

FOCUSED STUDY ACTIVITY WORK PLAN

General Information

Work Plan Unique Identifier:	W-MD-2-1718
Focused Study Activity Title:	Develop a method that accurately measure seepage from tailings ponds and evaluate its toxicological significance.
Focused Study Category:	Investigation of Cause or Potential Ecological Impact
Geographic Location (<i>choose from drop-down menu. If Project Location is in more than one area choose from second drop-down</i>)	Athabasca Oil Sands Region
Monitoring Site(s) Coordinates (<i>latitude and longitude</i>)	N/A
Project Leader:	Mark Hewitt and Richard Frank
Organization and contact information:	<p>Environment and Climate Change Canada Water Science and Technology Directorate Burlington ON mark.hewitt@canada.ca richard.frank@canada.ca</p>
Date Study initiated:	
Monitoring Category: <i>(From OSM long-term plan; choose from drop-down menu)</i>	Watershed Monitoring
Strategic Objective of Focused Study: (<i>From OSM long-term plan; choose from drop-down menu</i>)	Objective W2: Aquatic Contaminant Source Identification
Hypotheses: <i>(Briefly outline the specific hypotheses that your focused study is aiming to address)</i>	<ol style="list-style-type: none"> 1. <i>The Source Identification methodologies being employed are capable of differentiating complex mixtures in industrial process waters from natural bitumen sources.</i> 2. <i>Effects-Directed Analysis (EDA) allows for better characterization of both industrial and natural bitumen sources. Biological responses to generated chemically-distinct fractions from these sources will further enable the prioritization of chemical classes of interest.</i>
Deliverables: <i>What tangible goal (s) and/or</i>	<p>Goals:</p> <ol style="list-style-type: none"> 1. The work will advance our understanding of migratory

<p><i>product(s) will the monitoring produce and when?</i></p>	<p>compounds of interest and their inherent chemical variability within the relevant industrial and natural source materials investigated. Understanding this variability is required in validating the analytical methodology against the range of industrial and natural sources.</p> <ol style="list-style-type: none"> 2. The work will further our understanding of toxicologically relevant compounds within bitumen-influenced waters and will be integrated into the OSM network to better discriminate natural vs. anthropogenic sources under the risk based framework. Prioritized compounds and/or chemical classes will also be integrated into OSM framework with future objective of quantitative assessment. 3. The work will characterize the Certified Reference Materials (CRMs; Project S1-2-1-1617) under development for all stakeholders and further our understanding of toxicologically relevant compounds within bitumen-influenced waters. This supports the risk based framework by identifying which compounds and/or chemical classes within those sources pose the greatest risk to aquatic ecosystems and should be integrated into the OSM framework. <p>Products:</p> <ol style="list-style-type: none"> 1. Methodology to qualitatively detect tailings seepage into aquatic systems for OSM. 2. Chemical and toxicological characterizations of new Certified Reference Materials for industrial and natural bitumen-derived organics. 3. Effects directed analyses of groundwaters contaminated with tailings will begin to assess any risks presented by tailings seepage, supporting the risk based framework. This aspect addresses the question of whether tailings leakage is toxic, and if so, what are the toxic components within these mixtures. Characterizing the toxicity of migratory mixtures is of paramount importance, with subsequent investigations prioritizing and quantitatively assessing the toxic compounds and/or chemical classes, and eventually their fluxes to surface waters. 4. Initiate examination of biological samples from OS region (i.e., fish bile) for signatures of tailings seepage will begin to assess risks of associated by seepage via chemical exposure of biota. 5. Publications in the scientific peer-reviewed literature of
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	results.
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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 that describe this project. Use commas to separate them:

analytical methodology, tailings pond seepage, source identification, groundwater, bitumen soluble organics, toxicological significance, certified reference materials, effects directed analysis

Describe how you will test your hypothesis:

We will build on our previous studies and address the following key recommendation from our March 2016 Edmonton Workshop on ***“Analytical Methods for Monitoring Ambient Waters Potentially Influence by Bitumen in the Athabasca Region”***:

“To validate and refine analytical methodologies that allow for the discrimination of industrially-derived chemicals from those that arise from naturally-occurring bitumen deposits in groundwater and surface waters in the Athabasca Basin.”

