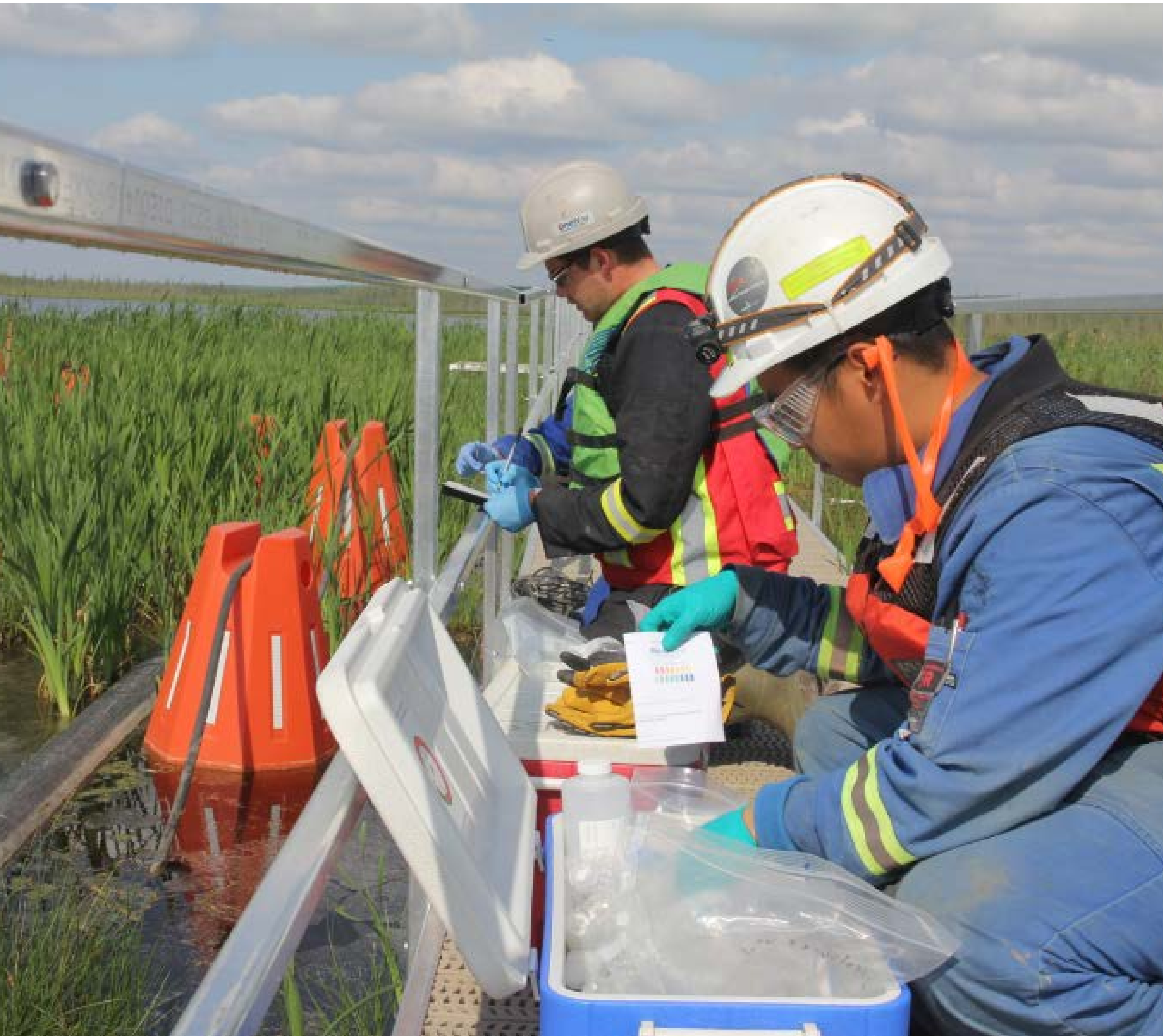
2023

Water Mining Research Report

December 2024 v1



INTRODUCTION

This report summarizes progress for research projects that were active in 2023 related to improving the use and management of water by the Mining Subcommittee of Canada's Oil Sands Innovation Alliance (COSIA) Water Environmental Priority Area (EPA). COSIA is the innovation arm of Pathways Alliance. In 2022, COSIA became part of Pathways Alliance. Formed in 2012, COSIA is focused on collaborative action and innovation in oil sands environmental technology, under four key environmental priority areas: tailings, water, land and greenhouse gases. Each summary was written by the research provider, and the opinions expressed are theirs and are not necessarily the opinions of Pathways Alliance nor its members.

Please contact the Industry Champion identified for each research project if any additional information is needed.

The COSIA Water EPA Mining Subcommittee participants during the period of this report were: Canadian Natural, Imperial Oil Resources Ltd., Suncor Energy, and Syncrude Canada Ltd.

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- Canadian Natural
- Cenovus Energy Inc.
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- Syncrude Canada Ltd.

December 2024

Cover – Water monitoring program at Imperial's Kearl site

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Summary Report Title	Project Number	Topic	2023	2022	2021	2020	2019	2018
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NATURAL AND ANTHROPOGENIC INPUTS TO THE ATHABASCA WATERSHED

WE0057 - Metals Versus Minerals: Impacts of Atmospheric Dust Deposition on the Speciation of Trace Elements in Snowmelt and Peatland Surface Waters

COSIA Project Number: WE0057

Research Provider: University of Alberta

Industry Champion: Canadian Natural

Industry Collaborators: Imperial Oil Resources Ltd., Suncor Energy Inc., Syncrude Canada Ltd., Teck Resources Limited

Status: Year 5

PROJECT SUMMARY

Open pit bitumen mining in northern Alberta generates volumes of dust. This dust derives from the mines, wind erosion of dry tailings and gravel roads, construction activities, and quarries, in addition to natural sources, such as river banks and sand bars. The dusts themselves consist mainly of mineral particles, some of which are chemically reactive (such as calcite, a calcium carbonate). Others are effectively insoluble (such as quartz, a silicate). The extent of these emissions and their ecological significance is unclear. Most environmental impact studies to date have not clearly distinguished between TEs (such as cadmium and lead) from the combustion of fossil fuels needed for bitumen upgrading and TEs that are hosted within the crystal lattice of the mineral particles themselves. Trace elements that are emitted to the air during combustion at high temperatures tend to be very small (< 1 micron) and in soluble form (such as oxides), whereas mechanically-generated mineral dusts tend to be rather large (10 to 100 microns) and much less soluble (silicate minerals such as quartz and feldspar). Very small, soluble, metal-containing particles such as those from combustion may represent a threat to biota, depending on the pH of soil and water, and other factors. Large, insoluble particles, such as mechanically-generated mineral dusts, most likely do not. The main goal of this study is to clearly distinguish between these two sources of TEs to the air, using size-resolved analyses of snow and Sphagnum moss from bogs. The secondary objective is to understand what impact, if any, the two sources of TEs may have on the chemical composition of meltwater and peatland surface waters from bogs that drain into the Athabasca River.

PROGRESS AND ACHIEVEMENTS

1. Snow and dust (Dr. Fiorella Barraza)

Snow samples had been collected from five ombrotrophic peat bogs (MIL, JPH4, McK, McM, ANZ) within the industrial zone the Athabasca Bituminous Sands (ABS) region, and at a reference site (UTK), located 264 km southwest from the industrial area. These samples were used to develop an analytical method for the determination of TEs in dusty snow by Javed et al, 2022 (10.1039/d1ea00034a). To characterize the spatial variation in atmospheric deposition of TEs, snow was also collected from the east and west banks of the Athabasca River (AR) and its tributaries (Firebag River, MacKay River, Muskeg River, Steepbank River, Clearwater River). In 2016, 25 sites were sampled (20 Athabasca River sites and five tributaries); in 2017, 14 sites (11 Athabasca River sites and three tributaries). Snow was also collected from three very remote locations: Athabasca Glacier, Maligne Lake and Rock Lake.

The industrial (e.g. dry tailings, road construction material) and natural materials (e.g. soil and glacial till) provided by our partners are potential sources of airborne dusts. These samples have been already processed (physical, mineralogical, and chemical analyses) by the bioaccessibility project team. To determine the total concentrations of TEs, the above-mentioned samples were sent to a commercial lab (Activation Laboratories, Ontario), where they were digested using a mixture of acids including HNO3, HCl, HClO4, and HF, and analyzed using ICP-MS. These results were used to calculate TE ratios (selected elements) to be compared to their equivalent ratios in the acid-soluble fraction of snow (melted, leached in concentrated HNO3, and filtered snow).

Between March 2023 and February 2024, the chemical analyses of the snow samples were completed,. These included: (i) SEM-EDS (scanning electron microscope and energy-dispersive X-ray spectroscopy) and XRD (X-Ray diffraction) analyses of the particulate fraction (>0.45 µm) and (ii) fractogram deconvolution of the data generated by AF4-ICPMS (asymmetric flow field flow fractionation-inductively coupled plasma mass spectrometry) for TEs in the colloidal and «truly dissolved» fractions (1 kDa to 0.45 µm and <1KDa respectively; in unacidified, filtered snow). The manuscript about the chemical reactivity of dusts using TEs in snow was published earlier this year (Barraza et al, 2024).

1. **Chemical reactivity of dust in snow: acid-soluble and insoluble fractions (Winter 2016 and 2017)**

The acid-soluble fraction of snow was used to evaluate the site-specific variation of TEs in winter 2016 and 2017, from samples collected along the Athabasca River and its tributaries. Particulate matter was extracted from snow, and the mineralogical composition of the particles was examined using SEM-EDS. Their chemical reactivity was assessed by comparing TEs in acid leachates and acid digests (unfiltered snow digested with concentrated HNO_3, at elevated T and P).

The data is reproducible from one year to the next, with concentrations ranging from approximately one ng/L (Tl) to less than two mg/L (Al). Concentrations were greater throughout the industrial zone compared to the reference location (UTK), with the midpoint between the two central upgraders being especially impacted. Regardless of their geochemical class (lithophile: Al, Be, Cs, La, Li, Sr, Th; chalcophile: As, Cd, Pb, Sb, Tl; or enriched in bitumen: Mo, Ni, V), all TEs showed strong, positive correlations with Y, a conservative element which serves as a surrogate for the abundance of mineral particles. Nevertheless, Cd and Sb showed weaker correlations, suggesting other potential sources of these elements.

Ratios of V:Ni were calculated to help identify the dominant source of these elements to the snow, given that they are both lost from the organic fraction of bitumen during upgrading. The average V/Ni in the snow of the AR is approximately 1.2, which is similar to fly ash. However, there are three lines of evidence which argue against fly ash as an important source of these two metals: 1) the strong, positive, linear correlation between V and Y (r=0.98) as well as Ni and Y (r=0.90); 2) the failure to find fly ash particles in any of the snow samples examined using the SEM; 3) peat bog records show that fly ash particles are most abundant in peat from the 1950s and 1960s, indicating there has been a decrease in fly ash deposition during recent decades (Mullan-Boudreau et al., 2017a), following the introduction of electrostatic precipitators on bitumen upgraders. Among the geomaterials provided by our partners, one type of road construction material had a similar V/Ni to that of snow, and road dust has been shown to be an important source of fugitive dusts in the ABS region.

To document possible differences in particle density and dust mineralogy, La, Th, and Y (which are enriched in heavy minerals) were normalized to Al (which is commonly used in weathering studies as an indicator of the abundance of clays which are much lighter). In the Athabasca River snow, these metal/Al ratios were two to five times greater compared to snow from UTK, and six to 30 times greater than the corresponding crustal ratios. These ratios were also four to 33 times greater in the snow than the tailings. Given that these ratios in snow exceed their crustal ratios, heavy minerals appear to be preferentially enriched in the snow of the river, compared to light minerals. The considerable chemical stability of the heavy minerals (e.g. monazite, rutile, zircon) helps to explain the limited chemical reactivity of the dusts of the ABS region. The SEM analysis of the acid-insoluble particles revealed abundant insoluble silicate minerals (quartz, clays, feldspars), followed by S-rich particles.

The summary of the results presented here is part of a manuscript entitled «Interannual and spatial variations in acid-soluble trace elements in snow: comparison with the mineralogy of dusts from open pit bitumen mining» (submitted on February 22, 2024).

2. Total concentration of TEs in the particulate fraction (Winter 2016)

Filters containing the particulate fraction were digested with HNO_3 and HBF_4 prior to being analyzed for major elements (Al, Na, Ca, Mg, K, P, and S) and TEs using ICP-OES and ICP-MS respectively. SEM and XRD analysis were performed to identify the mineral hosts of TEs and to compare them to the acid-insoluble dust particles. The minerals identified were: silicates such as quartz, kaolinite and muscovite; carbonate minerals such as calcite and dolomite; and Ti-oxides such as anatase and rutile. These results are in agreement with previous publications about the composition of dust particles found in the ABS region. Due to the very small size of the samples on the filters, it was not possible to mass-transform the raw concentrations (ICP-OES and ICP-MS data). These results will be part of manuscript in preparation entitled «*Trace elements in particulate and sub-micron aerosols deposited on snow near the Athabasca Bituminous Sands (ABS) region in Alberta, Canada*».

3. Size-fractionation of TEs in snow (Winter 2016 and 2017)

Within the "dissolved" i.e. filterable fraction of melted snow, 78 samples (including replicates) were analyzed for 20 TEs using AF4-ICPMS (January, 2022). The purpose of these measurements is to quantify the TE fraction that is "truly dissolved" i.e. in the form of ions and small molecules, and directly bioavailable. Processing AF4 data is a complex, time-consuming procedure that requires expertise. Between March 2023 and February 2024, two PHD students from our group were responsible of performing fractogram deconvolution to separate overlapping peaks. This allows TEs in the colloidal fraction to be quantified by size and composition, including those associated with DOM (dissolved organic matter), small inorganic, and large inorganic species (Cuss et al, 2017).

Our preliminary results indicate that potentially toxic TEs, such as As, Cd, and Pb are mainly present in ionic form. While this is the most available form for aquatic organisms, the concentrations are extremely low. In 2016, <u>total</u> Pb in SAR-UP2 (site located ~37 km downstream of industry) was 280 ng/L: <u>dissolved</u> (i.e. filterable) Pb was only eight ng/L (three per cent of total Pb). At this site, 100 per cent of dissolved Pb was in ionic form (equal to eight ng/L). In snow from the Steepbank River (midstream of industry), total Pb was 24 times greater than at SAR-UP2, but dissolved Pb was only 4.6 ng/L (0.1 per cent of total Pb): here, ionic Pb was 4.5 ng/L (98 per cent of dissolved Pb). At Firebag River, located at the south end of the transect (~ 82 km downstream of industry), total Pb was 52 times lower than at Steepbank River whereas dissolved Pb was still only 4.7 ng/L (i.e. similar to what was found at midstream locations). Similarly, ionic Pb represented 100 per cent of the dissolved fraction. In summary, almost all of the "dissolved" Pb is in the form of ionic species and simple molecules (< 300 Da), but the concentrations are extremely low.

Lead concentrations in the filtered snow samples from the Athabasca River are remarkably consistent with the Pb data obtained from snow samples collected from ombrotrophic bogs in the ABS region which averaged 4.2 ± 0.7 ng/L (Javed et al, 2017). To put all of these results into context, Pb concentrations in ancient ice samples from a core collected in Nunavut, was approximately five ng/L (Zheng et al, 2007).

