FOCUSED STUDY ACTIVITY WORK PLAN

General Information

Work Plan Unique Identifier:	*A-IC-4-1718*	
Focused Study Activity Title:	Atmospheric Deposition – Identification of Sources of Contaminants in Snowpack and Lake Sediments	
Focused Study Category:	Investigation of Cause or Potential Ecological Impact	
Geographic Location (*choose from drop-down menu. If Project Location is in more than one area choose from second drop-down***)**	Athabasca Oil Sands Region	Peace Athabasca Delta
Monitoring Site(s) Coordinates *(latitude and longitude)*		
Project Leader (s):	Derek Muir, Chris Marvin, Amila De Silva and Jane Kirk	
Organization and contact information:	**Environment and Climate Change Canada, Aquatic Contaminants Research Division** **Email: Derek.Muir@canada.ca, Chris.marvin@canada.ca, Amila.desilva@canada.ca, Jane.Kirk@Canada.ca** **Phone: 905-319-6921**	
Date Study initiated:	**2017 (as a separate focus study)**	
Monitoring Category: *(From OSM long-term plan; choose from drop-down menu)*	Atmospheric Monitoring	
Strategic Objective of Focused Study: *(From OSM long-term plan; choose from drop-down menu)*	Objective A2: Detect and report levels and trends of oil sands related chemical substances being deposited from the atmosphere	
Hypotheses: *(Briefly outline the specific hypotheses that your focused study is aiming to address)*	Major contributors to atmospheric contaminant deposition have unique chemical signatures that can be identified and statistically separated by analyzing source materials (i.e., pet coke and road haul dust, bitumen ore) and environmental receptors (i.e. snow, lake sediments, water samples, and air) using novel techniques.	
Deliverables: *What tangible goal (s) and/or product(s) will the monitoring produce and when?*	Identification of major contributors (i.e., pet coke and road haul dust, bitumen ore) to atmospheric contaminant deposition within 125 km of the major OS developments (2018-2019).	

Detailed Study Plan

(Please provide detailed information on the specifics of your focused study including – (**keywords, hypothesis and the assumptions and constraints behind your hypothesis**)

Provide a maximum of 10 key words: snow, polycyclic aromatic compounds (PACs), organic aerosols, metals, mercury, source attribution

Describe how you will test your hypothesis:

We propose to combine several novel analyses, including 2-dimensional-gas chromatography-time-of-flight mass spectrometry (GCxGC-ToF-MS) and liquid chromatography-Orbitrap high resolution mass spectrometry, elemental isotope ratios (mercury, lead, sulfur, + others to be investigated), and carbon particle analysis of both sources (i.e., petroleum coke "pet coke" and road haul dust, bitumen ore) and environmental receptors (i.e. snow, lake sediments, water samples, and air) to identify and statistically separate key sources of atmospheric contaminant deposition. Source samples from different OS industries will be obtained COSIA. Snow and lake sediments will be obtained during our field campaign, water samples will be provided through the Water Quality Monitoring program (Chambers and Cooke), and air extracts for PACs from passive samplers will be obtained from Harner in the Air Quality Research Division.

Initial studies using GCxGC-ToF-MS have shown that snow, sediment, and air samples contain hundreds of PACs that are not being analysed by routine GC-MS methods (Manzano et al. 2016). This work has suggested that select sulphur-, nitrogen- and oxygen-based PACs and their alkylated derivatives show great potential as diagnostic source indicators. Pet coke appears to be a major source material for areas near upgraders based on the recent work of Zhang et al. (2016) using moss from bogs in the OS region, however, that work was based on a limited suite of PACs and did not include other indicators such as metal analyses. Preliminary work on pet coke samples provided by Dr Jon Martin (U of Alberta) has shown that they contain a novel suite of PACs which appear to be very useful for source attribution e.g. allowing the spatial distribution of pet coke to be mapped.

Petroleum coke is formed during bitumen upgrading, which increases the hydrogen-to carbon ratio by removing carbon from the bitumen. Syncrude carries out fluid coking whereas Suncor and CNRL use delayed coking. Delayed coking is done at temperatures of ~415–450 °C and fluid coking is done at ~ 480–565 °C (Jack et al 1979). In delayed coking-liquid feed is reacted with hydrogen in a large drum, and coke accumulates at the bottom with time (CNRL and Suncor) while for fluid coking liquid feed is sprayed into a bed of hot coke particles (Syncrude) (Scott and Fedorak 2004). The result is a carbonaceous, heterogeneous substance termed "pet coke". The difference in operating temperatures likely yields different contents of volatiles and other less volatile carbonaceous substances. The sheer volume of coke produced by oil sands companies precludes storing the coke in silos or other isolated structures and thus it is stored outside leading to its potential to disperse off site (Fedorak and Coy 2006).

