for Inland Waters (CCIW), in Burlington, Ontario, Canada before being melted in the dark. River water samples were analyzed either at the CCIW or the Biogeochemical Analytical Service Laboratory (BASL), at the University of Alberta, in Edmonton, Alberta, Canada. Snow and river samples were filtered through 0.45-µm nitrocellulose membranes using acid washed Nalgene filter units.

At CCIW, melted snow and river water concentrations of THg, f-THg(dissolved component of THg), MeHg, and f-MeHg (dissolved component of MeHg) were analyzed by cold vapor atomic fluorescence spectrophotometry (CVAFS) following EPA methods 1631E (THg) and 1630 (MeHg). Unfiltered and filtered THg concentrations were determined by BrCl oxidation, SnCl<sub>2</sub> reduction, dual gold trap amalgamation, and detection by cold vapor atomic fluorescence spectrophotometry (CVAFS) using a Tekran<sup>©</sup> model 2500 Hg analyzer. Unfiltered and filtered MeHg concentrations in melted snow were determined by distillation, aqueous phase ethylation, and detection by CVFAS using a Brooks Rand MERX automated MeHg analyzer. For THg and MeHg analyses, the method detection limits (MDLs), calculated as three times the standard deviation of the blanks, were 0.03 and 0.010 ng L<sup>-1</sup>, respectively, using ~ 40 mL of

sample. All THg samples and 20% of MeHg samples were analyzed in duplicate, and were within 10% of each other with spike recoveries >90% for both analyses.

At BASL THg and f-THg were analyzed by CVAFS following EPA method 1631E. MeHg and f-MeHg were measured using a 2700 Methyl Mercury Analyzer coupled to Agilent 7900 ICP Mass Spectrometer (ICP-MS). The use of an ICP-MS is necessary because the MeHg samples were first spiked with the known amount of enriched methylmercury isotope (<sup>201</sup>MeHg) as an internal standard. The spiked samples are distilled at 127 °C by Tekran 2750 Methyl Mercury Distillation System with the addition of ammonium 1-pyrrolidinecarbodithioate (APDC) and hydrochloric acid (HCI) to remove matrices that may interfere with the ethylation process. Ascorbic acid is added to distillate to remove any trace of free chlorine. In a glass vial, the distillate is adjusted to pH 4.9 with acetate buffer. Sodium tetraethyl borate (NaTEB) is added to distillate for ethylation of MeHg to volatile MeHgEt. The ethylated samples are loaded on to the Tekran 2700 Methyl Mercury Analyzer coupled with Agilent 7900 ICP-Mass Spectrometer (ICP-MS) (Water)/ Elan DRC-e ICP-Mass Spectrometer (ICP-MS) (Solid). On the Tekran 2700 Methyl Mercury Analyzer, volatile ethylated mercury compounds in the sample are stripped from the liquid phase with argon gas, trapped and desorbed on the Tenax trap, separated mercury species by capillary GC and temperature ramping GC oven, then pyrolytic break down of mercury compounds to Hg (0). The elemental mercury is then introduced to ICP-MS to detect for mercury isotope 202 and 201. The concentrations are measured based on the ratio of mercury isotope with the correction of internal standard.

Water chemistry was measured at the National Laboratory for Environmental Testing (NLET) in Burlington, ON, Canada including 45 trace elements using inductively coupled plasma-mass spectrometry (ICP-MS).

## Discharge measurements and river load calculations

Mean daily discharge measurements were from the Water Survey of Canada (WSC: <u>http://wateroffice.ec.gc.ca/</u>) and from the Oil Sands Monitoring (OSM) Program (<u>https://www.canada.ca/en/environment-climate-change/services/oil-sands-monitoring.html</u>). Discharge was not measured at the upstream Steepbank site (S66) until after 2014. Therefore, to model pre-2014 discharge at this site, we used a linear regression between the WSC gauge near the river mouth (07DA006) and the OSM gauge S66 from 2014–2017. Discharge at the two sites is significantly related (r<sup>2</sup>=0.99), even when split between high-flow (r<sup>2</sup>=0.99) and low-flow (r<sup>2</sup>=0.98) seasons. Water quality data were in-filled between sampling events at daily frequency using linear extrapolation. Daily tributary river loads were then calculated by multiplying measured and extrapolated concentrations by the mean daily discharge.

Freshet was defined both by visually examining the hydrograph for each watershed and by monthly field visits that recorded the presence and extent of snow cover. Graphs of the mean daily discharge from the six tributary rivers were superimposed and the onset of freshet in a given hydrologic year was defined as the first increase in spring mean daily discharge, in any river. The end of freshet was defined as the inflection point between the first and second hydrograph peaks. This second increase in discharge is often associated with summer precipitation, and field observations made during water quality sampling recorded no snow on the ground by this date in any of the watersheds sampled. The freshet discharge peak for HY2012 occurred between March 27<sup>th</sup> and June 11<sup>th</sup>, between April 26<sup>th</sup> and June 8<sup>th</sup> in HY2013, and between April 6<sup>th</sup> and May 14<sup>th</sup> in HY2014.