These results summarized here will become part of manuscript entitled «. *Size-resolved fractionation of dissolved As, Cd and Pb (< 0.45 µm) into colloidal (1 kDa to 0.45 µm) and ionic (< 1 kDa) forms in snow from the Athabasca Bituminous Sands (ABS) region in Alberta, Canada* » (in preparation).

2. *Peat bog waters (Sundas Butt, PHD candidate)*

2.1. Peat pore waters

Peat porewaters were collected from four bogs in the ABS region: JPH4, McKay (McK), McMurray (McM), and Anzac (ANZ), listed in order of their decreasing proximity to mining activities, and a bog in a remote area, Utikuma (UTK). Samples were obtained in the autumn over three years (2019 to 2021) from excavated pits (30 to 40 cm deep) at the surface of the bogs. Samples were analyzed for dissolved TEs (<0.45 µm) using ICP-MS. Conservative (Al, Th and Y) and mobile lithophile elements (Fe, Li, Mn and Sr), and bitumen-enriched elements (Mo, Ni and V), all showed an increase in concentration toward industry. This trend corresponds to the increase in the rates of dust deposition (Mullan-Boudreau et al., 2017a), and reflects the dissolution of dust particles. Among the chalcophile elements, only As increases in concentration toward industry. No such trend is seen in regard to Cd, Pb, Sb, or Tl. Only Mn was enriched in the waters by more than 10x at all sites near the mining area, compared to its concentration at the reference site: the enrichments of all other elements were <10x. These findings were recently published (Butt et al, 2024).

2.2. Sphagnum moss waters

Sphagnum moss waters were squeezed from living moss that had been collected as noted earlier for peat bog porewaters. Water was also extracted from moss samples collected from 30 bogs in the ABS region, along with two additional bogs in remote areas: Caribou Mountains Wildland (CMW) and Birch Mountain Wildland (BMW). These additional moss samples had been collected in 2015 for a separate study (Mullan-Boudreau et al. 2017b), and kept frozen. The dissolved fractions (0.45 µm) of the expressed waters were analyzed for TEs, using ICP-MS. Most lithophile elements (Al, Fe, Li, Sr, Th, and Y) increase in concentration toward the mining area, again corresponding to the increase in dust deposition (Mullan-Boudreau et al. 2017b). Similar trends were observed for bitumen-enriched (Ni and V) and chalcophile elements (As, Cd, Pb, Sb, Tl). In comparison to the abundance of TEs at the remote sites, lithophile elements, such as Y, Fe, and Th, showed enrichments up to 600, 400, and 140x, respectively, closer to the mining activities. In contrast, bitumen-enriched and chalcophile elements were only enriched up to 50 and 20x, respectively. These findings suggest that the dust emitted from open-pit bitumen mining activities dissolves to some extent in these naturally acidic waters (pH 4), but the elements most affected are the lithophile elements. However, the presence of elevated concentrations of elements such as Y and Th, most likely associated with stable minerals such as zircon and monazite, suggests that some of the elements may occur in colloidal form.

The findings presented herein are part of a manuscript being drafted «*Trace elements in Sphagnum moss waters as indicators of the chemical reactivity of contemporary atmospheric dust inputs from mining activities in the Athabasca Bituminous Sands (ABS) region*», to be submitted by the end of March.

2.3. Peat porewaters from age-dated peat cores

Our next goal is to study the chemical reactivity of dust deposition over time, since the beginning of commercial mining and upgrading operations. Using age-dated peat cores with known histories of dust deposition, TEs will be measured in porewaters from bogs near industrial activities, as well as remote locations. First, the challenges of porewater extraction must be overcome: extracting sufficient porewater for ICP-MS analyses while avoiding oxidation of the samples and achieving low blank values for all of the elements of interest. Acid-cleaned centrifuge tubes equipped with built-in 0.45 µm PES membrane filters yielded acceptable blank values for the elements of interest. Centrifugation experiments showed that a five-gram sample of wet peat would yield sufficient porewater (four mL) to allow all necessary chemical analyses. Dissolved concentrations of Fe in porewaters extracted under a N_2 atmosphere in a glove box versus extraction in a clean air cabinet under ambient conditions showed no significant differences. Thus, porewater extractions of the age-dated peat cores can now proceed, within the metal-free, ultraclean SWAMP laboratory.

LESSONS LEARNED

1. Snow

Trace elements in the acid-soluble fraction of snow collected on the shores of the Athabasca River and its tributaries, showed considerable spatial variation, with increasing concentrations closer to the bitumen mining and upgrading operations. Compared to the reference site UTK, located 264 km southwest from the industrial area, sites located downstream, midstream, and upstream of industry showed greater TE concentrations, especially the conservative elements (i.e. Al, Th, Y) which are indicators of mineral dust deposition, as well as some of the elements enriched in bitumen (V and Mo). The dominant hosts of TEs appear to be the minerals which compose the ABS. Road dust may also be important at some sites. So far, the presence and relative abundance of insoluble silicate minerals such as quartz, may explain the low concentrations observed, and therefore the limited chemical reactivity of the TEs reported in this study. For instance, less than one-fifth of the V and Ni is liberated from these dust particles using 0.5 per cent of HNO_3. Carbonate minerals dissolve during the extreme pH conditions employed here (pH <1), and release any TEs they may contain. However, the potential to release some of these TEs into the surface waters of the river and its tributaries would be minimal given the fact that river water is saturated in respect to calcium carbonate. The size distribution of TEs (particulate, colloidal, and truly dissolved forms) in snow will provide an improved assessment of the potential impacts on surrounding ecosystem.

2. Porewaters expressed from Sphagnum moss and peat

Porewaters expressed from *Sphagnum* moss and the underlying peat are useful for evaluating the chemical reactivity of atmospheric dusts, and the subsequent release of TEs to naturally acidic (pH 4) waters. Considerably higher concentrations of most TEs are found in moss waters compared to peat porewaters, suggesting that contemporary and past atmospheric deposition is different in regard to quantity, reactivity, or both. To study the effects of contemporary dust and aerosols, preference should be given to sampling of moss waters. In regard to the reactivity of dusts in the past, porewaters must be extracted from age-dated peat cores in which the chronology of atmospheric deposition is known.

PRESENTATIONS AND PUBLICATIONS

Journal Publications:

Published

Barraza, F., Javed, M.B., Noernberg, T., Schultz, J., Shotyk, W., 2024. Spatial variation and chemical reactivity of dusts from open-pit bitumen mining using trace elements in snow. Chemosphere 141081. https://doi.org/10.1016/j.chemosphere.2023.141081

Butt, S., Barraza, F., Devito, K., Frost, L., Javed, M.., Oleksandrenko, A., Shotyk. W. Butt, S., Barraza, F., Frost, L., Javed, M.B., Oleksandrenko, A., Shotyk, W. 2024. Spatio-temporal variations in the concentration of trace elements in peat bog acrotelm waters due to the dissolution of dusts generated from open-pit mining activities in the Athabasca Bituminous Sands (ABS) region. Environmental Pollution 123470. https://doi.org/10.1016/j.envpol.2024.123470

Chen, N., Barraza, F., Belland, R.J., Javed, M.B., Grant-Weaver, I., Cuss, C.W., Shotyk, W., 2024. Estimating the bioaccessibility of atmospheric trace elements within the Athabasca Bituminous Sands region using the acid soluble ash fraction of Sphagnum moss. Environmental Science: Atmospheres 10.1039.D3EA00071K. https://doi.org/10.1039/D3EA00071K

Dennett, J.M., Dersch, A., Chipewyan Prairie First Nation, Barraza, F., Shotyk, W., Nielsen, S.E., 2023. Trace elements in the culturally significant plant *Sarracenia purpurea* in proximity to dust sources in the oil sands region of Alberta, Canada. Science of The Total Environment 165142. https://doi.org/10.1016/j.scitotenv.2023.165142

Shotyk, W., Barraza, F., Butt, S., Chen, N., Cuss, C.W., Devito, K., Frost, L., Grant-Weaver, I., Javed, M.B., Noernberg, T., Oleksandrenko, A., 2023. Trace elements in peat bog porewaters: indicators of dissolution of atmospheric dusts and aerosols from anthropogenic and natural sources. Environmental Science: Water Research & Technology 10.1039.D3EW00241A. https://doi.org/10.1039/D3EW00241A

Submitted, under review

Barraza, F., Hamann, A., Noernberg, T., Schultz, J., Shotyk, W. Interannual and spatial variations in acid-soluble trace elements in snow: comparison with the mineralogy of dusts from open pit bitumen mining. Submitted to *Atmospheric Pollution Research* on February 22, 2024, *Under review* since March 1, 2024.

In preparation

Barraza, F., Ibanez, Q., Luu, A., Noernberg, T., Wang, Y., Shotyk, W. Size-resolved fractionation of dissolved As, Cd and Pb (< 0.45 µm) into colloidal (1 kDa to 0.45 µm) and ionic (< 1 kDa) forms in snow from the Athabasca Bituminous Sands (ABS) region in Alberta, Canada.

Barraza, F., et al. Trace elements in particulate and sub-micron aerosols deposited on snow near the Athabasca Bituminous Sands (ABS) region in Alberta, Canada.

Butt, S., Barraza, F., Chen, N., Shotyk, W. Trace elements in *Sphagnum* moss waters as indicators of the chemical reactivity of contemporary atmospheric dust inputs from mining activities in the Athabasca Bituminous Sands (ABS) region.

Conferences, presentations, and workshops:

Barraza, F., Javed, M.B., Shultz, J., Noernberg, T., Shotyk, W. Trace elements in particulate and sub micron aerosol fractions in snow from the Athabasca Bituminous Sands (ABS) region in Alberta, Canada. 1st Joint International Conference on the Biogeochemistry of Trace Elements (ICOBTE) and Conference on Heavy Metals in the Environment (ICHMET). Wuppertal, Germany. September 6-10, 2024 (in person; awarded one of the top-10 posters out of 160).

Butt, S.A., Barraza, F., Chen, N., and Shotyk, W. Trace elements in Sphagnum moss waters as indicators of the chemical reactivity of contemporary atmospheric dust inputs from mining activities in the Athabasca Bituminous Sands (ABS) region. Poster presentation in Bentley Lecture event organized by the University of Alberta, Edmonton, Canada. February 13, 2024. (in person; awarded one of the top three posters out of 30)

Shotyk, W., Barraza, F.*, Butt, S., Chen, N., Cuss, C.W., Dennett, J., Devito, K., Frost, L., Grant-Weaver, I., Javed, M.B, Oleksandrenko, A., Noernberg, T, Wang, Y. Trace elements in peat bog surface waters and plant fluids: indicators of dissolution of natural and anthropogenic dusts and aerosols. 1st Joint International

Conference on the Biogeochemistry of Trace Elements (ICOBTE) and Conference on Heavy Metals in the Environment (ICHMET). Regular Session 9 «Other topics related to Trace Elements». Wuppertal, Germany. September 6-10, 2024. (*presented by F.Barraza; in person, invited)

Shotyk, W. Trace elements (TEs) in the environment of northern Alberta: which are bioavailable or bioaccessible, and which are not. 2023 COSIA Mine Water Management Science Workshop. Edmonton, Canada. October 12-13, 2023 (in person, invited).

RESEARCH TEAM AND COLLABORATORS

Institution: University of Alberta

Principal Investigator: William Shotyk

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Fiorella Barraza	University of Alberta	PHD, Research Associate		
Sundas Butt	University of Alberta	PHD candidate	January 2020	December 2024

WE0077 - Athabasca River Project: Creation of Artifacts During Sample Filtration

COSIA Project Number: WE0077

Research Provider: University of Alberta

Industry Champion: Syncrude Canada Ltd.

Industry Collaborators: Canadian Natural, Shell Canada Ltd., Imperial Oil Resources Ltd., Suncor Energy Inc., Teck Resources Limited

Status: Complete

PROJECT SUMMARY

The development of the Athabasca Bituminous Sands has received considerable attention due to serious concerns about potential contributions of trace elements (TE) from industrial activities to the surrounding ecosystems. Comprehensive and scientifically sound analyses are required to assess the extent of such releases, and their impacts on the environment. Trace elements within the dissolved fraction (< 0.45 µm) of natural waters are of special concern due to their greater mobility, bioaccessibility, and potential bioavailability than those within the corresponding particulate fraction (> 0.45 µm). These elements can be roughly divided into three major fractions based on their composition: 1) free ions and simple molecules, 2) organically-bound species that consist of metal ions (e.g., Cu2+) or small metallic particles complexed with dissolved organic matter (DOM), 3) primarily inorganic species such as oxyhydroxides of Al, Fe, or Mn with TEs adsorbed to their surface or encapsulated inside the lattice structure. Filtration through 0.45 µm filters is generally used to represent the "dissolved" fraction of TEs in natural waters. Following filtration, the concentrations of TEs within the dissolved fraction are usually determined using spectrometry-based approaches. Asymmetric flow field flow fractionation (AF4) coupled with inductively coupled plasma mass spectrometry (ICP-MS) goes one step further. Dissolved molecules and colloids are first separated according to their size, allowing size-resolved analyses of TEs. However, artifacts can be introduced into the samples during filtration, mainly due to filter clogging, and sometimes because of adsorption. The method used to filter the water, and its physicochemical characteristics, may impact the measured concentrations and size distribution of dissolved trace elements. The problems generated by filtration artifacts and their quantitative importance, have received limited attention. These issues may be of particular importance in rivers such as the Athabasca, where TE concentrations are very low.

This project aims to:

- Determine the magnitude of the errors introduced into the measurement of dissolved TE concentrations and colloidal forms that are caused by filtration artifacts.
- Develop, validate and apply an analytical method for analyzing the colloidal forms of TEs over a size continuum from ca. one nm to five µm, to avoid filtration through 0.45 µm filters.

PROGRESS AND ACHIEVEMENTS

1. Filtration artifacts

The filtration procedures described below were performed in triplicate. Membrane filters (0.45 µm) were used to assess the impact of filtration on water samples from the Athabasca River (AR; pH 7.2, TOC 15 mg/L), the Clearwater River (CL; pH 6.9, TOC 13 mg/L), and a peat bog porewater (pH ca. 4 and 93 mg/L TOC). Cartridge filters were also evaluated using water from the Athabasca River. The cumulative volumes of water processed ranged from 0.5 to 16 mL for membrane filtration and from 15 to 160 mL for cartridge filtration. The maximum volume of sample that could be processed using a given filter was identified by a dramatic increase in back pressure. To investigate the mechanisms underlying the artifacts resulting from filter clogging, a one µm PTFE membrane filter was employed as a prefilter for the 0.45 µm membrane filter. The pre-filtered water samples were subsequently filtered using the 0.45 µm membrane filter with incremental volumes of sample. Filtration artifacts were assessed by calculating the per cent of each TE recovered in the filtrates, relative to the TE concentration in the initial filtrate.

1. Membrane filtration

1.1. Dissolved concentrations

In river waters, there was a noticeable decrease in the dissolved concentrations of TEs as the processed volume increased. This applies to Al, V, Cr, Mn, Fe, Co, Ni, Cu, As, the REE, Pb, and Th. The per cent recovery ranged from 15 per cent to 78 per cent, with Al, Pb, the REE (e.g., La and Ce), Fe, Th, and V showing recoveries below 40 per cent. Bog waters exhibited distinct filtration artifacts compared to boreal rivers: compared to the initial filtrate, Cu was significantly lost (ca. 70 per cent), while losses of Cr, Ni, Mo, and Cd were on the order of 25 per cent.