The methods developed will be applied to OSM, enabling the identification of the sources, pathways and environmental levels of migratory waterborne oil sands mixtures beyond tailings containments, at sites where migrations have been documented or indicated (Roy et al. 2016). Effects directed analysis, a powerful tool used widely in monitoring programs (Brack et al. 2016) will assess the toxicological significance of the chemical classes of interest within migratory mixtures. These mixtures include, but are not limited to, acid extractable organics (AEOs), perfluorinated flame retardants, artificial sweeteners and new unknown substances recently identified as unique to oil sands process-affected water (OSPW) and groundwater containing migratory OSPW-derived mixtures (Milestone et al. 2017). We will accomplish these objectives according to the following 2 work packages:

1. **Analytical Toolbox.** We will apply our analytical toolbox (Hewitt et al. 2017), being finalized for detecting tailings migrations in ground/surface waters, to new source materials being collected for creation of Certified Reference Materials (CRMs; Project S1-2-1-1617). (OSPW collected by COSIA in 16/17-17/18; ground/surface water collections planned for 17/18; Bauer et al. 2017). Our work has recently shown that extensive sampling is required from tailings ponds to capture the range of chemical variability inherent to such large containments (Frank et al. 2016). Sampling for the creation of CRMs creates the logical opportunity to construct a database on the target analytes used for tracking migratory OSPW. These analyses will also need to be applied to the other 2 CRMs being prepared for surface and groundwaters, when they are generated (Project S1-2-1-1617), and initiated on biological samples (i.e., fish bile) from Athabasca River white sucker that will examine whether exposure to migratory mixtures can be detected (collaboration with M. McMaster).

- a. Addresses “high priority research need” from March 2016 Workshop: *“Characterizing the compositional ranges of bitumen-influenced waters (i.e. expand survey of OSPW, if possible, and natural).”*
 - b. By focusing on the certified reference materials that will be shared with all stakeholders, this work will maximize the knowledge gained and make the most efficient use of resources.
 - c. This work was initiated in 2016/17 and the methods developed will be applied to work package 2, below.
2. **Effects Directed Analysis (EDA).** Complete EDA method development (Tier 2 sub-fractionation) of 4 bulk in-house samples to identify toxicologically relevant compound classes from natural, industrial and OSPW-contaminated groundwater sources. Apply the EDA methodology developed in 2016/17 to new bulk samples collected for creation of Certified Reference Materials (Project S1-2-1-1617, described above).
- a. Addresses recommendation from March 2016 Workshop: *“Bitumen relevant reference materials are needed for method development and toxicity tests.”*
 - b. Addresses “high priority research need” from March 2016 Workshop: *“Differentiating identities of components of concern: identifying toxic substances and their potential to accumulate in sediments and bioaccumulate/biomagnify.”*
 - c. By applying the methodology to the Certified Reference Materials, we will maximize the knowledge generated as it will be used by all stakeholders, thereby making the most efficient use of resources.

Assumptions and Constraints behind the hypothesis and the testing method:

Assumptions

1. We will apply the analytical toolbox developed for tracking OSPW migrations to a range of OSPW samples that were collected via coordinated efforts by COSIA in 2016/17, with more extensive sampling of OSPW as well as natural surface and groundwater sources planned for 2017/18.
2. Methodology for fractionating groundwater to identify the chemical classes of interest at sites contaminated by tailings and natural bitumen-influenced sites are valid with existing standard protocols and protocols that will be finalized in 2017.

Constraints

1. Continued financial support and ability to secure and maintain human resources (dedicated term EG-03), and laboratory consumables including extraction resins, is essential.
2. Ability to maintain analytical instrumentation for analysis.
3. Ability to conduct complete range of bioassays contingent upon generation of sufficient quantities of groundwater fractions from existing samples.

References:

- Bauer, A.E., R.A. Frank, J.W. Roy, G. Bickerton, C.B. Milestone, D.G. Dixon and L.M. Hewitt. 2017. A preparative method for the isolation and fractionation of dissolved organics from bitumen-influenced waters. *Manuscript in preparation*.
- Brack, W., S. Ait-Aissac, R.M. Burgess, N. Creusot, C. Di Paolo, E. B.I., L.M. Hewitt, K. Hilscherova, J. Hollender, H. Hollert, W. Jonker, J. Kool, M. Lamoree, M. Muschket, S. Neumann, P. Rostkowski, C. Ruttkies, J. Schollee, E.L. Schymanski, T. Schulze, T.-B. Seiler, A.J. Tindall, G. De Aragão Umbuzeiro, B. Vrana and M. Krauss. 2016. Effect-directed analysis supporting monitoring of aquatic environments – An in-depth overview. *Sci. Tot. Environ.* 544: 1017-1118.
- Frank, R.A, G. Bickerton, J.W. Roy, S.J. Rowland, J.V. Headley, A.G. Scarlett, C.E. West, K.M. Peru, M. Conly and L.M. Hewitt. 2014. Profiling oil sands mixtures from industrial developments and natural groundwaters for source identification. *Environ. Sci. Technol.* **48**(5): 2660-2670.
- Frank R.A., Milestone C., Kavanagh R.J., Headley J.V., Rowland S.J., Scarlett A.G., West C.E., Peru K.M. and L.M. Hewitt. 2016. Assessing variability of acid extractable organics within two containments of oil sands process-affected water. *Chemosphere*, **160**: 303-313.
- Hewitt, L.M., Roy J.W., Bickerton G., De Silva A., Rowland S.J., Headley J.V., Scarlett A.G., West, C.E., Peru K.M., Milestone, C.B., and R.A. Frank. 2017. Chemical tracers for tracking migration of oil sands process waters in northern Alberta, Canada. *Manuscript in preparation*.
- Milestone, C.B, Roy, J.W. Bickerton, G., Frank R.A. and L.M. Hewitt. 2017. Using untargeted chemometrics approaches to identify tracers of oil sands process water migrations in the Athabasca oil sands region of Canada. *Manuscript in preparation*.
- Roy, J.W., Bickerton G., Frank R.A., Grapentine L. and L.M. Hewitt. 2016. Assessing risks associated with constituents detected in shallow riparian groundwater near a tailings pond in the Athabasca oil sands region of northern Alberta, Canada. *Groundwater*, **51**(4): 545-558.

Data Management

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

Deliverables	Timeframe
Data Collection Period: <i>Field work</i>	Start : 2017-05-01 End: 2017-10-31
Data Analysis Period: <i>Laboratory analysis and QA/QC of data</i>	Start : 2017-04-01 End: 2018-03-31
Data Release Date: <i>Metadata and data consistent, complete and meet basic standard format for publication in Open Data; on or linked to JOSM portal</i>	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
Chemical fractionation of bitumen influenced waters for toxicological assessments. (Frank et al. 2017).	Methodology used for fractionating OSPW has now been applied to bitumen-influenced groundwaters, allowing for more detailed chemical and toxicological characterization.	2017
Toxicological assessments of bitumen-influenced waters (Bauer et al. 2017).	1 st Tier EDA of groundwaters in-house.	2017
Chemical tracers for tracking migration of oil sands process waters in northern Alberta, Canada.	Analytical toolbox for measuring OSPW migrations.	2017

(Hewitt et al. 2017)		
Using untargeted chemometrics approaches to identify tracers of oil sands process water migrations in the Athabasca oil sands region of Canada. (Milestone et al. 2017).	Chemometric analysis of bitumen influenced waters to identify new tracer compounds for OSPW migrations.	2017
Variability OSPW manuscript from 2016-2018 samples. (Hewitt et al. 2018).	Include tracer compounds, chemometrics profiling of samples used for OSPW CRM.	2018
EDA analysis of bitumen-influenced groundwaters. (Frank et al. 2018).	2 nd Tier EDA of groundwaters in-house.	2018
EDA of OSPW CRM (Rodrigues et al. 2019).	Multi-tier EDA analysis.	2019

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 (ECCC)	Hewitt: Project coordination, organic acid and chemometric analyses, effects-directed analyses (chemical fractionation and characterization). Frank: Effects-directed analyses (chemical fractionation and bioassay coordination)	Mark Hewitt/Richard Frank
Component Lead (ECCC)	Project oversight	Ian Droppo
Co-Investigators (ECCC)	-Fire suppressing PFCs analyses (<i>A. de Silva</i>) -Artificial sweeteners analyses (<i>J. Roy, G. Bickerton</i>)	A. de Silva J. Roy G. Bickerton

	-Early life stage fish bioassays (<i>J. Parrott</i>) -Invertebrate bioassays (<i>R. Frank, A. Bartlett, P. Gillis</i>)	J. Parrott A. Bartlett P. Gillis
Technical Support (ECCC)	-Technical support for completion of analyses described above in EC laboratories	R. Vanderveen, S. Batchelor, M. Rudy (Hewitt/Frank) C. Spencer (De Silva) K. Shires, C. Sullivan (Parrott) L. Brown (Bartlett)