#### Additional details of snowpack modeling methods

Snowpack was collected in HY2012 and HY2013 from all watersheds except the High Hills. However, HY2012 and HY2013 snowpack sampling was designed for a different study. Evaluation of the HY2012 and HY2013 snowpack data, showed and insufficient number of samples, and poor spatial coverage in the Steepbank, Firebag, Ells and MacKay watersheds. Thus, from the HY2012 and HY2013 snowpack data sets, only the Muskeg Watershed had sufficient spatial coverage for credible modeling snowpack loads at the watershed and subbasin scales.

Model parameters were selected to retain the broad range in snowpack loads calculated from individual site measurements and to minimize data normalization. Although the HY2014 followed a gridded pattern, which provided a good base for the modeled surface, the full extent of the MacKay, Ells, Firebag, and High Hills watersheds were not sampled. To extend the spatial coverage of the modeled geostatistical surface to the full extent of the tributary watersheds boundaries, additional false points were added to the data set. False points were created, at the perimeter of the watershed boundaries, where there was no snowpack data for more than 50 km. For every parameter modeled, each false point was then assigned a conservative average load (ng/m<sup>2</sup>) from the closest sample sites. The modeled surfaces are thus a conservative estimate of snowpack loads in the MacKay, Ells, Firebag, and High Hills watersheds.

Prior modeling of snowpack THg and MeHg loads prioritized evaluating the overall spatial pattern of atmospheric deposition at a broad regional scale.<sup>1,3</sup> ArcGIS modeling used selected parameters for the Simple Kriging method, which is a two-step process. First, the snowpack loads from individual sites are modeled to create a geostatistical surface. Second, the geostatistical surface is resampled in a gridded manor, producing the modeled snowpack loads for each cell. Kriging normalizes the data (snowpack loads), which has been useful for discerning overall Oil Sand Region spatial trends in snowpack loads (e.g., Kirk et al.<sup>1</sup>). Our objective, however, was different. We sought to quantify spatial differences in snowpack loads at the sub-watershed scale. It was critical therefore to retain the precise geospatial location for sites with measured snowpack loads relative to the modeled surface, and to generate credible modeled loads in the outer reaches of the study area where we have fewer measurements. Using an Inverse Distance Weighting (IDW) method was found to produce modeled snowpack loads that did not normalize the data while also minimizing the geospatial distortion of the modeled snowpack loads relative to measured loads from individual sites.

## Details of the Inverse Distance Weighting (IDW) method

Geostatistical analysis was used to create a surface model from snowpack loads for each sample site using ArcGIS 10.5 Inverse Distance Weighting (IDW). IDW method property

parameters used for analysis were: power (optimized); neighborhood type (smooth); smoothing factor value (0.1); angle (150°, representing the dominant surface wind direction for the study region); major semi axis (0.8); and minor semi axis (0.64). The data set of snowpack loads was used to create a geostatistical surface for the entire study area (excluding sites with 0 values). This geostatistical surface was converted to a raster dataset (with x and y cell size 0.001249 of an arc degree). The raster dataset was then re-projected from a Geographic World representation into local UTM Zone 12N Projection (x and y cell size in meters). This entire surface coverage was then clipped for each of the watersheds and the sub-basins to calculate the snowpack loads for the watershed or sub-basin.

## **SI Figures**



**Figure S1.** Bar charts of modeled (using IDW) % particulate THg, % particulate MeHg, and % MeHg (relative to THg) within each of the six watersheds during HY2014 and within the Muskeg watershed over all three hydrologic years.

# **SI Tables**

**Table S1.** Watershed and sub-watershed land-cover and land-use areas for the year 2014 for all watersheds and for the years 2012 and 2013 in the Muskeg watershed. The % oil sands disturbed refers developed areas where there is no natural exchange of water with the rest of the watershed (e.g. tailings ponds) as determined by the Regional Aquatics Monitoring Program (RAMP; <u>www.ramp-alberta.org</u>) while the % disturbed refers to total human footprint from the Alberta Biodiversity Monitoring Institute.<sup>4</sup>