1.2. Size distributions

As expected, TEs occurring in river waters mainly as simple ions such as Li, Sr, Cd, and Ba, were minimally affected by filter clogging. In contrast, TEs that readily hydrolyze and occur primarily in colloidal phases showed notable decreases in the concentrations of both the ionic and large inorganic fractions: this applies to Al, V, Cr, Mn, Fe, Co, Pb, and Th. From 20 to 80 per cent of primarily ionic species were excluded, while almost 100 per cent of the large inorganic species were excluded (i.e. lost). The exclusion of particles followed a size-dependent trend, with larger particles (ca. 200 nm) being excluded more rapidly than smaller particles (ca. 50 nm), suggesting a reduction in pore size as filtration progressed. Regarding DOM-associated and small inorganic species, approximately 20 per cent of these colloids were deposited on the filter during the first two mL of filtration. Thereafter, the TE concentrations remained similar in subsequent aliquots. The effect of filter clogging on bog waters was minimal. Only large inorganic TEs (e.g., Al, V, Cr, Pb, Th, and U) were significantly lost.

The impact of filter clogging was substantially mitigated when water samples were prefiltered using one µm membrane filters. As the processed volume increased, there was no significant loss of dissolved TEs ($p > 0.05$). These findings suggest that microparticles were effectively removed through prefiltration.

2. Cartridge filtration

2.1. Dissolved concentrations

The measurements of dissolved TEs in Athabasca River waters are greatly influenced by cartridge filtration. Based on the variation pattern with increasing processed volume, these TEs can be classified into three distinct groups. The first group, comprising Li, V, Cr, Fe, Ni, As, Rb, Sr, Mo, Sb, Ba, and Th, showed increases in the dissolved concentrations of 20 to 50 per cent until 90 ml had been filtered, followed by stable concentrations thereafter. On the other hand, the second group, consisting of Al, Mn, Co, Cu, Y, Cd, Cs, the lanthanides, and Pb, decreased after filtering 90 mL of the sample. Uranium was anomalous in that it exhibited significant adsorption onto the cartridge filter.

2.2. Size distributions

The primarily ionic species had higher concentrations in the first 90 mL of filtrate aliquots compared to the subsequent filtrates. Almost 100 per cent of colloidal species were excluded at the beginning of filtration, and their concentrations gradually increased with increased volume of sample processed. Once the processed volume reached 140 ml, the concentrations of colloidal species stabilized.

2. Development of AF4-ICPMS methods to analyze trace elements <5 μm

2.1. Method development

For the Athabasca River samples, a method was developed for analyzing TEs in microparticles (one to five µm), inorganic colloids (nine kDa to 1000 nm), macromolecules (0.3 to two kDa), and primarily ionic species (<0.3 kDa) using AF4-UV-ICP-MS, utilizing both normal and steric modes. To evaluate the accuracy of the concentration measurements, the recovery of size standards was employed. The retention ratio was also employed to determine the size or molecular mass. These size standards included bromophenol blue, sodium polystyrene sulfonate (PSS), polystyrene (PS), and SiO_2 standards, ranging from 0.69 kDa to 4000 nm.

Challenges arose from insufficient recoveries and shifting retention ratios for particles whose sizes (>500 nm) approach or exceed the inversion point between normal and steric modes. These variations are attributed to membrane-particle interactions, which are governed by the balance of attractive van der Waals and repulsive electrostatic forces. The dominant factor affecting recovery is the attractive van der Waals force, while the repulsive electrostatic force mainly contributes to the retention ratio shifting.

2.2. Size distribution of TEs in the Athabasca River

2.2.1. Concentrations

The abundance of TEs occurring as mainly ionic species and small molecules (i.e. those ≤ 0.3 kDa) was compared with their bulk concentrations (i.e. < 5 µm). In order of decreasing relative abundance, more than 80 per cent of the Li, Mg, As, Sr, U, and Mo were in ≤ 0.3 kDa fraction: Ba and Cd (> 60 per cent); Ni, Cu, and Co (> 40 per cent); Cr and Y (> 20 per cent). Conservative lithophiles elements (Al, Mn, Fe, and Th) and Pb occurred only to a very small extent (< ca. 10 per cent) in this fraction. These findings have direct environmental relevance, given the primarily ionic species and small molecules are known to exhibit greater mobility and bioavailability, compared to their colloidal counterparts. In the case of Pb, it is worth noting < 10 per cent of this element occurs in the fraction that is directly bioavailable. In regard to DOM-associated species (0.3–2 kDa), the proportion of elements in this fraction ranged from 90 per cent of Zn, gradually decreasing through Cu, Ni, Y, Cr, Co, Th, As, U, Fe, Pb, Mn, and V to Al (approximately 0.2 per cent).

The fraction consisting primarily of inorganic colloids and particles exhibited a wide size distribution, ranging from nine kDa to five µm. All elements except Li occurred in this fraction. Inorganic species were predominantly colloidal (< one µm) for elements such as Cr, Co, Ni, Cu, Zn, Sr, Y, Mo, Cd, and U. Microparticles (one to five µm) were only observed for Mg, Al, V, Mn, Fe, Ba, Pb, and Th, with their proportion decreasing in this order from 89 per cent (Mg) to three per cent (Th).

2.2.2. Size distributions

In regard to the small colloid fraction (<10 nm), which ranges from 0.3 to 20 kDa, the DOM-associated species can be further categorized into two size fractions: 1) small organic colloids with an average molecular mass of 0.86 ± 0.04 kDa, and 2) mixed Fe/Al-organic colloids with an average molecular mass of 1.4 ± 0.2 kDa. Many macronutrients necessary for animals were only associated with small organic colloids, such as V, Co, Ni, and Zn. Potentially toxic elements (e.g., Cr, and Pb) as well as lithophile elements (Al, Mn, Fe, Y, and U) were associated with Fe/Al-organic colloids. In the Athabasca River, small inorganic species (9.0 ± 0.2 kDa) occur, but only for Fe and Pb.

Regarding primarily inorganic species ranging from 100 nm to five µm, there was an abundance of Mg-bearing, Al-bearing, Fe-bearing, and Pb-bearing particles. Typically, Mg-bearing particles contained Sr, and Ba with sizes ranging from 187 to 3,780 nm. In the micrometer range, Al, V, Mn, and Fe displayed a similar size distribution, with notable particles of 4,120, 3,130, and 1,900 nm. These particles could be chlorite due to the co-occurrence of Al and Fe. In the nanometre size range, Al-bearing particles (824 and 506 nm) predominantly contained V and Mn, while Fe-bearing particles (167 nm) contained Pb. A significant positive correlation was found between V and Al ($p<0.01$), suggesting that much of the V may occur in the form of clays. A significant positive correlation was observed between the sizes of Fe and Pb ($p<0.05$). Evidence points to a role for Fe-bearing compounds as carriers for Pb, particularly in regard to clays (> one µm) and Fe oxyhydroxides (< one µm). The Pb-bearing particles (ca. 1,140 nm) found in the river water samples are consistent with findings from our previous study using spICP-TOFMS (Montaño et al., 2022).

LESSONS LEARNED

The operational definition of “dissolved” TEs as species capable of passing through a 0.45 µm membrane filter probably dates from the commercial introduction of filter materials with pores of this diameter. However, it is well known that polyvalent metal ions such as Al^{3+} and Fe^{3+} hydrolyze at low pH to form colloidal species and hydroxides of very low solubility. Thus, the determination of “dissolved” Al and Fe as defined in this way was always a considerable overestimate of the “truly dissolved” concentration: this difference has profound ramifications for the bioavailability of these elements. The data obtained in this study using AF4-ICP-MS provides a clear distinction between the conventionally defined “dissolved” fraction and truly dissolved species (i.e. ions and simple molecules), for these and many other elements. Moreover, the artifacts created during membrane filtration have now been quantified for both Athabasca River water (pH 8) and peat bog porewater (pH 4). These waters differ not only in pH, but also in ionic strength, alkalinity, abundance of major ions and in regard to concentrations of DOM. Not surprisingly, the artifacts created differ between these two extreme types of solutions.

As expected, membrane filtration mainly influenced TEs that were associated with large inorganic colloids, such as Al, Mn, Fe, As, the REE, Pb, and Th. It yields larger variations in primarily ionic and large inorganic species for AR waters compared to bog waters. The deposition of microparticles on 0.45 µm membrane filters appear to be most responsible for the exclusion of TEs when the filters become clogged. There are two possible solutions to the problem of filter clogging, and the artifacts they create. First, for laboratories fortunate enough to have AF4-UV-ICP-MS, or access to such instrumentation, TEs can be directly determined across an extremely broad size range, from particles in the range of micrometers, through macromolecules in the range of a few kDa, to primarily ionic species <0.3 kDa. The method developed here exploits both normal and steric modes to analyze the size distribution of all TEs smaller than five µm in river waters. However, the instrumentation is expensive, complicated to operate, and time consuming, making it practical only for academic research laboratories. The alternative is to simply employ a one µm pre-filter in the field, before filtering through a 0.45 µm filter, to eliminate most of the artifacts described here. Given the extremely low concentrations of dissolved TEs in the AR and the peat bog porewaters of the region, metal-free, ultraclean procedures and protocols must be used throughout any field campaign, from sample collection, through processing, to analysis.

Cartridge filtration tends to yield higher proportions of primarily ionic TEs in the filtrates than membrane filtration. This finding may be relevant for studies of the bioavailability of TEs in boreal waters.

PRESENTATIONS AND PUBLICATIONS

Journal Publications:

Published

Wang Y.; Cuss C. W.; Shotyk W. Application of asymmetric flow field-flow fractionation to the study of aquatic systems: Coupled methods, challenges, and future needs. *J. Chromatogr. A* 2020, 1632, 461600. https://doi.org/10.1016/j.chroma.2020.461600.

Wang Y.; Cuss C. W.; Pei L.; Shotyk W. Resolving uncertainties in the quantification of trace elements within organic-rich boreal rivers for AF4-UV-ICP-MS analysis. *Anal. Chem.* 2024, 96, 6889-6897. https://doi.org/10.1021/acs.analchem.3c05198

Wang Y.; Cuss C. W.; Shotyk W. Applications, challenges, and considerations for trace element analysis in natural waters using AF4-UV-ICPMS (Chapter). In Baalousha M, Gueguen C, & Williams K. R. (Eds), Field Flow Fractionation: Principles and Applications (Book). Wiley-VCH Verlag GmbH, 2024, ISBN13: 9783527340682. (In press)

Submitted, under review

Wang Y.; Cuss C.; Barraza F.; W.; Luu A.; Oleksandrenko A.; Shotyk W. Filtration artifacts on potentially bioavailable forms of trace elements in rivers and bog waters in boreal zone. Water Res.

Wang Y.; Butt A. S.; Cuss C. W.; Pei L.; Xue J. -P.; Luu A.; Barraza F.; Shotyk W. Addressing challenges of membrane clogging in AF4-UV-ICPMS analysis for accurate size determination of trace elements in acidic peat bog waters. Anal. Chem.

In preparation

Wang Y.; Cuss C. W.; Shotyk W. Understanding recovery variations and retention ratio shifts in AF4-UV-ICPMS analysis of sub-5 µm particles due to membrane-particle interactions.

Conferences, presentations, and workshops:

Wang Y.; Cuss C. W.; Shotyk W. Extension of the AF4-ICP-MS method to a higher size range to account for filtration artifacts. Presented at the Annual COSIA Science Committee meeting, Edmonton, Alberta, Dec. 08, 2020 (Oral presentation).

Wang Y.; Cuss C. W.; Butt S.; Lei P.; Luu A.; Oleksandrenko A.; Shotyk W. Filtration artifact study, and routine analysis of trace elements in “truly” dissolved and dissolved fractions of bog waters using AF4-UV-ICP-MS. Presented at the COSIA Science Committee meeting, Edmonton, Alberta, Dec. 14, 2021 (Oral presentation).

Wang Y.; Cuss C. W.; Butt S.; Lei P.; Luu A.; Oleksandrenko A.; Shotyk W. The impact of 0.45 µm membrane filtration on dissolved trace elements in natural waters. Presented at the semi-annual COSIA Science Committee meeting, Edmonton, Alberta, Dec 3, 2022 (Oral presentation).

Wang Y.; Cuss C. W.; Luu A.; Oleksandrenko A.; Bujaczek T.; Shotyk W. Impact of filtration on the concentration and size distribution of dissolved trace elements in natural waters. The sixth annual ALES Graduate Research Symposium, University of Alberta, Edmonton, Alberta, March 28, 2023 (Oral presentation).

RESEARCH TEAM AND COLLABORATORS

Institution: University of Alberta

Principal Investigator: William Shotyk

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Yu Wang	University of Alberta	PHD Candidate	Sept. 2019	Apr. 2024

WE0098 - Lake Surface Sediment Sampling Across the Peace-Athabasca Delta after Widespread Flooding to Assess for Pollution and Generate Baselines for Contaminant Concentrations Prior to Release of Treated Oil Sands Process Water into the Athabasca River

COSIA Project Number: WE0098
Research Provider: Roland Hall and Brent Wolfe / PIs
Industry Champion: Pathways Alliance Inc. / COSIA
Industry Collaborators: Chris Godwaldt
Status: Year 1 of 2

PROJECT SUMMARY

1. The scope of the project

Concern persists over degradation of aquatic ecosystems in the Peace-Athabasca Delta (PAD) by releases of substances of concern from upstream oil sands development along the Lower Athabasca River and other industrial activities in the watershed. The PAD is a dynamic floodplain located ~200 river kilometres downstream of Alberta's oil sands development, at the terminus region of the Athabasca River where its load of sediment and associated compounds of concern is deposited. Eighty per cent of the delta is protected within Wood Buffalo National Park (WBNP). The remainder is First Nations and Métis or Crown land. Knowledge of concentrations of compounds of concern in sediment of flood-prone lakes in the PAD before release of treated OSPW (i.e., 'pre-release' baselines) is required to allow for comparison of Athabasca River sediment quality ***before*** versus after releases of treated OSPW into the Athabasca River occur. Such knowledge is needed by a broad range of stakeholders 1) to identify if discharge of treated OSPW and other industrial activities in the watershed begin to affect aquatic ecosystems within the PAD, and should this occur, 2) to signal that changes may be needed to industrial operations to ensure downstream environments are adequately protected.

2. Summarize the key objectives of the project/program/study

This project will analyze recently-deposited sediment collected in May 2023 from 40 lakes in the PAD after widespread flooding from the Athabasca and Peace rivers occurred during 2020-2022 to 1) evaluate if sediment deposited by the recent floodwaters are enriched in three classes of compounds of concern (metals, total mercury (THg), polycyclic aromatic compounds (PACs)) relative to natural concentrations that existed before 1920 (i.e., 'pre-disturbance' baseline), in surface sediment collected from lakes in 2017 following a period without widespread flooding, and in surface sediment collected in 2018 from a subset of the lakes that had flooded that, and 2) generate scientifically rigorous definition of 'pre-release' baseline concentrations of the three classes of compounds of concern in advance of release of treated OSPW into the Athabasca River.

The project takes advantage of rare widespread flooding in the delta during 2020-2022 that deposited water, sediment, and associated compounds of concern from the Athabasca and Peace rivers into a substantial number of lakes. Collection and analysis of the recently deposited sediment allows us to determine concentrations of the compounds of concern in river sediment before any permitted releases of treated OSPW into the Athabasca River.