Preliminary analyses show that only low concentrations of mercury and methyl mercury are present in pet coke (older samples provided by Dr Jon Martin, U of Alberta). A relatively large suite of elements (43) were

determined in lichen by ICP-MS by Landis et al (2012) and source identification was investigated with samples of haul road dust, overburden, pet coke and other process materials, as well as upgrader stack particulates. They used 28 elements for the source identification study and concluded that largest impact on elemental concentrations was related to fugitive dust.

Data for other chemical signatures in source materials is gradually emerging due to research sponsored by WBEA as well as independent university based studies. Studabaker et al (2012) analysed a suite of 18 unsubstituted PAHs and 2 alkylated PAHs in refinery process material, mine mineral, haul road dust, and forest fire ash and found distinctly different patterns which could partially distinguish sources. Studabaker et al (2012) also found that Al, Fe, V, molybdenum, cerium, neodymium, samarium, and praseodymium in lichen correlated with total (unsubstituted and alkylated) PAH concentrations, suggesting that similar transport mechanisms are involved for crustal metals and PAHs near mines. Oil sands facility soils show abundances for almost all 36 PACs (unsubstituted and alkylated PAHs), while only a few species, notably chrysene, are abundant in the forest soils (Wang et al. 2015).

Metal isotopes have also been used to access sources of emissions in the oil sands region (Huang et al 2015). Stack emission particulates from oil sand upgraders have been shown to have different lead isotope ratios to lichen and forest soils (Graney et al 2012). Blum et al (2012) determined mercury isotope ratios in lichen from the oil sands region and found that Hg isotope ratios (Δ199Hg and Δ201Hg) were higher within 25 km of the oil sands development area. They speculated that this is due to isotope fractionation during partial photochemical reduction and loss of Hg from lichen surfaces. However, they did not investigate source materials. In future work we intend to apply ICP-multicollector mass spectrometry to determine isotope ratios of selected elements in oil sands environmental samples.

Jariyasopit et al (2016) determined PAC transformation products, including nitrated polycyclic aromatic hydrocarbons (NPAHs) and oxygenated polycyclic aromatic hydrocarbons (OPAHs) in air in the oil sands region. They found PACs were elevated near mining activities and declined with distance from the source region, while NPAHs and OPAHs exhibited a more variable spatial distribution with the highest levels in Fort McMurray. No previous work has been done on NPAHs and OPAHs in depositional samples. Ultra-high performance liquid chromatography-atmospheric pressure photoionization-tandem mass spectrometry (UHPLC-APPI-MS/MS) has been used for simultaneous analysis of PAHs and NPAHs (Lung and Liu 2015). When combined with high resolution mass spectrometry, UHPLC may be very useful for separating and identifying a broader array of PAC degradation products in oil sands environmental media.

Liggio et al. (2016) assessed of the magnitude of secondary organic aerosol (SOA) production from oil sands emissions and concluded that atmospheric oxidation of low-volatility organic vapours was responsible for the majority of the observed SOA mass. Under the project “Studying OS Air Pollution Emissions, Transformation and Fate”, Liggio and colleagues are studying SOA in more detail using a laboratory based approach. As part of that study this project (de Silva and Muir) will identify SOA compounds ie C10-C20 carboxylates and other oxidized hydrocarbons, using UHPLC-Orbitrap mass spectrometry. If the lab based SOA results are successful, the analyses will be extended to extracts of snow from the OS area.