Watershed	Location	Contributing area (km²)	% Bog	% Fen	% Marsh	% Open water	% Swamp	% Oil sands disturbed (RAMP)	% Disturbed (ABMI)
	Downstream	1405	3.3	33.7	0.1	0.5	21.7	9.4	22.2
Muskey (2012)	Upstream	418	2.8	33.5	0.0	0.2	24.4	1.4	15.2
Muckog (2012)	Downstream	1405	3.5	35.1	0.1	0.5	22.6	9.7	-
wuskey (2013)	Upstream	418	2.9	34.9	0.0	0.2	25.7	1.4	-
Muckog (2014)	Downstream	1405	3.3	33.5	0.1	0.5	21.6	11.6	22.9
Muskey (2014)	Upstream	418	2.8	32.6	0.0	0.2	24.1	2.3	17.2
Steenberk	Downstream	1317	15.1	37.2	0.2	0.5	16.3	1.2	3.6
Steepballk	Upstream	1195	16.0	39.1	0.2	0.6	15.8	0.1	2.4
Ello	Downstream	2419	11.4	22.7	0.3	6.7	6.8	0.3	2.0
Elis	Upstream	2272	11.8	23.2	0.3	7.1	6.8	0.0	1.5
Maalfass	Downstream	5550	18.8	30.4	0.2	0.8	12.9	0.8	3.6
Machay	Upstream	4174	19.9	32.7	0.2	0.7	13.7	0.4	3.3
Firebag	Downstream	6370	4.8	26.6	0.3	1.8	10.0	0.5	2.2
High Hills	Downstream	1345	3.5	19.5	0.2	0.3	4.2	0.0	0.1

**Table S2.** List of each watershed including the number of snowpack and river samples collected during each hydrologic year for total mercury (THg) and methylmercury (MeHg).

		Number of Snow Samples			Number of River Samples					
Watershed	Sub-watershed				THg	MeHg	THg	MeHg	THg	MeHg
		2012	2013	2014	2012	2012	2013	2013	2014	2014
Muskog	Upstream	5	6	4	-	-	31	26	43	41
WIUSKEg	Downstream	12	12	12	31	23	41	36	45	44
Stoophank	Upstream	-	-	5	-	-	-	-	38	38
Steepballk	Downstream	2	-	36	36					
File	Upstream	-	-	5	-	-	-	-	40	39
LIIS	Downstream	-	-	2	-	-	-	-	39	39
	Upstream	-	-	9	-	-	-	-	37	37
WIACKAY	Downstream	-	-	8	-	-	-	-	37	37
Firebag	Downstream	-	-	15	-	-	-	-	127	124
High Hills	Downstream	-	-	4	-	-	-	-	36	36

**Table S3.** The number of exceedances of the Alberta Surface Water Quality Guideline for chronic long-term ( $\geq$  4 days) Hg exposure (5 ng/L) and acute ( $\geq$  1 hour) Hg exposure (13 ng/L). Exceedances are based on daily concentration values for HY2014 where each value was either a measured concentration or estimated by linear extrapolation. The higher (acute) Canadian Water Quality Guideline for the protection of aquatic life (26 ng/L THg) was not exceeded.

Watershed	Station	Number of exceedances of chronic (5 ng/l) guideline	Number of exceedances of acute (13 ng/l) guideline	
MacKay	Downstream	55	7	
Ινίαζκαγ	Upstream	57	3	
<b>F</b>	Downstream	76	28	
EIIS	Upstream	70	16	
Firebag	Downstream	8	0	
Muskeg	Downstream	0	0	
	Upstream	0	0	
Characher als	Downstream	52	8	
Steepballk	Upstream	16	0	
High Hills	Downstream	93	23	

**Table S4.** Results of permutation and non-parametric tests for paired upstream and downstreamsamples.

Paired mean (PermMatched) results (*p-value<0.05, **p-value<0.01)								
Watershed	THg	THg	THg	MeHg	MeHg	MeHg		
	Concentrations	Loads	Yields	Concentrations	Loads	Yields		
Muskeg	0.01*	0.009**	0.6	0.9	0.04*	0.02*		
Steepbank	0.002**	0.002**	0.002**	0.04*	0.02*	0.02*		
Ells	0.006**	0.003**	0.003**	0.9	0.6	0.7		
МасКау	0.02*	0.03*	0.007**	0.007**	0.04*	0.1		

Permutation tests for paired upstream and downstream samples

Non-parametric tests for paired upstream and downstream samples

Paired median (pairwise.wilcox.test	results (p-value<0.05, p-value<0.01	L)
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Watershed	THg	THg	THg	MeHg	MeHg	MeHg
_	Concentrations	Loads	Yields	Concentrations	Loads	Yields
Muskeg	0.010**	0.010**	0.9	1.0	0.1	0.03*
Steepbank	0.002**	0.002**	0.002**	0.1	0.01*	0.02*
Ells	0.006**	0.004**	0.004**	0.2	0.9	0.8
МасКау	0.01*	0.03*	0.01*	0.01*	0.04*	0.3

Among watershed permutation tests of differences in mean Freshet concentrations, loads, and yields (Perm1way) p-values < 0.05, p-values < 0.01

THg	THg	THg	MeHg	MeHg	MeHg
Concentrations	Loads	Yields	Concentrations	Loads	Yields
0.001**	0.0004**	0.0000**	0.40	0.09	0.06

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