The compound classes analyzed in the study include substances known to be harmful to wildlife and humans, including a suite of metals, THg and PACs. In this report, we present results for vanadium (V), nickel (Ni) and THg. V and Ni serve as key indicator metals of emissions from oil sands development because their concentrations are elevated in McMurray Formation bitumen relative to other geological sources and in mining wastes. While concentrations of mercury are typically below acute and chronic guidelines for the protection of aquatic life in OSPW, mercury remains a concern for many stakeholders. Mercury can be converted to methylmercury, a neurotoxin that may bioaccumulate and biomagnify through food webs and pose risks to higher trophic levels including humans. We will report results of the analysis of PAC concentrations in the surface sediment samples in a final report. PACs are a concern because many of the compounds in bitumen are known or suspected human carcinogens and have been associated with toxicological effects in fish.

Surficial sediment samples (uppermost ~one cm) were collected in May 2023 from 40 lakes distributed across the PAD (22 in the Athabasca sector, 18 in the Peace sector) to take advantage of unusually extensive flooding of lakes in the PAD during 2020-2022 (Figure 1). The sediment samples were collected using a gravity corer deployed near the centre of each lake. Due to extensive flooding prior to sample collection, many of the lakes received input of river floodwaters, with concentrations of the compounds in the sediment samples that are representative of Athabasca River and Peace River sediment. For the lakes that flooded prior to sample collection, a visually distinctive light grey mineral-rich surficial layer of river sediment was skimmed off from underlying darker organic-rich lake sediment to ensure the chemical analyses characterize the concentrations of compounds of concern in recently deposited river-transported sediment.

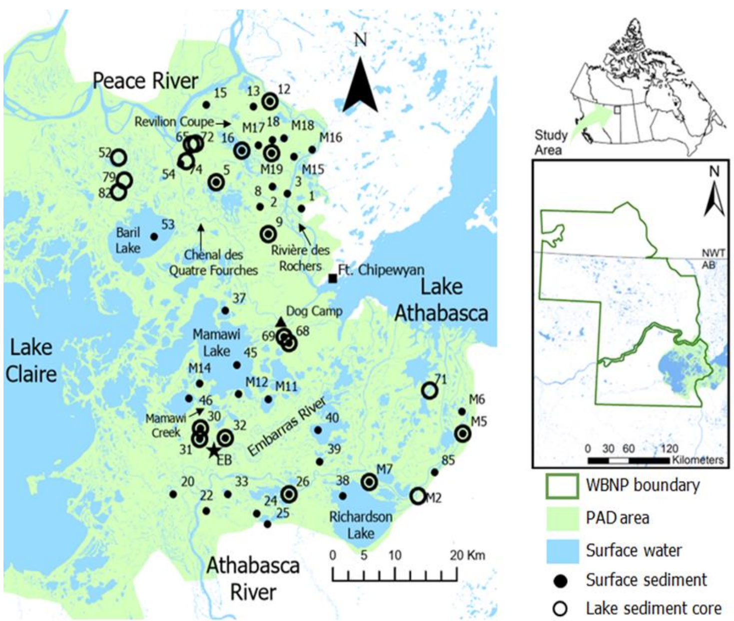

Figure 1. Maps showing locations of the lakes in the Peace-Athabasca Delta sampled for surface sediment in May 2023 (solid circles), and the sediment cores (open circles) and riverbank samples (solid triangles) used to determine pre-disturbance (i.e., pre-1920) baseline concentrations of substances of concern. The delta is identified in light green in the maps, and the boundary of Wood Buffalo National Park is identified as a bark green line in the inset maps along the right margin.

Concentrations of a suite of metals and trace elements were determined on well-mixed subsamples of freeze-dried sediment at ALS Canada following EPA method 200.2/6020B (aqua regia hot block digestion and analysis by CRC-ICP-MS). Concentrations of total mercury were determined on subsamples of freeze-dried sediment at the Biotron Laboratory, Western University, using thermal decomposition and atomic adsorption spectrophotometry, and following EPA Method 7473. These analytical methods are consistent with the methods used in our prior research. The samples have not yet been processed for analysis of PACs.

Consistent with our prior studies, changes in elemental concentrations between the sediment samples collected in 2023 and the pre-disturbance baselines are quantified as Enrichment Factors (EFs). This permits us to determine if the sediment deposited by recent floodwaters is enriched in these metals. Here, we report EFs for Ni, V and THg. For Ni and V, the EFs are based on aluminum-normalized concentrations and were computed using the equation: $EF = (X/Al)_i/(X/Al)_{pre\text{-}1920}$; where X_i is the measured metal of interest concentration and Al_i is the measured concentration of Al for a specific sediment sample (i), and $X_{pre\text{-}1920}$ is the expected value for a metal of interest in sediment deposited before 1920 as derived from the equation of the regression line for the relation between the metal of interest and Al when $Al_{pre\text{-}1920} = Al_i$. Our program has continuously improved the pre-disturbance baselines for V and Ni by increasing the number of sites and samples beyond those presented in previous publications. Here, we present the most updated pre-disturbance baselines established using radiometrically dated sediment cores from seven lakes in the Athabasca sector (PAD 26, 30, 31, 32, 71, M2, M7), three lakes in the Peace sector (PAD 52, 65, 67) and riverbank exposures from both rivers. Separate baselines were derived for the Athabasca and Peace sectors because elemental concentrations are naturally higher in sediment transported by the Peace River.

The relation between concentrations of THg and Al (and other commonly used geochemical normalizers) is not statistically significant. Thus, EFs for THg were computed using a simplified equation: $EF = THgi/THg_{pre\text{-}disturbance}$ where THg_i is the concentration of THg for a specific sediment sample and $THg_{pre\text{-}disturbance}$ is the pre-1920 average THg concentration. The equations were applied separately to lakes in the Peace and Athabasca sectors of the delta.

PROGRESS AND ACHIEVEMENTS

To date, the surficial sediment samples have been analyzed for concentrations of a suite of metals and THg. In this interim report, we present results for the oil sands-indicator metals V and Ni, and for THg.

Concentrations of V and Ni in the surface sediment samples collected in May 2023 from lakes in the Athabasca sector (red circles) and Peace sector (blue circles) fall close to the linear relations of these metals with Al in sediment deposited before 1920 (pre-disturbance baseline) and mainly within the 95 per cent prediction intervals, which represent the range of natural variation of individual samples (**Figure 2**). This indicates little to no enrichment of V and Ni concentrations, because values in the 2023 surface sediment remain largely within the range of natural variation that existed before 1920. Samples with lower concentrations of the metals in these plots are associated with coarser grained sediment supplied by higher energy floodwaters, whereas higher concentrations are associated with finer grained sediment deposited under conditions of lower energy of flow (i.e., weaker floodwater input or absence of flooding). High coefficients of determination for the relations between Ni and V with Al ($R^2 = 0.802\text{-}0.978$) in pre-disturbance sediment demonstrate the effectiveness of Al as a geochemical normalizer.

Enrichment Factor (EF) is a commonly used metric to quantify how much the concentration of a compound of concern has increased relative to a pre-disturbance baseline. An EF of 1.0 identifies no change relative to baseline, whereas EFs of two and five, for example, represent two-fold (doubling) and five-fold increases above baseline, respectively. Thresholds and terminology presented in a widely cited comprehensive review by Birch (2017. *Determination of sediment metal background concentrations and enrichment in marine environments – a critical review. Science of the Total Environment 580: 813–831*) provide internationally consistent categorization of the degree of enrichment above pre-disturbance baseline. EFs ≤1.5 represent the range of natural variability or 'pristine conditions', EFs >1.5–3.0 represent 'minimal enrichment', EFs >3.0–5.0 represent 'moderate enrichment', EFs >5.0–10.0 represent 'considerable enrichment' and EFs >10.0 represent 'severe enrichment'. EFs and these thresholds have been used to evaluate paleolimnological records in the PAD and Lower Athabasca River.

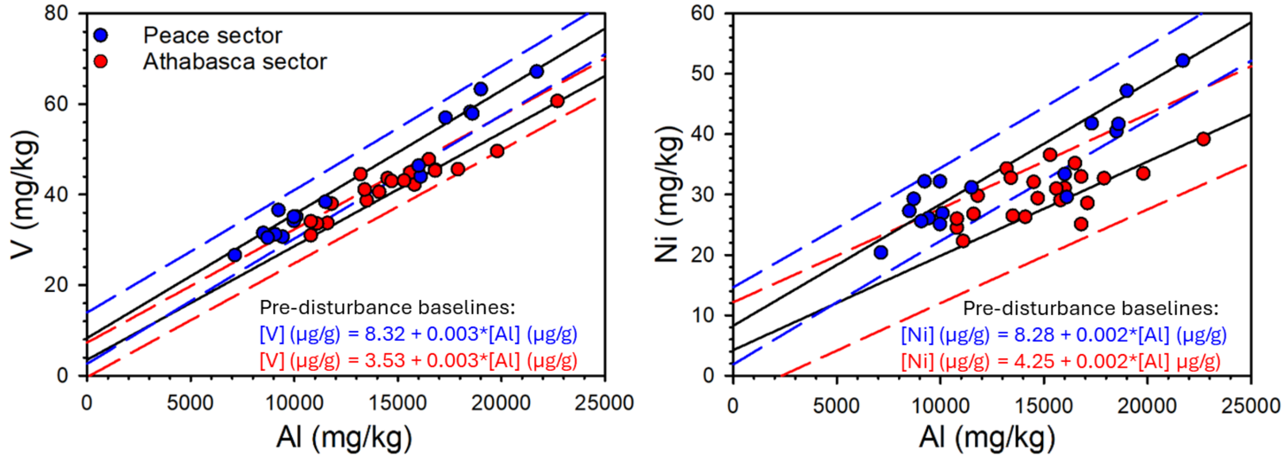

Figure 2. Graphs showing concentrations of vanadium (V) and nickel (Ni) and their relations with aluminum (Al) concentration in surface sediment samples obtained in May 2023 from lakes in the Athabasca sector (red circles) and Peace sector (blue circles) of the Peace-Athabasca Delta. The data are presented relative to sector-specific pre-disturbance baseline relations (regression lines and 95 per cent prediction intervals) for sediment deposited before 1920 into lakes and riverbanks in the delta. Equations for the pre-disturbance baselines are presented at the bottom right of the graphs (correlation coefficients (R^2) for the Athabasca and Peace sector pre-disturbance baselines, respectively, are 0.978 and 0.963 for V and 0.802 and 0.860 for Ni).

EFs computed for V and Ni in surface sediment samples collected in 2023 from the lakes in both sectors of the delta are close to 1.0 and well below the threshold for 'minimal enrichment,' identifying no enrichment above pre-disturbance concentrations (**Figure 3**). Moreover, the distribution of EFs and median values for the surface sediment samples collected in 2023 are comparable to the values in surface sediment collected in 2017, which captured a period of little flooding, in surface sediment collected in 2018 from lakes that had received recent input of floodwaters, and in sediment deposited before 1920. Display of the data as EFs in **Figure 3** enhances communication of the evidence for little to no enrichment of key oil sands-indicator metals in river-supplied sediment to lakes in the PAD beyond presentation of the base data as scatterplots in **Figure 2**.

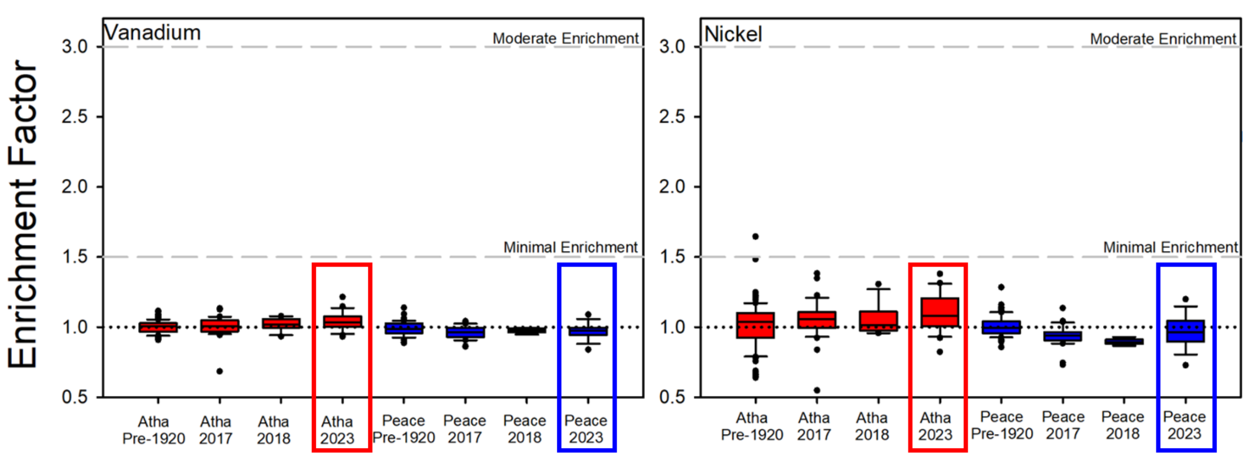

Figure 3. Boxplots showing the distribution of Enrichment Factors (EFs) for vanadium and nickel in surface sediments collected in May 2023 from lakes in the Athabasca sector (red) and Peace sector (blue) of the Peace-Athabasca Delta (outlined with a box), and how they compare to distributions of values for surface sediment collected in 2017 after a period of minimal flooding, in 2018 after widespread flooding, and in sediment deposited prior to 1920 before evidence of enrichment by long-range atmospheric transport of metals to the region.

Consistent with the findings for V and Ni, EFs for THg in surface sediment samples collected in 2023 from the lakes in both sectors of the delta are also close to 1.0 and below the threshold for 'minimal enrichment,' identifying no enrichment above pre-disturbance concentrations, yet EFs for THg are slightly higher in the Athabasca sector than in the Peace sector (**Figure 4**).

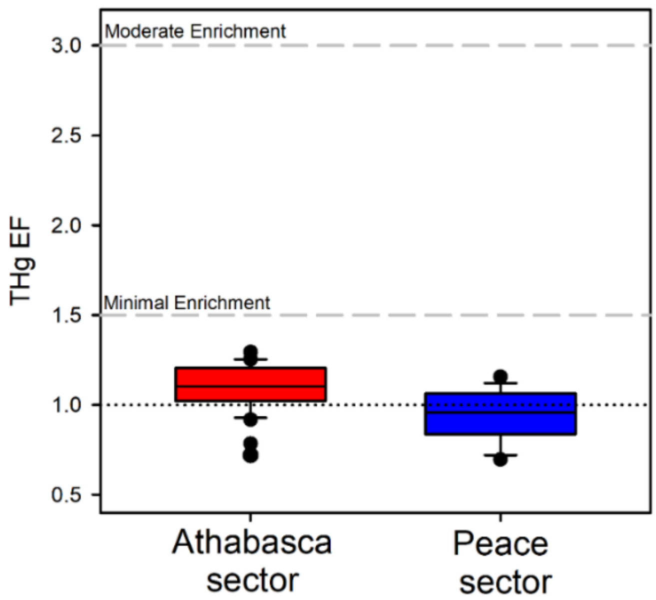

Figure 4. Boxplots showing the distribution of Enrichment Factors (EFs) for total mercury (THg) in surface sediments collected in May 2023 from lakes in the Athabasca sector (red) and Peace sector (blue) of the Peace-Athabasca Delta.