Assumptions and Constraints behind the hypothesis and the testing method:

1. Critical to the source identification focus of this study is the ability to obtain source samples from industry. This has been done in 2016 through COSIA but only from one of 4 upgrader and bitumen

mining and processing sites so additional samples are required in 2017-18. Future access to source materials from all major industries in the OS region is important to fully investigate atmospheric sources and this depends on cooperation of the industries and help of COSIA. 2. There could be other sources of PACs and other contaminants such as mercury, methyl mercury, as well as the 45 elements that are being measured by ICP-MS, besides pet coke, road haul dust, and bitumen ore. These include forest fires, vehicle emissions (particularly from diesel engines), low temperature waste burning, and volatilization from tailings ponds (Parajulee and Wania 2014) 3. Additional analytical method development may be necessary to optimize GCXxGC and UHPLC separations of PACs, and degradation products of PACs and SOA. 4. Ability to put analytical contracts in place in a timely fashion. 5. Ability to bring in a post-doctoral fellow for the GCxGC studies and to hire a term employee for instrument and analytical support. 6. For 2018-19 the study design will be strengthened to include field work, coordinated with the 'Atmospheric Deposition to Lakes and Snowpack" project to include sampling near sources (eg haul roads, coke piles) using a geometrical approach to better assess chemical signatures for source identification and quantification.	
Deliverables: *What tangible goal (s) and/or product(s) will the monitoring produce and when?*	1. Identification of major contributors (i.e., pet coke and road haul dust, bitumen ore) to atmospheric contaminant deposition within 125 km of the major OS developments (2018-2019). 2. Identify novel PACs and other contaminants including PAC degradation products, and multi-element suites, not routinely measured in oil sands environmental media, and assess their usefulness for future source tracking and for monitoring. 3. All raw data uploaded to the portal in a timely fashion. 4. Data published in the peer reviewed literature and presented at conferences. 5. Data shared with industry partners through the Canadian Oil Sands Innovation Alliance (COSIA) to design effective mitigation strategies if needed.

References:

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Graney, J.R., Landis, M.S., Krupa, S., 2012. Chapter 15 - Coupling Lead Isotopes and Element Concentrations in Epiphytic Lichens to Track Sources of Air Emissions in the Athabasca Oil Sands Region, in: Kevin, E.P. (Ed.), Developments in Environmental Science. Elsevier, pp. 343-372.

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Manzano, C.A., Muir, D., Marvin, C., 2016. Separation of thia-arenes and aza-arenes from polycyclic aromatics in snowpack samples from the Athabasca oil sands region by GC×GC/ToF-MS. International Journal of Environmental Analytical Chemistry 96, 905-920.

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Summers, J.C., Kurek, J., Kirk, J.L., Muir, D.C.G., Wang, X., Wiklund, J.A., Cooke, C.A., Evans, M.S., Smol, J.P., 2016. Recent warming, rather than industrial emissions of bioavailable nutrients, is the dominant driver of lake primary production shifts across the Athabasca Oil Sands Region. PLoS ONE 11.

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Zhang, Y., Shotyk, W., Zaccone, C., Noernberg, T., Pelletier, R., Bicalho, B., Froese, D.G., Davies, L., Martin, J.W., 2016. Airborne Petcoke Dust is a Major Source of Polycyclic Aromatic Hydrocarbons in the Athabasca Oil Sands Region. Environmental Science & Technology 50, 1711-1720.

Data Management

If this work generates data please summarize your project-level data management plan.

Deliverables	Timeframe
Data Collection Period: *Field work*	Start : 2016-09-14 End: 2017-09-14
Data Analysis Period: *Laboratory analysis and QA/QC of data*	Start : 2016-09-14 End: 2018-03-31
Data Release Date: *Metadata and data consistent, complete and meet basic standard format for publication in Open Data; on or linked to JOSM portal*	2018-03-31

Reporting and Publications

Provide information on the anticipated reports / publications. (Insert additional rows if needed)

Expected Subject/Titles of Publications or Reports	Short Description of Publication or Report	Expected Year of Publication
Spatial and temporal trends of novel PACs in snow, sediments and air in the oil sands region. In prep.	Reports on the determination of novel PACs in environmental media previously analysed for conventional PACs	2017
Identification of novel PACs in pet coke, road haul dust and bitumen from the Alberta oil sands region	Reports on the analysis of source materials from the oil sands region received in 2016-17	2018
Metal isotope ratios in pet coke, road haul dust and bitumen and environmental samples	Reports on the analysis of source materials from the oil sands region received in 2016-17	2018

Technical / Professional Roles and Responsibilities

Identify members of the monitoring team/organization, their roles and responsibilities. Identify monitoring organization leads if different from overall monitoring activity lead. (Insert additional rows if needed)

