FOCUSED STUDY ACTIVITY WORK PLAN

General Information

*** Decision Pool B: Workplan approved with contingency** *** Approved at $189,246 with contingency** * Report for 2017-18 is required prior to funds being released for 2018/29. * This project is to be completed in the 2018/19 year. *Funding expectations: as a minimum a final report is required by March 31, 2019. All publications or products resulting from this work requires acknowledgement of funding from the Oil Sands Monitoring Program and are to be provided to the Oil Sands Monitoring Secretariat for tracking and any programmatic communications purposes. Work funded through the Oil Sands Program will be available for public dissemination.		
Work Plan Unique Identifier:	*W-MD-1-1718*	
Focused Study Activity Title:	Develop an Accredited Standard Method for Quantitative Analysis of Naphthenic Acids Concentrations	
Focused Study Category:	Monitoring Design and Method Improvement	
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	Choose an item.
Monitoring Site(s) Coordinates *(latitude and longitude)*		
Project Leader:	Richard Strub	
Organization and contact information:	**Environment and Climate Change Canada** **Water Science and Technology Directorate** **Richard.Strub@canada.ca**	
Date Study initiated:		
Monitoring Category: *(From OSM long-term plan; choose from drop-down menu)*	Watershed Monitoring	
Strategic Objective of Focused Study: *(From OSM long-term plan; choose from drop-down menu)*	Objective S1: Evaluate and update Standard Operating Procedures	
Hypotheses: *(Briefly outline the specific hypotheses that your focused study is aiming to address)*	*1. The Source Identification methodologies being employed are capable of differentiating complex mixtures in industrial process waters from natural bitumen sources.*	

	2. 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.
Deliverables: *What tangible goal (s) and/or product(s) will the monitoring produce and when?*	This project will produce two deliverables: • ***Certified*** Standard Reference Materials for analyzing water soluble bitumen organics, including NA/AEOs. These include Oil Sands Processed Water (OSPW), relevant ground and surface waters. • Synthesis of a Primary Naphthenic Internal Standard as required for CALA ***Accredited*** analytical methods for NAs. These deliverables follow the recommendations made by experts at the Naphthenic Acid Methodology Workshop held in Edmonton on March 14, 2016.

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**)

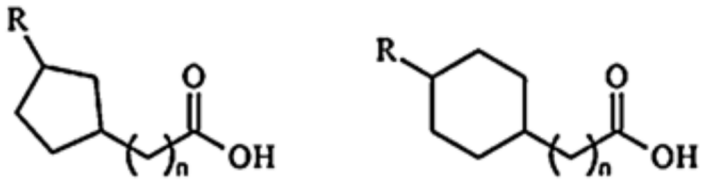
Provide a maximum of 10 key words that describe this project. Use commas to separate them:

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 water.* It was agreed that at present the definition of NAs would be a simple carboxylic acid with two oxygen atoms and the R group can be multi-cyclic and aromatic but does not include heteroatoms (no C or H) or any other functionalities:



- Bitumen-relevant reference materials for method development and toxicity tests were highlighted as a key gap to be addressed in order to support monitoring and research into this family of chemicals. Since most analytical instrumentation is comparative, it requires a sample of known composition (reference material) for accurate calibration. These reference materials are produced under stringent manufacturing procedures and differ from laboratory reagents in their certification and the traceability of the data provided.

The deliverables for 2018-19 include the following, representing work ongoing from 2017-18:

- Bitumen Relevant Standard Reference Materials for water soluble organic chemicals, including NA and other organic substances. Materials to be used in NA Analytical Methodology Development, Toxicity Testing and Effect-Directed Analyses by multiple stakeholders. A representative sample has been sent to the Burlington laboratory from COSIA of bulk tailings water in order to prepare a concentrated NA standard reference sample for analytical method development and toxicity testing. The tailings water sample will be processed by ECCC to generate concentrated extracts of water soluble organics. The extraction process is based on a method developed by ECCC and validated against OSPW and bitumen-influenced groundwater (Bauer et al. 2016 in preparation). ECCC has been certified by American Association for Laboratory Accreditation (A2LA) to be a developer of reference materials. The resulting samples will be characterized by ECCC and other parties using the approved analytical methods and SOPs. The reference materials will be characterized, certified and available nationally by the appropriate supplier of reference materials. The reference materials will benefit the NPRI and international oil spill research efforts.
- Continued work on preparation of the three certified reference materials (RMs) in this focused study (OSPW, groundwater and surface water) will continue in year 2017-18 with completion in year 2018-19. These RMs are relevant sources of bitumen-derived organics to the Athabasca watershed (surface water, groundwater and process water).