Based on analysis of V, Ni, and THg concentrations in the surface sediment samples collected in May 2023, the project has generated new sector-specific 'pre-release' baselines which can serve as benchmarks for evaluating enrichment of these elements in aquatic sediment within the Peace-Athabasca Delta by future releases of treated OSPW into the Athabasca River and other industrial activities. The pre-release baselines for V and Ni are based on linear regression with the geochemical normalizer (Al), as reported in Table 1. For THg, the pre-release baseline is the average concentration in sediment samples collected in May 2023.

Table 1. Sector-specific 'pre-release' baselines for V and Ni concentrations in aquatic sediment in the Peace-Athabasca Delta, based on surface sediment collected from 40 lakes in May 2023. The pre-release baselines for V and Ni are based on linear regression with the geochemical normalizer (Al). The pre-release baselines for THg are the average concentration in sediment samples collected in May 2023. Concentrations of all elements are expressed per gram of dry sediment mass.

Sector	Metal	Regression Equation	Adj. R^2	P-value
Athabasca	V	[V] μg/g = 0.003*([Al] μg/g) + 7.08	0.953	$1.36x10^{-11}$
	Ni	[Ni] μg/g = 0.002*([Al] μg/g) + 11.51	0.802	$7.13x10^{-07}$

	THg	[THg] (ng/g) = 67.31 ng/g		
Peace	V	[V] µg/g = 0.003*([Al] µg/g) + 5.45	0.915	$3.51x10^{-10}$
	Ni	[Ni] µg/g = 0.002*([Al] µg/g) + 9.84	0.739	$2.95x10^{-06}$
	THg	[THg] (ng/g) = 75.56 ng/g		

LESSONS LEARNED

1. Analysis of sediment deposited into floodplain lakes in the Peace-Athabasca Delta can be used to determine important benchmarks, or baselines, for concentrations of compounds of concern transported by the Athabasca River and Peace River and to quantify how much concentrations have increased over time due to industrial activities operating within their watersheds.

2. The results reveal that concentrations of V, Ni and THg in the surface sediments collected in 2023 are not elevated above 'pre-disturbance' baselines, which characterize the concentrations in sediment deposited before the 1920s, when enrichment from long-range atmospheric transport is detectable. The methodology has strong ability (>99 per cent power) to detect a 10 per cent enrichment of V and Ni (or a rise in EF by 0.1 units) in lake surface sediment (Owca et al., 2020). The study, thus, demonstrates no enrichment of these metals relative to naturally occurring concentrations in aquatic sediment at the Peace-Athabasca Delta.

3. The study generated 'pre-release' baselines for concentrations of V, Ni and THg from analysis of surface sediment collected from delta lakes in 2023 after widespread flooding in 2020-2022. These pre-release baselines provide informative benchmarks for evaluating enrichment of these elements in aquatic sediment within the Peace-Athabasca Delta by future releases of treated OSPW into the Athabasca, and other industrial activities in the Athabasca and Peace river watersheds.

PRESENTATIONS AND PUBLICATIONS

Journal Publications:

Published

Kay, M.L., L.A. MacDonald, J.A. Wiklund, C.A.M. Girard, B.B. Wolfe, R.I. Hall. 2024. 'Paleofloodscapes': application of sediment source fingerprinting to track flood regime change over space and time at the Peace-Athabasca Delta, Canada. Science of the Total Environment 912: 169538. https://doi.org/10.1016/j.scitotenv.2023.169538.

Conferences, presentations, and workshops:

Kay, M.L., B.B. Wolfe, R.I. Hall. 2023. Use of widespread flooding at the Peace-Athabasca Delta in 2020-2022 to evaluate enrichment of substances of concern in Athabasca River sediment. Canada's Oil Sands

Innovation Alliance 2023 Mine Water Management Science Workshop. Edmonton, AB. October 12-13, 2023.

Reports:

Hall, R.I., B.B. Wolfe. 2024. First Interannual Report to Parks Canada for Parks Canada Research and Collection Permit WBNP-2023-45299for the Project “Lake surface sediment sampling across the Peace-Athabasca Delta after widespread flooding to assess for pollution and generate baselines for contaminant concentrations prior to release of treated oil sands process water into the Athabasca River”. May 26, 2024.

RESEARCH TEAM AND COLLABORATORS

Institution: University of Waterloo

Principal Investigator: Roland Hall

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Brent Wolfe	Wilfrid Laurier University	Professor and Associate VP and Dean of the Faculty of Graduate and Postdoctoral Studies		

OIL SANDS PROCESS-AFFECTED WATER CHEMISTRY AND TOXICITY

WE0072 - Bioavailability and Bioaccessibility of Trace Elements in Natural and Industrial Particles of the Lower Athabasca River Watershed

COSIA Project Number: WE0072

Research Provider: University of Alberta

Industry Champion: Canadian Natural

Industry Collaborators: Imperial Oil REsourcesLtd., Suncor Energy Inc., Syncrude Canada Ltd., Teck Resources Limited

Status: Year 4 of 5

PROJECT SUMMARY

This study looks at the potential environmental impacts and ecological significance of trace elements (TEs) from open pit bitumen mining and upgrading, including from the eventual release of treated oil sands process water (OSPW) to the Athabasca River. In many if not most cases, total concentrations of TEs in environmental media have been interpreted as having some biological significance, regardless of the chemical form of the element. This has led to many misunderstandings and, often, concern that may be exaggerated.

The overall objective of this work is to examine, understand, and communicate the risks to the health of aquatic ecosystems represented by TEs associated with industrial particles. This includes by-products and residua of bitumen mining and upgrading (dry tailings, coke, soil, and overburden) that may be added to the Athabasca River by wind and water erosion. Samples of these materials were provided to us by COSIA members for study.

The particles will be reacted in synthetic gastrointestinal fluids to estimate bioaccessibility and bioavailability to invertebrates, fish, and other aquatic life. As a control for this approach, the gradient in bioavailability and bioaccessibility of TEs, represented by natural particles suspended in the Athabasca River, will be examined at selected locations. The potential bioaccessibility of TEs in aquatic particles, using rigorous experimental studies of their chemical reactivity in synthetic gastric fluid, will be evaluated.

All of the analytical work will be undertaken in the metal-free, ultraclean SWAMP lab. For perspective and context, selected samples representative of urban runoff, as well as the dominant rock-forming minerals of the earth's crust (plagioclase feldspar, potassium feldspar, mica, quartz, and calcite) will be also examined.

PROGRESS AND ACHIEVEMENTS

1. *Geomaterials (Dr. Matthias Oursin)*

1.1. Total and quasi total concentrations

Geomaterials provided by our partners (Imperial, Suncor, Canadian Natural, and Syncrude) include overburden, soils, tailings, road construction materials, and cokes from the Athabasca Bituminous Sands region (ABS). The geomaterials where divided into four size fractions: medium sand (>250 µm), fine sand (>64 µm), silt (>10 µm), and silt/clay (<10 µm).

These samples have been processed and analyzed, including SEM and XRD analyses for physical, mineralogical characterization, and ICP-MS and ICP-OES for determination of trace and major elements respectively. To ascertain the total concentrations of TEs, the samples were analyzed at a commercial laboratory (Activation Laboratories, Ancaster, ONT). ACTLABS provides complete dissolution of mineral and organic samples through a mixture of acids including HNO_3, HCl, $HClO_4$, and HF. The latter two acids are not used in the SWAMP lab (for safety reasons), hence the need to outsource this work. The concentrations obtained using ICP-MS analyses of these samples represent "true total" concentrations. In the SWAMP lab, "quasi total" concentrations of TEs were determined in bulk samples of these same materials, after digestion in concentrated HNO_3 using a high-pressure microwave system.

The results show that total concentrations are greater than quasi-total concentrations for all TEs and size-fractions. For instance, the total concentrations of Pb are on average 20 per cent greater than the "quasi total" concentrations. This trend is most evident in coarse tailings, where the concentration difference in the bulk fraction is 60 per cent. Because ACTLABS employs HF, even the most refractory silicate minerals are dissolved, leading to greater total concentrations of TEs.

Two materials were selected for more detailed comparison: sandy till and clay till. Comparing the TE concentration data for each size fraction (sand, fine sand, silt and silt/clay) shows the disparity between quasi-total and total concentrations decreases with decreasing particle size. In the sandy till, Pb showed a difference of 55 per cent for the fraction greater than two mm, 32 per cent for the fraction between two mm and 250 µm, 39 per cent for the fraction between 250 and 64 mm, 16 per cent for the fraction between 64 and 10 µm and two per cent for the fraction less than 10 µm. Similar results were obtained for the clay till. The trend in decreasing discrepancy between the two digestion methods was anticipated because mineral dissolution rates are proportional to surface area, and surface area increases with decreasing particle size. The analysis of total and quasi-total concentrations of the other elements across different size fractions also shows significant variability, both within elements and particle sizes, ranging from one per cent for Eu to 75 per cent for Mo in the <10 µm size fraction. Hereafter, both total and quasi-total concentrations will be used to calculate bioaccessibility because the quasi total concentrations will yield more conservative estimates of bioaccessibility (see below). The extractable concentrations of TEs and the quasi total concentrations are both obtained in the SWAMP lab on the same ICP-MS instrument operated by the same analyst. Moreover, total concentrations can only be obtained after complete dissolution of mineral particles. This requires the use of HF, an acid not present in digestive fluids.

1.2. Bioaccesibility of trace elements in HCl alone

The bulk fraction (< two mm) of each geomaterial was leached as follows: ambient temperature, 16 hours of reaction time at a pH of 2 (obtained using high purity HCl). Bioaccessibility was calculated for each element as:

$$Bioaccessibility(\%) = \frac{C_{extractableTE}}{C_{totalTE}} \times 100$$

Overall, bioaccessibility showed great variability between elements, geomaterial type and particle size. Soils showed the greatest bioavailability among the natural materials, most likely due to their high surface area-to-volume ratio, providing reactive sites for dissolution and the release of TEs into solution. For Pb, the peat/subsoil/topsoil material showed the greatest bioaccessibility: 31 per cent. For context, the bioaccessibility of Pb ranged from 0.5 per cent for coarse sand tailings to 15 per cent for fine tailings. For some elements, such as Rb, the average bioaccessibility ranges from zero to four per cent for all geomaterials, except for the soils: 15 per cent for the litter sample, and 26 per cent for peat/subsoil/topsoil. Bioaccessibility of TEs within the organic fraction of soils may be very different from the mineral fraction. Physically separating and analyzing these two main soil fractions separately may be worthwhile.

Except for the soils, the other geomaterials show similar behaviour. Road construction materials, tailings and overburden all show similar bioaccessibility for most of the elements.

Among the elements, aluminum is the least bioaccessible, ranging from zero to one per cent: again, soil is exceptional, with five per cent Al bioaccessibility from litter and 13 per cent from peat/subsoil/topsoil. Rare earth elements show a similar bioaccessibility among the geomaterials, with bioavailability increasing with atomic number, suggesting a similar behaviour during the digestion.

1.3. New samples collected

In June 2023, Hammerstone Infrastructure Materials Ltd, one of the largest limestone quarries in Western Canada, provided us with samples from their quarry at Fort McKay, including small rocks used to fill roads and larger stones used for drainage. These limestone samples will also undergo the same process as the other geomaterials: physical and chemical characterization, separation by particle size, digestion with HNO3, extraction with SGF, and determination of the bioaccessible fraction.

1.4. Trace elements in more complex formulations of SGF and SIF

The bioaccessibility experiments undertaken to date have used HCl alone, and have been successful because of the extremely low blank values in high purity HCl. Hydrochloric acid at pH 2 provides appropriate conditions for the dissolution of mineral matter, but enzymes are required to simulate the digestion of carbohydrates, fats, and proteins.

Two formulations of Synthetic Intestinal Fluid (SIF) were studied. The first composition was pancreatin (two mg/mL) and ox-bile (four mg/mL). The second was sodium taurocholate and bovine serum (BSA, five mg/mL). Both formulations resulted in unacceptably high background concentrations of TEs. An attempt to lower the blank values for TES using Chelex-100 resin was unsuccessful, and other cleanup treatments will be evaluated.

The formulation of Synthetic Gastric Fluid also needs to be improved. Initial tests showed that pepsin also has unacceptably high concentrations of TEs and needs to be purified before use. Other cleanup treatments will be explored.

2. Suspended solids from the Athabasca River (Pamela Gascon, M.Sc. candidate)

The bioaccessibility of TEs in suspended solids from the Athabasca River will be examined using simulated gastric fluid representative of teleost fish. The initial project activities that have been completed include the review of relevant literature and selection of appropriate samples from the inventory of suspended solids obtained in the past from the main stream of the river and its tributaries.

The samples consist of suspended particles retained on 0.45 µm PTFE membrane filters. Most of the samples were collected between 2017 and 2019 from the main stem of the Athabasca River upstream, midstream, and downstream of the industrial region. Samples were also collected from the surrounding tributaries (Pierre River, Tar River, Ells River, McKay River, Muskeg River, Beaver Creek, Steepbank River, Clearwater River, Horse River, and Little Fishery Creek). A representative subset of these samples will form the basis of the experiments to assess the bioaccessibility of TEs in the particles retained by the filters. The best method to extract the particles is currently under development, and requires consideration of the unique challenges presented by the very small mass of material deposited on the filter membranes (e.g. variation in particle density and size, and adsorption characteristics) as well as the practical limitations with the removal and handling of the membranes. In the past, the PTFE membranes were removed from the polypropylene filter housing by precise cutting using a lathe operated by Tommy Noernberg, our mechanical engineering technologist. He has since constructed a hand-operated press to allow the membranes to be recovered easily, precisely, and rapidly, by hand. The next step to be undertaken is to accurately determine the mass of solids retained on these filters, using an analytical microbalance in the National Institute of Nanotechnology (NINT).

LESSONS LEARNED

From the detailed investigations conducted on TEs in the geomaterials examined, three valuable lessons have emerged.

First, the distinction between total concentrations and "quasi total" concentrations of TEs is important for accurately assessing bioaccessibility. Total dissolution of these samples versus digestion in concentrated HNO_3 alone, at elevated temperature and pressure reveals significant differences in concentrations, particularly in regard to coarse particles such as tailings. Quasi-total concentrations, obtained in the metal-free, ultraclean SWAMP laboratory, will provide more conservative estimates of TE bioaccessibility. Within the fine fraction of soils and sediments, the discrepancy between total and quasi total concentrations of TEs, is modest.

Second, the concept of bioaccessibility is a key factor in understanding the potential risks posed by TEs to aquatic organisms. The in vitro experiments using synthetic gastrointestinal fluids have already shown the variation in Pb bioaccessibility for different size fractions, with smaller particle sizes generally associated with greater bioaccessibility. One of the implications of these results is bioaccessibility of TEs in suspended solids may vary with water velocity, implying that TE bioaccessibility is expected to be lower in spring when streams and rivers are transporting relatively more large particles. The samples of suspended solids recovered from filters will provide insight regarding spatial variation in TE bioaccessibility, and provide a comparison with the results obtained from potential sources of these solids to the river (i.e. the geomaterials provided by industry).

Third, ongoing efforts to refine experimental methodologies, such as improving the TE blank values by purifying the reagents used to create the synthetic intestinal fluids, and the adaptation of procedures for obtaining and leaching suspended particles from the Athabasca River, highlight the importance of continual innovation.