Role	Responsibilities	Resource Name/Organization
Project Lead (Environment and Climate Change Canada)	- Project coordinator and principal investigator on PACs in snow, water, air, and sediments	Derek Muir
Project Lead (Environment and Climate Change Canada)	- Project coordinator and principal investigator on metals and methyl mercury in snow and mercury in sediments	Jane Kirk
Project Lead (Environment and Climate Change Canada)	- Principal co-investigator on PACs in snow, water, air and sediments	Chris Marvin
Project Lead (Environment and Climate Change Canada)	- Principal co-investigator on PACs degradation products analyzable by UPLC-Orbitrap MS	Amila de Silva
Post-doctoral fellow (Environment and Climate Change Canada)	- Interpretation and write up of PACs data in snow - Identification and quantification of novel PACs in snow, sediments, water and source materials using GCxGC – Time of Flight-Mass Spectrometry	Leah Chibwe (Jan 1 2017-Dec 31st 2019)
Post-doctoral fellow (Environment and Climate Change Canada)	- Interpretation and write up of metals data in snow - Source attribution studies to identify relative importance of pet coke/fugitive dusts etc. to contaminants loads (using metal isotope ratios, carbon particle analysis)	Yamini Gopalapillai (Jan 1 2017-Dec 31st 2019)
1 CH-01 Term	- support for GCxGC-time of flight mass spectrometry analysis of source materials and environmental samples including extractions, isolation steps and servicing of the instrument (changing gases, GC columns)	TBD
1 EG-04 Term (Environment and Climate Change Canada)	- Processing of water chemistry and metals in snow samples - Extraction of PACs in snow	Amy Sett
1 EG-04 Term	- Analysis of trace methyl mercury in snow and	Amber Gleason

(Environment and Climate Change Canada)	total mercury analysis in lake sediments - QA/QC and data uploads to the portal	
Technical Support (Environment and Climate Change Canada)	- Analysis of PACs in snow	Dayue Shang and staff (Pacific and Yukon Laboratory for Environmental Testing)
1 EG-05 (Environment and Climate Change Canada)	- Extraction of snow (separate filtered particles and dissolved phases) - GC-MS analysis of selected PACs and reference materials	Camilla Teixeira

Deliverables **(Year 1)** If your Focus Study is longer than 1 year then complete **Appendix C** for multi-year deliverables breakdown

Provide a summary of tangible quarterly deliverables. Identify major project areas (deliverables) and results that can be identified as a tangible goal. This could include: field work, lab work/ analysis, evaluation, data, reports, publications, SOPs etc. Do not define process as your Deliverable e.g. 'fly to Ft. McMurray to conduct fieldwork' or 'seek Director approval for report'.

Deliverable(s) (please provide enough information to support status reporting)
Q1 – April to June
Lab analyses of source materials and existing and new sample extracts for PACs in OS snow and sediment cores by use of 2D-GC-TOF-MS.
Q2 – July to September
Publication on "Spatial and temporal trends of novel PACs in snow, sediments and air in the oil sands region" which reports on the determination of novel PACs in environmental media previously analyzed for conventional PACs.
Q3 – October to December
SETAC North America presentation on "Spatial and temporal patterns of novel PACs in snow in the Athabasca oil sands region (Alberta, Canada)."
Q4 – January to March
Initial report cataloging novel PACs in snow and other environmental media – for output to the portal

Detailed Financial Breakdown – Year 1 of 3 (2017-2018)

Also complete **Appendix B** for the multi-year financial breakdown

Budget requirements – List areas that require budget expenditures: (ADD OR DELETE BUDGET CATEGORIES AS REQUIRED)	**OS Funding**	**External Funding (*outside JOSM*)**
O&M - Operations and Maintenance:		
Helicopter Costs	-	**$**
Data Management	-	**$**
Publication costs (open access)	**$1,500**	
TMU related analyses (multielement suite and water chemistry at NLET; PAC analysis by PYLET)	-	
Internal Lab Analysis (mercury and methyl Hg analyses in Kirk lab; core dating by Muir/Yang)	-	**$**
Consumable Materials & Supplies (GCxGC, UPLC consumables)	**$29,080**	**$**
Sub-Total (not corrected with spreadsheet info)	**$30,580**	**$**
O&M - Travel		
Field Work	-	**$**
Conferences (identify conference) SETAC North America X 1 ($3100)	**$3000**	**$**
Meeting (identify meeting) OS Symposium, Integration workshop, and/or meetings with AEP and ASTD as needs arise (=$2000)	**$2000**	**$**
Training – 2D-GC-TOF maintenance	**$3000**	
Sub-Total (not corrected with spreadsheet info)	**$8000**	**$**
O&M - External Contracts :		
Goods and Services Contract (*describe contractor*) Service contract for GCxGC	**$20,000**	**$**
External Lab Analysis Contract to specialized paleolimnology laboratory	-	**$**
Sub-Total (not corrected with spreadsheet info)	**$20,000**	**$**
Salaries:		
Principal Investigator	**$**	**$21,586**
Technical / Professional Assistants	**$**	**$23,022**