Deliverables (Year 1) If your Focus Study is longer than 1 year then complete **Appendix 3** 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
<p>Coordinate sample collection list of required source waters (OSPW, ground/surface waters) to be collected by COSIA.</p> <p>Continue drafts of publication(s), commenced in 2016/17, related to 1st tier fractionation and associated characterization of bitumen-influenced waters.</p> <p>Continue characterizations of OSPW samples collected in 2016/17.</p>
Q2 – July to September
<p>Commence toxicological characterizations of isolated 2nd tier fractionations of 2016/17 groundwater fractions.</p> <p>Continue/complete drafts of publication(s) related to 1st tier fractionation and associated characterization of bitumen-influenced waters collected in 2016/17.</p> <p>Oversee collection and sub-sampling of required source waters being collected by COSIA in 2017/18 for the development of CRMs (Project S1-2-1-1617).</p> <p>Commence characterizations of bitumen-influenced samples collected for CRMs in 2017/18 (OSPW, ground/surface waters, Project S1-2-1-1617).</p>
Q3 – October to December
<p>Continue toxicological characterizations of isolated 2nd Tier groundwater fractions.</p> <p>Complete drafts of publication(s) related to 1st tier fractionation and associated characterization of bitumen-influenced waters collected in 2016/17.</p> <p>Continue oversight of collection and sub-sampling of required source waters being collected by COSIA for the</p>

development of CRMs (Project S1-2-1-1617).

Continue characterizations of bitumen-influenced samples collected in 2017/18 (OSPW, ground/surface waters, Project S1-2-1-1617).

Commence drafts of publication(s) related to 2nd Tier fractionation and associated characterization of bitumen-influenced waters collected in 2016/17.

Commence fractionation and characterization of CRMs under development (Project S1-2-1-1617) from 2017/18 samples, using methods developed on the 2016/17 groundwater fractions.

Q4 – January to March

Complete toxicological characterizations of isolated 2nd Tier groundwater fractions.

Complete sub-sampling of required source waters being collected by COSIA for the development of CRMs (Project S1-2-1-1617).

Continue characterizations of bitumen-influenced samples collected in 2017/18 (OSPW, ground/surface waters, Project S1-2-1-1617) and initiate characterizations of fish bile from Athabasca mainstem white sucker (collaboration with M.McMaster).

Continue drafts of publication(s) related to 2nd Tier fractionation and associated characterization of bitumen-influenced waters collected in 2016/17.

Continue EDA of CRMs under development (Project S1-2-1-1617) from 2017/18 samples.



Detailed Financial Breakdown – Year 1 of 3 (2017-2020)

Also complete **Appendix 2** 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	\$	\$
Field Costs	\$	\$
Data Management	\$4k	\$
Internal Lab Analysis (NLET)	\$15k	\$
Consumable Materials & Supplies	\$90.2k	\$
Sub-Total	\$	\$
O&M - Travel		
Field Work	\$	\$
Conferences (SETAC, 2 individuals)	\$8k	\$
Meeting (identify meeting)	\$	\$
Sub-Total	\$	\$
O&M - External Contracts :		
Goods and Services Contract <i>University of Alberta HRMS - \$25.0K</i> <i>Agilent QToF maintenance contract - \$25.0K</i> <i>Sheridan College data analysis -\$10.0K</i>	\$60k	\$
External Lab Analysis	\$	\$
Sub-Total	\$	\$
Salaries:		
Principal Investigator	\$	\$
Technical / Professional Assistants (1 year term EG-03)	\$72.8k	\$
Field Staff	\$	\$
Sub-Total	\$	\$
Total Salaries	\$72.8k	\$

Budget requirements – List areas that require budget expenditures: (ADD OR DELETE BUDGET CATEGORIES AS REQUIRED)	OS Funding	External Funding <i>(outside JOSM)</i>
Total O&M	\$177.2k	\$
2017-2018 GRAND TOTAL *	\$250,000	\$

Appendix 1 - Approvals

Project Submitted by:		
Name: Mark Hewitt and Richard Frank		
Organization: ECCC	Signature:	Date:
Project Approved by:		
Dr. Monique Dubé (AEP)		Dr. Kevin Cash (ECCC)
Signature 		Signature 
Date		Date