PRESENTATIONS AND PUBLICATIONS

Journal Publications:

In preparation

Review paper “Application of in vitro fluid digestion methods for estimating the bioaccessibility of sediment-associated contaminants to aquatic organisms: A review” (to be submitted in spring 2024).

List of authors: Mandy Krebs, Fiorella Barraza, Pamela Gascon, Matthias Oursin and William Shotyk

Proposed Journal: Environmental Research Letters

RESEARCH TEAM AND COLLABORATORS

Institution: University of Alberta

Principal Investigator: William Shotyk

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Dr. Fiorella Barraza	University of Alberta	Research Associate		
Pamela Wescott	University of Alberta	MSc Candidate	5 September 2023	Fall 2025
Dr. Matthias Oursin	University of Alberta	Postdoctoral Fellow		

WE0085 - Petroleum Hydrocarbons in Oil Sands Mine Waters

COSIA Project Number: WE0085

Research Provider: Four Elements Consulting Ltd.

Industry Champion: COSIA Water Mining Subcommittee

Industry Collaborators: Canadian Natural, Imperial Oil Resources Ltd., Suncor Energy Inc., Syncrude Canada Ltd.

Status: Year 2 of 3

PROJECT SUMMARY

One measure of organic constituents in surface water used by the Government of Alberta is called "petroleum hydrocarbons," although the corresponding analytical method can capture a very broad range of organic constituents. The Government of Alberta has surface water quality guidelines and analytical methods for petroleum hydrocarbons adopted from the Canada-Wide Standard for Petroleum Hydrocarbons in Soil (PHC CWS) developed by the Canadian Council of Ministers of the Environment (CCME 2001, 2008). This study was completed to evaluate the laboratory performance of the CCME analytical method for OSMW samples. Analytical methods for hydrocarbons include fractions based on boiling point (BP) ranges for the corresponding straight-chain alkane (described by nCX, where X is the number of carbons). The CCME analysis includes four fractions: "F1" (volatile, gasoline range; nC<10; BP <164.6°C), "F2" (light hydrocarbons, diesel range; nC10-16; BP 164.6-277.1°C), "F3" (lubricant range; nC16-34; BP 277.1-496.9°C), and "F4" (heavy lubricant range; nC>34; BP >496.9°C). Alberta has draft acute guidelines for the protection of aquatic life for the F1 and F2 fractions of 150 μg/L and 110 μg/L, respectively (GOA 2018). The measure and the associated surface water quality guidelines were developed to support the assessment of potential ecological and human risks at sites where soils have been contaminated by petroleum products (CCME 2001, 2008), and their suitability for assessment of surface waters has not been fully vetted.

The first year of the project included an evaluation of the Alberta guidelines for the protection of aquatic life for the F1 and F2 fractions as well as a preliminary evaluation of the laboratory performance of the CCME analytical method for oil sands mine water samples. The second year included a more comprehensive evaluation of the analytical method.

One component of the method is the use of silica gel "cleanup" (SGC), which removes polar organics, such as fats, humic acids, and naphthenic acids, from the sample prior to analysis. The SGC is susceptible to intra- and inter-laboratory variation, particularly for waters with high concentrations of polar organics, such as oil sands mine waters (CCME 2001, 2008; BCMECCS 2023; WSDOE 2023; Zemo et al. 2013). The CCME standard method includes SGC for the F2 to F4 fractions and allows for either in-situ SGC, where the silica gel is added directly to the sample, or ex-situ (column) SGC where the sample extract is dispensed through the top of a glass column packed with silica gel (CCME 2001, 2008). The column SGC is considered more robust but is not routinely offered by commercial laboratories.

PROGRESS AND ACHIEVEMENTS

For this study, over 20 samples were collected over several years from a range of natural waters and OSMWs, including: 1) water from a natural spring more than 10 km away from any oil sands mines, 2) groundwater from monitoring wells on mine sites, 3) depressurization water (groundwater, often with high salinity, pumped from below active mining areas to prevent seepage into the mining area, and stored indefinitely in lined ponds), 4) reclamation water (from waterbodies such as end pit lakes that may contain reclaimed liquid or solid tailings material that are intended to be integrated with the reclaimed landscape and discharged following treatment to receiving waters such as the Athabasca River), and 5) oil sands process water (water from active tailings facilities. Sample analysis using in-situ and column SGC was completed at Bureau Veritas Laboratories (BV Labs). A capric acid reverse surrogate was added prior to SGC. Capric acid is a fatty acid that should be 100% removed by the SGC and is required as part of the SGC for the British Columbia standard method (BCMECCS 2023).

The analysis using the column SGC method resulted in lower, and more precise hydrocarbon measurements relative to the in-situ SGC method and were typically below detection for a range of OSMWs, including reclamation water and tailings pond water. Recovery of the capric acid reverse surrogate was 0% for all of the analyses with column SGC. Recovery percentages for the analyses with in-situ SGC varied between 1 and 32%.

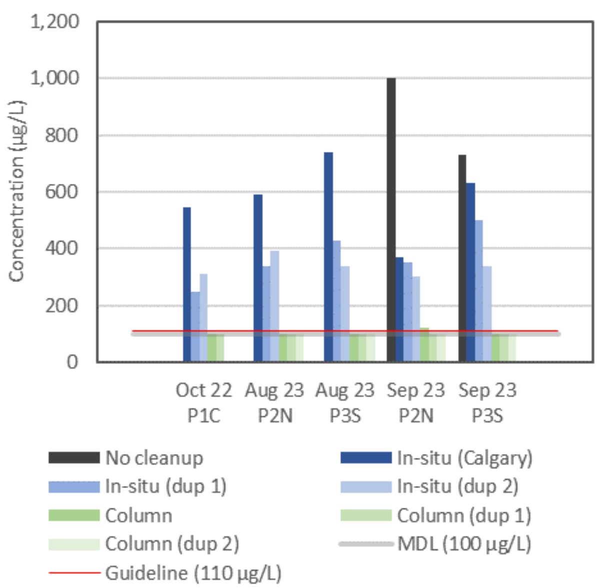

Fig 1. F2 Hydrocarbons measured in samples collected from a reclamation waterbody at three locations over three years. For the samples collected in August 2023, an additional analysis with column SGC was completed shortly after sample collection and was treated as a second duplicate in addition to the full laboratory analysis completed in December. The concentration of naphthenic acids and total organic carbon in these samples were 26 to 31 mg/L and 26 to 36 mg/L, respectively.

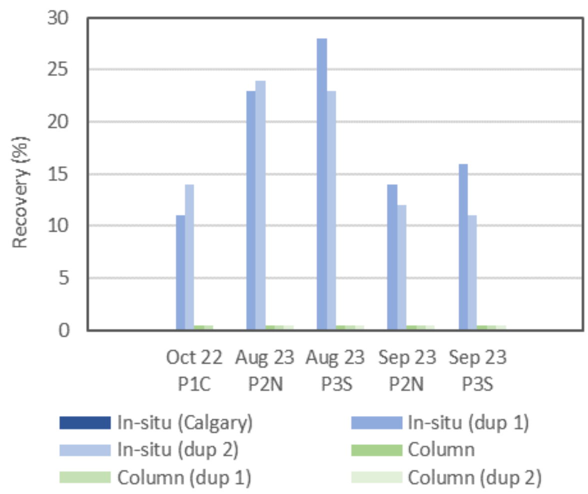

Fig. 2. Capric acid recoveries for samples shown in Figure 1.

LESSONS LEARNED

The study confirmed that The measurement of F2 hydrocarbons in oil sands mine water can be confounded by high levels of polar organic substances has demonstrated that the in-situ SGC is not reliable for the analysis of hydrocarbons in oil sands mine waters, including the historical data collected. Future analysis should use the column SGC with the capric acid reverse surrogate, unless further refinement of the in-situ SGC method is undertaken to improve performance and define performance measures.

Dissolved organic material in OSMWs, including naphthenic acids, has been studied extensively. The challenges with measurement, interpretation, and assessment are similar for naphthenic acids and petroleum hydrocarbons: there are a myriad of approaches to measurement that are mostly not available in commercial laboratories, the chemical species measured are very broad, and there is a poor correspondence between concentration and toxic effects. Because of these limitations, direct measurement of toxicity using whole-effluent toxicity testing may be a more suitable measure to support regulation of OSMW release than either petroleum hydro-carbons or naphthenic acids, consistent with applicable guidance (AEP 1995,1996; CCME 2003).

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Zemo, D.A., K.A. Synowiec, R.I. Magaw, and R.E. Mohler. 2013. Comparison of shake and column silica gel cleanup methods for groundwater extracts to be analyzed for TPHd/DRO. Groundwater Monitoring & Remediation 33(4): 108–112.

PRESENTATIONS AND PUBLICATIONS

Conferences, presentations, and workshops:

Rosner, T.D. 2023. Petroleum Hydrocarbons in Oil Sands Mine Waters. 2023 COSIA Mine Water Management Science Workshop. Edmonton, Canada.

RESEARCH TEAM AND COLLABORATORS

Institution: Four Elements Consulting Ltd.

Principal Investigator: Tammy Rosner, Aquatic Ecologist

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Heather L. Lord	Environmental Standards Inc.	Forensic Chemist		

WE0087 - Scientific basis for acute mixing zone

COSIA Project Number: WE0087

Research Provider: Four Elements Consulting Ltd.

Industry Champion: COSIA Water Mining Subcommittee

Industry Collaborators: Canadian Natural, Imperial Oil Resources Ltd., Suncor Energy Inc., Syncrude Canada Ltd.

Status: Ongoing

PROJECT SUMMARY

The scope of work for this project includes an analysis of cases in Albertan other jurisdictions where effluent concentrations or effluent limits are greater than either acute guidelines or chronic guidelines, based on this analysis describing the scientific justification for acute mixing zones for the substances in Oil Sands Mine Waters (OSMW) that could potentially exceed Alberta's acute guidelines for the protection of aquatic life, which are dissolved aluminum, dissolved iron, chloride, and CCME F2 hydrocarbons. CCME F2 hydrocarbons was removed from the analysis based on a parallel study that found that the measured concentrations in OSMWs were erroneous.

In addition to describing the justification for the use of acute mixing zones for treated OSMW releases, a more general analysis of the use of mixing zones was included in the study to address broader concerns with mixing zone policy.

Note: Alberta Environment and Protected Areas (AEPA) guidance on the use of mixing zones comes primarily from the Water Quality Based Effluent Limits Procedures Manual (WQBELs procedures manual; AEP 1995).

PROGRESS AND ACHIEVEMENTS

Information was compiled to support ongoing discussion of mixing zone policy, and an evaluation of the use of acute and chronic mixing zones was also completed. For both analyses, information from other jurisdictions and specific examples of policy implementation in Alberta was used as a point of reference. The work included an evaluation of justification for acute and chronic mixing zones for OSMWs and an evaluation of the existing Alberta guidance in relation to guidance from other jurisdictions and existing Alberta authorizations for water release.

LESSONS LEARNED

Analysis and Examples of Existing Alberta Release Water Quality and Effluent Limits

Alberta EPEA approvals do not explicitly authorize either acute or chronic mixing zones; however, authorization can be inferred for cases where treated effluent concentrations or effluent limits are greater than guidelines or other effects thresholds or when acute or chronic toxicity is observed based on whole-effluent toxicity testing.

The report includes many examples of releases in Alberta where effluent concentrations or effluent limits are greater than either acute guidelines or chronic guidelines, including chronic guidelines for inherently toxic or bioaccumulative constituents such as selenium, mercury, lead, and arsenic. Regulations under the Canadian Fisheries Act, which apply to Alberta releases in the mining, pulp and paper, and municipal sectors, include effluent limits that exceed acute guidelines for total suspended solids, copper, lead, nickel, and zinc and chronic guidelines for arsenic, lead, and selenium. Additionally, regulations under the Fisheries Act required 50% or greater survival for the rainbow trout and Daphnia magna bioassays, whereas Alberta acute guideline for whole effluent toxicity is 0.3 toxic units (i.e, 30% of the percent release water corresponding to the lethal concentration to 50 percent of the organisms is 100% effluent, then the corresponding acute guideline is 30% release water), which is equivalent to less than 1% mortality in 100% effluent. Historically, mining effluents in Canada have exceeded acute guidelines for ammonia, chloride, copper, nickel, zinc, and cyanide, as well as chronic guidelines for arsenic, lead, and selenium.

Examples: Municipal and industrial releases on the Athabasca River, upstream of Fort McMurray and on the North Saskatchewan River near Edmonton exceed acute guidelines for ammonia, total suspended solids, nitrate, dissolved aluminum, copper, lead, nickel, mercury, and zinc. EPEA approvals typically require 50% or greater survival for the rainbow trout bioassay, although some EPEA approvals require actions such as toxicity identification studies if survival is less than 90%. Most EPEA approvals do not have survival requirements for Daphnia magna or other bioassays.

Application to OSPW

Substances in the OSMW profiles that could potentially exceed Alberta's acute guidelines for the protection of aquatic life are–dissolved aluminum, dissolved iron, and chloride. Considerations specific to these constituents are as follows:

- Effluents and surface waters frequently exceed acute guidelines for dissolved iron and aluminum without adverse effects.

- The concentrations of dissolved aluminum and dissolved iron in OSMW are lower than concentrations in the Athabasca River.
- The report summarizes previous studies which show that the treatment of chloride in OSMWs is neither economically feasible nor desirable from an environmental perspective. Extensive analysis has shown that release of OSMW with chloride concentrations above the acute guideline would not result in lethality to passing organisms or other adverse effects on the Athabasca River.

Comparison to Other Jurisdictions

Alberta's current policies for the use of both acute and chronic mixing zones and the implementation of those policies in the authorizations for existing releases are consistent with those of other jurisdictions. All jurisdictions require that there be no lethality to passing organisms and that mixing zones are not used as an alternative to reasonable and practical treatment. Additionally, best practices for outfall site selection and design implemented in other jurisdictions are similar to those implemented in Alberta, such as: selecting sites and designing outfalls to maximize near-field mixing, including setbacks from secondary channels and riparian areas, and assessing potential changes in sediment quality.

Although the Alberta policy related to water release and to mixing zones is equivalent to other jurisdictions, there are some limitations of the existing Alberta framework related to documentation. Guidance for some jurisdictions provide more detailed information on mixing zone restrictions and best practices for outfall siting and design.

In Alberta, best practices have not been formally documented and have not always been implemented consistently by engineers responsible for outfall design. Outfall site selection is one of the most important factors that can minimize potential effects by enhancing mixing in the near-field and before interaction with the riverbed, banks, secondary channels, and flooded riparian areas. There are examples where best practices related to outfall design have not been implemented in Alberta and have had serious economic and environmental consequences.

Additionally, there has been a lack of consensus about certain elements of the WQBELs manual. The Alberta framework would benefit from additional clarity related to the use of mixing zones and the definition of "adequate justification." A proposed list of criteria that would constitute adequate justification is provided in the final section.

Comparison to the Lower Athabasca Region Tailings Management Framework

Specific to OSMWs, the Lower Athabasca Region Tailings Management Framework for the Mineable Athabasca Oil Sands (GOA 2015) outlines requirements similar to anticipated requirements under EPEA. For example, it requires that all other options be evaluated based on net environmental effects prior to release, that technology-based effluent limits be developed, and that a comprehensive evaluation of potential ecosystem and human health risks be undertaken.