Budget requirements – List areas that require budget expenditures: (ADD OR DELETE BUDGET CATEGORIES AS REQUIRED)	OS Funding	External Funding (*outside JOSM*)
Field Staff (overtime) (Includes CSS Costs of salary*14.6% and EPB costs of salary*CSS*20%)	-	$
Visiting Fellow (2017-18) – O&M not salary (both post-docs are starting work January 1, 2017 and continuing as of April 1; 1 X $60,000 (directly invoiced by NSERC)+ 4.1% CSS	**$60,000**	$
Technical / Professional Assistants: 1 term CH-01 (Includes CSS Costs of salary*14.6% and EPB costs of salary*CSS*20%)	**$69,816**	
Students	-	$
Total Salaries	**$129,816**	**$44,608**
Total O&M/Salaries (not including overhead)	**$188,396**	
Total Overhead (Includes O&M/Salaries)	**$41,604**	$
2017-2018 GRAND TOTAL (in agreement with spreadsheet)	**$230,000**	**$44,608**

Appendix A - Approvals

Project Submitted by:		
Name:		
Organization:	Signature:	Date:

Project Approved by:		
Dr. Monique Dubé (AEP)		**Dr. Kevin Cash (ECCC)**
Signature 		Signature 
Date		Date

APPENDIX B – Detailed Multi-year Financial Breakdown (Complete the following detailed financial breakdown; add or delete categories as required)

Budget requirements	Year 1 (201X- 201Y)		Year 2 (201X- 201Y)		Year 3 (201X- 201Y)	
	Cash	In-kind	Cash	In-kind	Cash	In-kind
1) Salaries and benefits						
a) Investigators						
b) Technical/professional assistants	**$69,816**					
c) Field Staff						
d) Visiting Fellows	**$60,000**					
2) Operations and maintenance						
a) Facilities						
b) Equipment						
c) Lab analysis						
d) Data management						
e) Field work						
3) Consumable Materials and supplies						
a) GCxGC, UPLC consumables	**$29,080**					
b) Goods and Services Contract	**$20,000**					
4) Travel						
a) Conferences and meetings	**$5000**					
b) Field work /Training	**$3000**					

c) Project-related travel						
5) Dissemination & Engagement						
a) Publications/Reports	**$1,500**					
b) Translation (if required)						
c) Communications						
d) Stakeholder Engagement						
e) Indigenous Peoples Engagement						
6) ECCC Overhead						
a) Overhead	**$41,604**					
Grand Total	**$230,000**					

APPENDIX C –Years 2 and 3 Deliverables (Complete the following detailed breakdown. Provide a summary of tangible quarterly deliverables and your anticipated expenditures. Identify major project areas (deliverables) and results that can be identified as a tangible goal.)

Year 2 (2018- 2019)
Deliverable(s) (please provide enough information to support status reporting)
Q1 – April to June
Continuation of lab analyses of source materials and existing and new sample extracts for PACs in OS snow and sediment cores by use of 2D-GC-TOF-MS and LC-Orbitrap. Contract for application of ICP-multicollector mass spectrometry to determine isotope ratios of selected elements in oil sands environmental samples
Q2 – July to September
Planning for geometrical approach to better assess chemical signatures for source identification and quantification with cooperation of COSIA
Possible peer reviewed publication on identification of oxidized hydrocarbon compounds in secondary organic aerosols in the oil sands region
Q3 – October to December
SETAC North America presentation on "Spatial patterns of novel PACs in snow in the Athabasca oil sands region."
Q4 – January to March
Field work coordinated with the 'Atmospheric Deposition to Lakes and Snowpack" project to include sampling near sources (eg haul roads, coke piles) using a geometrical approach to better assess chemical signatures for source identification and quantification.
Updated report cataloging novel PACs and elemental isotope ratios in snow and other environmental media – for output to the portal