The following deliverable from 2017-18 will be completed in that fiscal year:

- Synthesis of a mono-aromatic NA primary standard prevalent in OSPW and natural bitumen-influenced groundwater; the structure of which has been proposed by academic and ECCC researchers as representative of 1 class of water soluble NA acids. This traceable, authentic and relevant internal standard will also be isotopically labelled to assist laboratories involved in analysis of Naphthenic acids as part of the delivery of a robust quality assured analytical operational method

for NAs. This work has been started in 2016-17 and will be completed in 2017-18.

Assumptions and Constraints behind the hypothesis and the testing method:

Assumptions

A synthetic primary internal standard will be an adequate first proxy to begin to quantify the range of molecular structures associated with bitumen-related Naphthenic Acids.

Oil sands process water, and future planned samples of groundwater and surface water are sufficiently representative of the range of variation in these waters that they can be used to define an appropriate and certifiable reference material.

Constraints

Scope: There are constraints and risks inherent in undertaking custom synthesis of unknowns. The structure proposed is that of Prof. Steve Rowland based on work with ECCC. Prof. Rowland has led the identification work on new compound classes within the NA umbrella and is the global lead authority in this area. A comprehensive review of the available data behind Professor Rowland's proposed structure was conducted by the private synthetic laboratory which has costed the synthesis and would conduct the work (Sneickus Innovations) and a jointly agreed-upon structure with Professor Rowland was finalized based on new data.

It is important to note that the proposed compound is detected in both OSPW and groundwater influenced by bitumen, as 1 of 8 isomers of a family of mono-aromatic acids. All members of this family are enriched substantially in OSPW, with strong potential for use as a tracer for OSPW migrations (Hewitt et al. 2016, in prep).

It is also important to note that should the proposed structure ultimately prove to not be one of the 8 isomers present in bitumen influenced waters, several positive outcomes will nevertheless be realized:

The synthetic route will generate a mixture of isomers, in addition to the one targeted. It is possible one of these isomers will be present in bitumen and this will thus fulfill the original intent.

The targeted compound (and associated isomers also generated) will all be close structural analogs to what actually is present. As such, they will be better than anything that is commercially available at present and can still be used for analytical method development with continued financial support and ability to secure and maintain human resources (dedicated term EG-03), and laboratory consumables including extraction resins, is essential.

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: *Field work*	Start : 2018-05-01 End: 2017-11-01
Data Analysis Period: *Laboratory analysis and QA/QC of data*	Start : 2018-04-02 End: 2019-03-29
Data Release Date: *Metadata and data consistent, complete and meet basic standard format for publication in Open Data; on or linked to JOSM portal*	2019-03-29

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

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/Resource Name/Organization	Responsibilities
Project Lead (ECCC)	Project Design, Scientific Oversight and Management
Project Co-Lead (ECCC)	Advice on instrument SOPs, Standard Reference Materials preparation. Link to the Water Methodology Project (W2-1-1)
Program Scientist (ECCC)	Study design document preparation
Project Support (ECCC)	Data processing and administrative support
Project Support (ECCC)	Reference sample preparation, methods testing and validation, and sample characterization
Project Support (AEP)	AEP representation to assist in Scientific Oversight and AEP needs from this focused project

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
Coordinate sample collection list of required source waters (OSPW, ground/surface waters) to be collected by COSIA. Continue characterizations of OSPW samples collected in 2016/17.
Q2 – July to September
Oversee collection and sub-sampling of required source waters being collected by COSIA in 2017/18 for the development of CRMs Commence characterizations of bitumen-influenced samples collected for CRMs in 2017/18 (OSPW, ground/surface waters)
Q3 – October to December
Continue oversight of collection and sub-sampling of required source waters being collected by COSIA for the development of CRMs Continue characterizations of bitumen-influenced samples collected in 2017/18 (OSPW, ground/surface waters).
Q4 – January to March
Complete sub-sampling of required source waters being collected by COSIA for the development of CRMs. Continue characterizations of bitumen-influenced samples collected in 2017/18 (OSPW, ground/surface waters).