Justification for Release and Use of Acute and Chronic Mixing Zones

Adequate justification for the authorization of both acute and chronic mixing zones is required under the WQBELs procedures manual. The difference between the two cases is that for the acute mixing zone, compliance with the rule of thumb mixing zone restrictions must be demonstrated, whereas, with chronic guidelines, spatial restrictions can be used as an alternative.

Adequate justification for release, including the use of acute and chronic mixing zones, could reasonably be expected to require demonstrating the following key components:

- The release was part of an optimized water management strategy and is required for ongoing operations and to meet reclamation objectives. The need for release has been established and documented in life-of-mine closure plans. Whether release occurs during operations or at closure would be determined based on site-specific water management plan and associated net environmental effects evaluation.
- The release would meet technology-based effluent limits, and mixing zones were not used as an alternative to reasonable and practical treatment. Operators have committed to meeting technology-based effluent limits, which are currently under development by AEPA.
- The release would not result in human health effects or unacceptable effects on aquatic life, and a monitoring program would be implemented for confirmation. Recent studies have been completed that support this assessment for a hypothetical OSMW release. Additional assessment would be completed for each individual release as part of a regulatory application.
- The release would not result in acute lethality to passing organisms. This has been demonstrated based on a comprehensive modelling analysis described in a previous study.
- The release would meet the additional "rule of thumb" mixing zone restrictions described in the WQBELs manual as well as comparable criteria identified in other jurisdictions. These were evaluated as part of the mixing zone evaluation in this study.

- The outfall site selection and design were based on best practices currently used for comparable releases in Alberta. These were evaluated as part of the mixing zone evaluation in this study.

References

AEP (Alberta Environmental Protection). 1995. Water Quality Based Effluent Limits Procedures Manual. Environmental Protection. Edmonton. Available at: http://environment.alberta.ca/01216.html

PRESENTATIONS AND PUBLICATIONS

A draft report is currently under review.

RESEARCH TEAM AND COLLABORATORS

Institution: Four Elements Consulting Ltd.

Principal Investigator: Tammy Rosner

WJ0116 - Development of Microbial Fuel Cell Biosensor for Detection of Naphthenic Acids

COSIA Project Number: WJ0116

Research Provider: University of Alberta

Industry Champion: Imperial Oil Resources Ltd.

Industry Collaborators: None

Status: In progress

PROJECT SUMMARY

Naphthenic acids (NAs) contribute to the toxicity and endocrine-disrupting potential in oil sands process-water (OSPW) generated from mining operations in northern Alberta. There is a growing concern over the intrusion of NAs into surrounding aquatic ecosystems and subsequent adverse impacts on the environment. Therefore, monitoring NAs in water samples from tailing ponds, nearby groundwater wells, and surrounding surface water is critical to environmental monitoring by oil sands companies. Analytical tools commonly used for measurements of NAs include Fourier transform infrared (FTIR) spectroscopy, gas chromatography-mass spectrometry (GC-MS), and high-performance liquid chromatography (HPLC). However, analysis of NAs with these methods is time-consuming and expensive, and samples need to be sent to an analytical laboratory. Developing a low-cost and fast analytical method for on-site quantification and/or in-situ monitoring of NAs will help address these challenges.

Dr. Dhar's research lab at the University of Alberta has been developing a microbial electrochemical biosensor for in situ detection and quantification of NAs in OSPW samples. Microbial electrochemical biosensors use electroactive bacterial biofilms as biosensing elements to generate an electrical signal in response to an analyte, which can be a target environmental contaminant. This electrical signal can be correlated with the concentration of the target analyte. These biosensors can offer a viable method for measuring concentrations of NAs in OSPW. Biosensors can be also integrated into engineered remediation systems, such as constructed treatment wetlands and end pit lakes, for in-situ monitoring of NAs.

The project's key goals and timelines are as follows:

- Conducting proof-of-concept tests with model NAs (2017-2018, completed)
- Studying the impact of various environmental parameters (e.g. salinity, temperature, and petroleum hydrocarbon compounds) on the biosensor's response with model NA compounds (2018-2020, completed)
- Development of a more precise calibration method with commercial NAs (2020-2021, completed)
- Exploring the biosensor's ability to function as a dual platform for measuring both NA concentrations and their related toxicity (2021, completed)
- Investigating the potential of the microbial electrochemical biosensor as a dual platform for detecting both NA concentrations and their associated toxicity (2021, completed)

- Demonstration of microbial electrochemical biosensor for detecting NA concentrations in real OSPW samples and sensitivity improvement (2022-2023, completed)
- Design optimization toward developing a miniaturized version of the biosensor for field application (2023-present, in progress).
- Developing machine learning (ML) algorithms to analyze biosensor response under the interference of complex water matrices and varying environmental conditions in real OSPW (to be completed).

PROGRESS AND ACHIEVEMENTS

1. Demonstration of microbial electrochemical biosensor with real OSPW sample (2022-2023)

A significant portion of our research last year focused on demonstrating the microbial electrochemical biosensor for detecting NAs concentrations in real OSPW samples. For calibration with different concentrations, OSPW sample was diluted with deionized water to obtain the concentration (by volume) range of 20 per cent – 100 per cent (no dilution). The calibration curves were recorded at different standing periods under closed-circuit (CC) mode followed by charging-discharging (CD) cycles at optimal calibration parameters from our previous experiments (details can be found in our previous reports). Briefly, the calibration procedure involves a standing period under continuous CC operations to achieve stable current production (with less than five per cent variation over time), followed by CD cycles. The CD cycles alternate between open-circuit mode (for electron accumulation) and closed-circuit mode (for rapid discharge of electrons), generating transient peak currents. As shown in Fig. 1a, the average transient peak currents increased proportionally with the charging time up to 15 minutes and plateaued, suggesting that longer charging times did not lead to higher electron accumulation and peak current production. Our previous research indicated that a five-minute charging period was adequate for high current outputs with optimal sensitivity using model NAs and commercial NAs. However, the complex matrix of real OSPW requires a relatively longer charging duration for effective electron accumulation and peak performance. Therefore, a 15-minute charging period was used for further investigations.

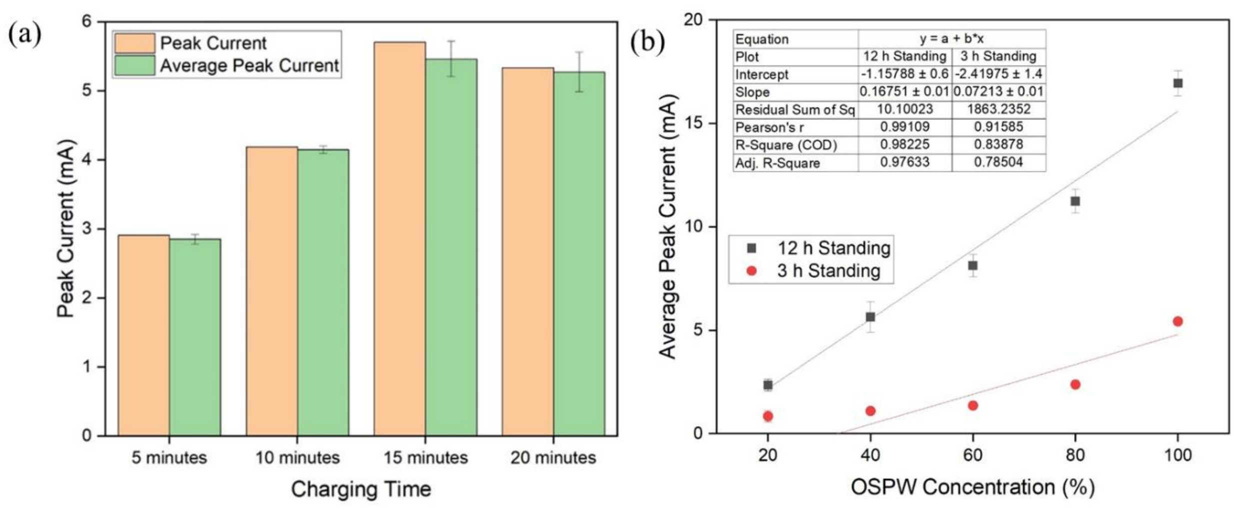


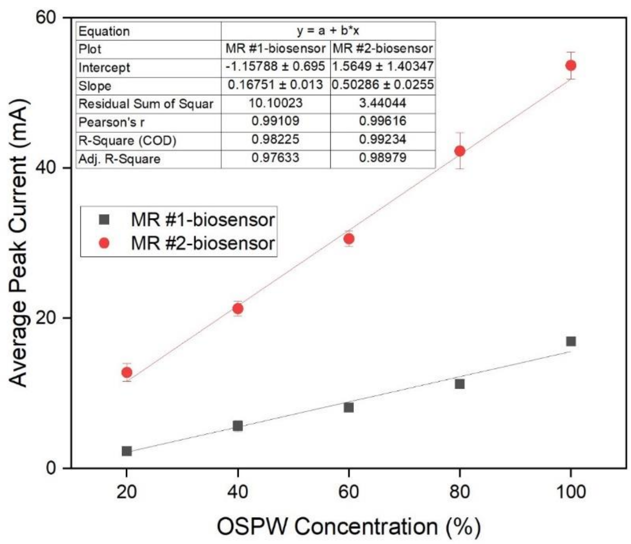
Fig. 1. (a) Peak and average peak currents obtained at different charging times during the CD cycles, and (b) A calibration curve built from two different standing periods (three hours and 12 hours) followed by CD cycles.

In the next stage, the biosensor was calibrated using two different standing periods: three hours and 12 hours. Initial observations showed stable current production for both intervals (Fig. 1b). After continuous CC operation, the biosensor was switched to CD mode to measure transient peak currents. The 12-hour standing period led to increased current responses and enhanced sensitivity, evident from the slope increase from 0.07213 to 0.16751 in the linear equation. This also improved the coefficient of determination (R2) from 0.839 to 0.982, indicating a stronger linear relationship between current output and OSPW concentration. While a longer standing period may extend detection time, it results in better sensitivity and increased current output, justifying the extended timeframe. Consequently, the 12-hour standing period followed by a CD cycle (15-minute charging and 1-minute discharging) was considered as optimum for further experiments.

2. Improving sensitivity with different inoculum sources (2023)

In the next phase, the impact of different inoculum sources was studied using effluents from two distinct mother reactors that were introduced to the biosensor as inoculums. Initially, the biosensor was fed with effluent from a mother microbial electrochemical reactor (MR #1), which had been enriched with mature fine tailings (MFT) from an oil sand tailing ponds in northern Alberta. This effluent also contained a medium with various model NA compounds (cyclohexane carboxylic acids, alkylated cyclopentane carboxylic acids) and OSPW for more than a year, allowing the biosensor to stabilize after inoculation (referred to as MR #1-biosensor, serving as the control for this study). Following this, the calibration curve was established using the previously described method. Subsequently, effluent from another mother microbial electrochemical reactor #2 (MR #2), which had been operating with a 25 mM acetate medium for over 6 years, was used to repopulate the anodic biosensing communities of the same biosensor. For example, the MR #1-biosensor was supplemented with effluent from MR #2, resulting in the MR #2-biosensor (indicating the MR #1-biosensor with the addition of MR #2 effluent). Once a steady state was achieved, a new calibration curve was generated.

Fig. 2 shows the calibration curves from different inoculum sources. The MR #2-biosensor performed better, producing notably higher current outputs compared to the MR #1-biosensor (control). The calibration data for the biosensor with MR #2 effluent showed an increase in current output of 3.8 to 5.4 times higher than that of the biosensor using only MR #1 effluent. Furthermore, the sensitivity of the biosensor improved with the use of MR #2, as evidenced by the rise in slope (m) from 0.16751 to 0.50286, which allowed for more precise detection of OSPW NAs and improved the correlation coefficient (R2) from 0.982 to 0.992.



Equation	y = a + b*x	
Plot	MR #1-biosensor	MR #2-biosensor
Intercept	-1.15788 ± 0.695	1.5649 ± 1.40347
Slope	0.16751 ± 0.013	0.50286 ± 0.0255
Residual Sum of Squar	10.10023	3.44044
Pearson's r	0.99109	0.99616
R-Square (COD)	0.98225	0.99234
Adj. R-Square	0.97633	0.98979

Fig. 2. Calibration curves constructed using two different inoculum sources: MR #1-biosensor, also known as the control, and MR #2-biosensor, known as MR #1-biosensor re-inoculated with MR #2 effluent. Note, the calibration curve was made using average peak currents obtained from CD operations.

LESSONS LEARNED

These results provide the first demonstration of our developed microbial electrochemical biosensor for measuring NA concentrations in real OSPW samples, as well as a further strategy to enhance the performance and sensitivity of the biosensor. The findings suggest the optimal calibration approach for the OSPW biosensor includes a 12-hour standing period followed by a 15-minute charging period within a CD cycle. Using an inoculum sourced from the effluent of a mother reactor running on acetate further improved biosensor's efficiency. The calibration curve derived under different optimized conditions showed high sensitivity, with a high linearity and a steep slope, enabling rapid and practical detection of OSPW NAs using the biosensor. The team is now working towards further development for field-scale applications.

PRESENTATIONS AND PUBLICATIONS

Journal Publications:

Published

Chung, T. H., Dhillon, S.K.; Zakaria, B.S.; Meshref, M. N., & Dhar, B. R. (2024). Detecting naphthenic acids in real oil sands process water with microbial electrochemical sensor: Impact of inoculum sources and quorum sensing autoinducer, under preparation.

Chung, T. H., Zakaria, B.S.; Meshref, M. N., & Dhar, B. R. (2021). Enhancing quorum sensing in biofilm anode to improve biosensing of naphthenic acids, emphasis on aromatic compounds. Biosensors and Bioelectronics, 210, 114275.

Chung, T. H., Meshref, M. N., & Dhar, B. R. (2021). A review and roadmap for developing microbial electrochemical cell-based biosensors for recalcitrant environmental contaminants, emphasis on aromatic compounds. Chemical Engineering Journal, 130245.

Chung, T. H., Meshref, M. N., & Dhar, B. R. (2020). Microbial electrochemical biosensor for rapid detection of naphthenic acid in aqueous solution. Journal of Electroanalytical Chemistry, 873, 114405.

Conferences, presentations, and workshops:

Chung, T.; Zakaria, B.S.; Dhar, B.R. (2019). Development of microbial electrochemical cell as a rapid biosensor for the detection of naphthenic acids, 11th Western Canadian Symposium on Water Quality Research, May 10, Edmonton, AB, Canada.

Chung, T.; Zakaria, B.S.; Dhar, B.R. (2019). Calibration of bio-electrochemical naphthenic acids sensor using electrical response from charging-discharging cycles, poster presented in Canada's Oil Sands Innovation Alliance (COSIA) Innovation Summit, June 7-8, Calgary, Alberta.

Barua, S.; Zakaria, B.S.; Dhar, B.R. (2018). Development of a self-powered biosensor for real-time monitoring of naphthenic acids, poster presented in Canada's Oil Sands Innovation Alliance (COSIA) Innovation Summit, June 7-8, Calgary, Alberta.

Barua, S.; Zakaria, B.S.; Dhar, B.R. (2018). Development of bioelectrochemical sensing device for naphthenic acids, poster presented in 53rd Central Canadian Symposium on Water Quality Research, February 22, Toronto, ON, Canada.