APPENDIX 2 – 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	63.3		63.3		63.3	
c) Field Staff						
d)						
2) Operations and maintenance						
a) Facilities						
b) Equipment						
c) Lab analysis	15.0		15.0		15.0	
d) Data management						
e) Field work					30.0	
3) Consumable Materials and supplies						
a)	97.7		106.0		106.0	
b)						
4) Travel						
a) Conferences and meetings	8.0		8.0		8.0	
b) Field work					13.7	
c) Project-related travel	2.0		2.0		2.0	

5) Dissemination & Engagement						
a) Publications/Reports	2.0		2.0		2.0	
b) Translation (if required)	2.0		2.0		2.0	
c) Communications						
d) Stakeholder Engagement						
e) Indigenous Peoples Engagement						
6) External Contracts						
a)	60.0		60.0		60.0	
Grand Total	250.0		258.3		302.0	

APPENDIX 3 –Years 2 and 3 Deliverables (Complete the following detailed breakdown. Provide a summary of tangible quarterly deliverables. 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
<p>Coordinate sample collection list of required source waters (ground/surface waters) to be collected by AEP/ECCC.</p> <p>Continue drafts of publication(s), commenced in 2017/18, related to fractionation and associated characterization of bitumen-influenced waters.</p> <p>Continue characterizations of CRM samples collected in 2017/18.</p>
Q2 – July to September
<p>Commence toxicological characterizations of isolated 2017/18 fractions.</p> <p>Continue/complete drafts of publication(s) related to fractionation and associated characterization of bitumen-influenced waters collected in 2017/18.</p> <p>Oversee collection and sub-sampling of required source waters collected by AEP/ECCC in 2018/19 for the development of CRMs (Project S1-2-1-1617).</p> <p>Commence characterizations of bitumen-influenced samples collected for CRMs in 2018/19 (ground/surface waters, Project S1-2-1-1617).</p>
Q3 – October to December
<p>Continue toxicological characterizations of isolated CRM fractions.</p> <p>Complete drafts of publication(s) related to fractionation and associated characterization of bitumen-influenced waters collected in 2017/18.</p> <p>Continue oversight of collection and sub-sampling of required source waters being</p>

collected by AEP/ECCC for the development of CRMs (Project S1-2-1-1617).

Continue characterizations of bitumen-influenced samples collected in 2018/19 (ground/surface waters, Project S1-2-1-1617).

Commence drafts of publication(s) related to fractionation and associated characterization of bitumen-influenced waters collected in 2017/18.

Commence fractionation and characterization of CRMs under development (Project S1-2-1-1617) from 2018/19 samples.

Q4 - January to March

Complete toxicological characterizations of isolated fractions.

Complete sub-sampling of required source waters being collected by AEP/ECCC for the development of CRMs (Project S1-2-1-1617).

Continue characterizations of bitumen-influenced samples collected in 2018/19 (ground/surface waters, Project S1-2-1-1617).

Continue drafts of publication(s) related to fractionation and associated characterization of bitumen-influenced waters collected in 2017/18.

Continue EDA of CRMs under development (Project S1-2-1-1617) from 2018/19 samples.

Year 3 (2019- 2020)

Deliverable(s) (please provide enough information to support status reporting)

Q1 - April to June

Continue drafts of publication(s), commenced in 2018/19, related to fractionation and associated characterization of bitumen-influenced waters.

Continue characterizations of CRM samples collected in 2018/19.

Initiate field collections of groundwaters, surface waters and biological samples (e.g.

fish bile) for tailings migrations.
Q2 – July to September
Complete field collections of groundwaters, surface waters and biological samples (e.g. fish bile) for tailings migrations.
Commence toxicological characterizations of isolated 2018/19 fractions.
Continue/complete drafts of publication(s) related to fractionation and associated characterization of bitumen-influenced waters collected in 2018/19.
Q3 – October to December
Commence analyses of 2019/20 collections of groundwaters, surface waters and biological samples (e.g. fish bile) for tailings migrations.
Continue toxicological characterizations of isolated CRM fractions.
Complete drafts of publication(s) related to fractionation and associated characterization of bitumen-influenced waters collected in 2018/19.
Q4 – January to March
Complete analyses of 2019/20 collections of groundwaters, surface waters and biological samples (e.g. fish bile) for tailings migrations.
Complete toxicological characterizations of isolated fractions.
Initiate drafts of publication(s) related to analyses of 2019/20 collections of groundwaters, surface waters and biological samples.
Complete EDA of CRMs under development (Project S1-2-1-1617).