Detailed Financial Breakdown – Year 1 of 2 (2017-2019)

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	**$**	**$**
Field Costs	**$**	**$**
Data Management	**$**	**$**
Internal Lab Analysis	**$21,000**	**$**
Consumable Materials & Supplies	**$142,361**	**$**
Sub-Total	**$**	**$**
O&M - Travel		
Field Work	**$**	**$**
Conferences	**$**	**$**
Meeting (*annual planning meeting in Burlington for 1 person on travel status)*	**$1,500**	**$**
Sub-Total	**$**	**$**
O&M - External Contracts :		
Goods and Services Contract *Primary standard continued contract*	**$50,667**	**$**
External Lab Analysis	**$**	**$**
Sub-Total	**$**	**$**
Salaries:		
Principal Investigator	**$**	**$**
Technical / Professional Assistants (2-1 year term EG-03, 1 CH-02 operations management), Lab FTEs	**$110,042**	**$**
Field Staff	**$**	**$**
Sub-Total	**$110,042**	**$**
Total Salaries	**$110,042**	**$**

Budget requirements – List areas that require budget expenditures: (ADD OR DELETE BUDGET CATEGORIES AS REQUIRED)	**OS Funding**	**External Funding (***outside JOSM***)**
Total O&M	**$215,528**	**$**
2017-2018 GRAND TOTAL (*before other related costs)	**$325,570**	**$**

Appendix A - Approvals

Project Submitted by:		
Name: Richard Strub		
Organization: ECCC	Signature:	Date:

Project Approved by:		
Signature		Signature
Date		Date

Activity Planning Review and Evaluation

To be completed by OSM Administration

Date Completed	**Review type**	**Validated by** (insert name and title)
	Program Management review completed	

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

Budget requirements	Year 1 (2017- 2018)		Year 2 (2018- 2019)		Year 3 (201X- 201Y)	
	Cash	In-kind	Cash	In-kind	Cash	In-kind
1) Salaries and benefits						
a) Investigators						
b) Technical/professional assistants	110,042		104,622			
c) Field Staff						
2) Operations and maintenance						
a) Facilities						
b) Equipment						
c) Lab analysis	21,000		21,000			
d) Data management						
e) Field work						
3) Consumable Materials and supplies						
a)	142,361					
4) Travel						
a) Conferences and meetings						
b) Field work						
c) Project-related travel	1,500		1,500			
5) Dissemination & Engagement						
a) Publications/Reports						

b) Translation (if required)						
c) Communications						
d) Stakeholder Engagement						
e) Indigenous Peoples Engagement						
6) External Contracts						
a)	50,667					
Grand Total (before other related costs)	325,570		127,122			

***Total Salary Costs for ECCC ($104,622) in 2018-19 with other related costs is $143,876. The total O&M costs for ECCC ($22,500) in 2018-19 with other related costs is $37,023). The Grand Total Cost for ECCC ($127,122) with other related costs is $180,900.**

*Total Salary Costs for ECCC ($110,042) in 2017-18 with other related costs is $151,330. The total O&M costs for ECCC ($215,528) in 2017-18 with other related costs is $238,670). The Grand Total Cost for ECCC ($325,570) with other related costs is $390,000.

APPENDIX C –Years 2 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
Coordinate sample collection list of required source waters (ground/surface waters) to be collected by AEP/ECCC. Continue characterizations of CRM samples collected in 2017/18.
Q2 – July to September
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). Commence characterizations of bitumen-influenced samples collected for CRMs in 2018/19 (ground/surface waters, Project S1-2-1-1617).
Q3 – October to December
Continue oversight of collection and 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). Commence fractionation and characterization of CRMs under development (Project S1-2-1-1617) from 2018/19 samples.
Q4 – January to March
Deliverable 1 • Announcement to stakeholders and other interested parties the availability of *Certified* Standard Reference Materials for analyzing water-soluble bitumen organics, including NA/AEOs. These include Oil Sands Processed Water (OSPW), relevant ground and surface waters. *Deliverable 2* • Announcement to stakeholders and other interested parties the availability of an authentic analytical Primary Naphthenic Acid Internal Standard as required for CALA *Accredited* analytical methods for determining NAs.