RESEARCH TEAM AND COLLABORATORS

Institution: University of Alberta

Principal Investigator: Dr. Bipro Dhar

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Tae Chung	University of Alberta	PHD Student	2021	2025
Dr. Basem Zakaria	University of Alberta	Postdoctoral fellow	2022	2023
Dr. Simran Kaur Dhillon	University of Alberta	Postdoctoral fellow	2023	2025

WJ0182 - Using BE-SPME Passive Samplers for Ecological Hazard Assessment of Oil Sands Process-Affected Water

COSIA Project Number: WJ0182

Research Provider: Meta Analytical Inc.

Industry Champion: Imperial Oil Resources Ltd.

Industry Collaborators: Canadian Natural, Syncrude Canada Ltd.

Status: Ongoing

PROJECT SUMMARY

Oil sands process-affected water (OSPW) is typically comprised of a complex mixture of organic and inorganic constituents generated during the bitumen extraction process used in the oil sands industry. Currently oil sands operations utilize large, on-site tailings ponds for storage OSPW, with over 92.7km2 being used to hold process water for recycling and reuse. Recent work by Redman et al. (2018) demonstrates that bio-mimetic solid phase microextraction (BE-SPME) based passive samplers may be useful tools for hazard assessment of OSPW, as these devices can effectively provide a surrogate measure of dissolved organic contaminant residues that can cause adverse effects in aquatic organisms. Before this approach can be deployed under the Oil Sands Monitoring (OSM) program or for end-of-pipe testing of treated OSPW, additional laboratory and field-based studies are required to establish effectiveness of the passive samplers. Figure 1 shows a schematic illustration of scope of the current project. The current project is part of a larger overall research program involving development and testing of BE-SPME passive samplers for hazard assessment of petroleum-derived dissolved organic chemicals (phase I-III) reported in the 2020 Water Mining Research Summary. The overall goal of this research is to demonstrate the efficacy of SPME-based passive samplers for robust, cost-effective hazard assessment of OSPW. The primary objectives for the present work on BE-SPME passive samplers for hazard assessment of OSPW (phase IV) include:

- using BE-SPME passive samplers to assess chronic effects of OSPW-derived dissolved organic chemicals in early life-stage fish, including rainbow trout (Oncorhynchus mykiss) and fathead minnow (Pimephales promelas).
- using BE-SPME passive samplers to assess chronic effects of OSPW-derived dissolved organic chemicals in early life-stage amphibians, i.e., wood frog embryos (Lithobates sylvaticus).
- comparing observed concentration-response relationships for chronic exposure in early life stage fish (rainbow trout) and amphibians (wood frogs) to previous results and evaluate species-sensitivity distributions.
- comparing to BE-SPME data, using high-resolution mass spectrometry (Orbitrap-MS) to measure speciated and total naphthenic acid (NA) concentrations in operational OSPW, treated OSPW and surface water samples for comparison to BE-SPME data,
- usingy BE-SPME passive samplers for hazard assessment of different operational OSPW, treated OSPW and receiving waters within the Lower Athabasca River watershed.

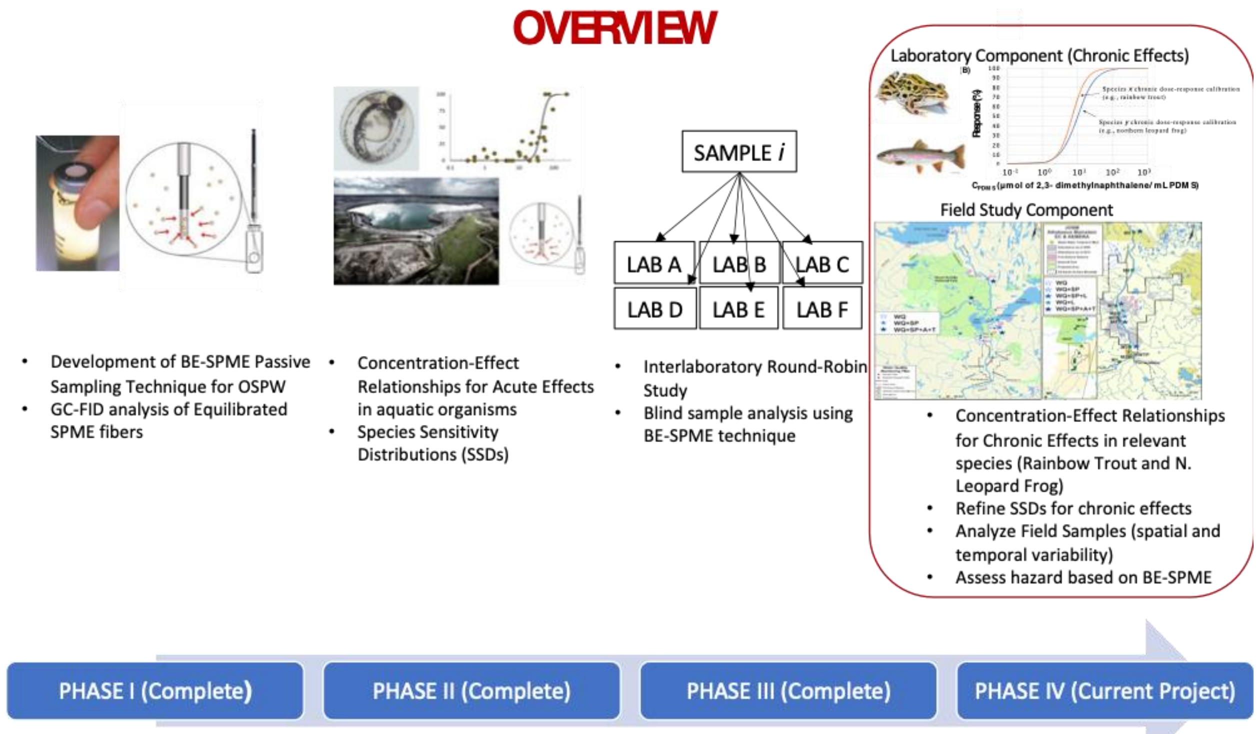


Figure 1. Schematic illustration of the scope of the current project (phase IV), as well as phases related to BE-SPME development and testing and interlaboratory comparison studies (phase I-III).

PROGRESS AND ACHIEVEMENTS

Sample Collections

In 2021, we collected three one m^3 totes of operational OSPW acquired from an oil sand operator (2021 OSPW), as well as 40-litre samples of constructed wetland influent and effluent (Day 0 and Day 15 temporal sampling at Kearl Treatment Wetland). We also collected several samples of surface water from existing oil sands monitoring sites (Athabasca River and Muskeg River surface water). These field samples consisted of two-litre grab samples collected during the months of June and October 2021. We used three sampling sites (corresponding to existing OSM sites), including one upstream of Fort McMurray and two sites near Fort McKay. Triplicate samples were taken at each site.

In 2022, we collected four one m^3 totes of operational OSPW acquired from an oil sand operator (2022 OSPW), as well as 40-litre samples of constructed wetland influent and effluent (Day 0 and Day 15 temporal sampling at Kearl Treatment Wetland). During this period, we also collected 300 litres of “aged OSPW,” which consisted of OSPW aged in a two-year old mesocosm experiment at the InnoTech Mesocosm facility in Vegreville, AB. Field surface water samples were collected from the Athabasca River and Muskeg River sites, comprised of two-litre grab samples collected in June and October 2022.

In 2023, we received samples of several water samples from another oil sand operator. Samples provided included one pit lake, three tailings ponds, three reclaimed wetlands and one freshwater reservoir. During this period, we also collected samples of advanced oxidation treated OSPW. Samples were submitted for

BE-SPME and total NA (Orbitrap-MS) analysis at InnoTech Alberta. Samples results are not shown as these samples are currently awaiting processing and analysis.

Chemical Analyses

For the current project, operational OSPW, treated OSPW and surface water samples are analyzed for the total bioavailable dissolved organics using the developed BE-SPME method and speciated naphthenic acid (NA) concentrations using high-resolution mass spectrometry (Orbitrap-MS). Specific samples analyzed included operational OSPW (2021 OSPW and 2022 OSPW totes), treated wetland influent and effluent (Kearl Treatment Wetland in 2021 and 2022), and surface water samples collected from Athabasca and Muskeg River. Table 1 shows the observed BE-SPME and total NA concentrations measured in these various samples.

Figure 2 shows the relationship between measured BE-SPME concentrations and total Naphthenic Acid concentrations measured via Orbitrap-MS for analyzed samples of operational OSPW and diluted operational OSPW used in exposure experiments.

Table 1. Results of BE-SPME measurements, total naphthenic acid (NAs) concentrations, pH, total dissolved solids (TDS), and total hardness in 2021 and 2022 operational OSPW, closed-loop treatment wetland, aged OSPW (two-year phytoremediation trial) and the Athabasca River watershed.

	2021					2022				
	BE-SPME (mM)	Total NAs (µg/L)	pH	TDS (mg/L)	Hardness (mg/L CaCO3)	BE-SPME (mM)	Total NAs (µg/L)	pH	TDS (mg/L)	Hardness (mg/L CaCO3)
OSPW [a]										
1% OSPW	-	-	8 ± 0.02	-	-	0.6	249	7.2 ± 0.0	-	-
2.2% OSPW	4.7 ± 1	369	8 ± 0.02	-	-	2.3	468	7.2 ± 0.02	-	-
4.6% OSPW	8.9 ± 1.9	807	8 ± 0.03	-	-	3.8	976	7.2 ± 0.02	-	-
10% OSPW	20.6 ± 4.5	1,910 ± 55.1	8 ± 0.02	-	-	8 ± 0.7	1,820	7.4 ± 0.02	-	-
22% OSPW	42.9 ± 16.2	5,220 ± 318	8.2 ± 0.02	-	-	16.3	4,170	7.7 ± 0.03	-	-
46% OSPW	81.7 ± 8.6	11, 000 ± 603	8.4 ± 0.05	-	-	33.9 ± 3.7	7,510	8.1 ± 0.05	-	-
100% OSPW	112 ± 7.3	15,300 ± 1,000	8.6 ± 0.06	808	227	60.7 ± 11.3	11,500 ± 439	8.3 ± 0.06	902	204
Aged/Treated OSPW										
Aged OSPW (2-year Mesocosm) [b]	-	-	-	-	-	34.2	6,870	8.5 ± 0.07	736	126
Constructed Wetland (Day 0) [c]	47.2	19,600	8.5 ± 0.07	848	240	50	12,200	8.4 ± 0.08	954	227
Constructed Wetland (Day 15) [c]	42.8	9,100	8.6 ± 0.09	810	302	46.3	9,480	8.5 ± 0.08	1,020	333
Athabasca River Watershed (Surface Water)										
Athabasca River [d]	N.D	8.6 ± 0.4	7.9 ± 0.07	202	133	N.D	12.3 ± 6.3	-	-	-
Muskeg River [d]	N.D	9.5 ± 1.9	-	-	-	N.D	17.1 ± 1.9	-	-	-

[a] Operational OSPW (i.e., 100 per cent OSPW) was obtained in 2021 and 2022. [b] Aged OSPW consisted of water from a small pond mesocosm involving OSPW at InnoTech Alberta. [c] Water was obtained in 2021 and 2022 from the Kearl closed-loop constructed wetland tests designed to study passive treatment of OSPW. [d] Field-collected surface water from existing monitoring sites. Coordinates for Athabasca River and Muskeg River sites were 57°08'09" N 111°36 '32"W and 57°07'59" N 111°36 '14"W, respectively.

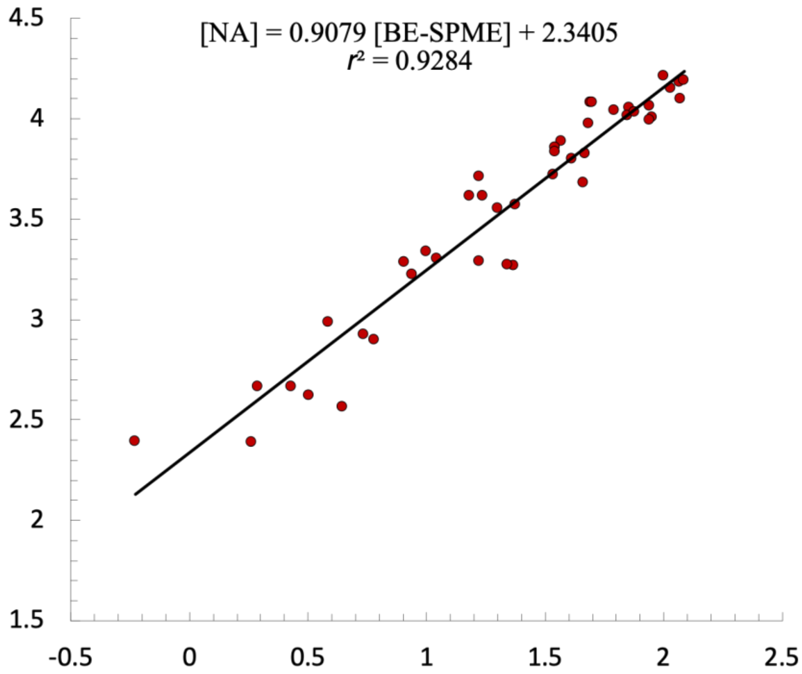


Figure 2: Relationship between measured BE-SPME (mM 2,3 dimethylnaphthalene equivalent) via GC-FID and total Naphthenic acids (ug/L) via high resolution Orbitrap mass spectrometry. Results from all analyses of 2021 and 2022 OSPW samples (n=47).

Chronic Toxicity Studies with Early Life-Stage Fish

We completed thirty-day chronic early life-stage toxicity experiments with rainbow trout (*Oncorhynchus mykiss*) using with 2021 and 2022 operational OSPW/diluted operational OSPW (100 per cent, 46 per cent, 22 per cent, 10 per cent, 4.6 per cent, 2.2 per cent, one per cent, Controls). We also completed exposure experiments involving treated and aged OSPW, including Kearl treatment wetland water and aged OSPW from a two-year mesocosm study.

For operational OSPW, the estimated LC50s for BE-SPME in 2021 and 2022 were 22.9 and 20.7 mM, respectively. The estimated LC50s for Total NAs in 2021 and 2022 were 2,290 and 3,390 µg/L, respectively. The lowest observable effect concentration (LOEC) related growth effects and deformities ranged between approximately 10 to 20 mM for BE-SPME and 1,000 to 2,000 µg/L total NAs. The observed dose-response relationship curves for rainbow trout chronic OSPW exposure is comparable to those previously reported for shorter-term/acute assays using different species. Significant total deformities observed from 10 per cent operational OSPW in 2021 and from 22 per cent operational OSPW in 2022, but not at lower concentrations.

OSPW treatment via a closed-loop constructed wetland system and via a two-year phytoremediation mesocosm (aged OSPW) significantly reduced mortality and deformities. Compared to high mortality observed in constructed wetland influent (Day 0 water), no significant mortality was observed in treated constructed wetland effluent (Day 15 water) in 2021 and 2022. Constructed wetland effluent (Day 15 water) only exhibited significant difference in craniofacial deformities in 2021.

To investigate species-sensitivity differences in chronic effects related to operational OSPW exposure, we completed an additional 14-day chronic toxicity assay using fathead minnow (*Pimephales promelas*). Exposure experiments were conducted by Nautilus Environmental and included assessment of two toxicological endpoints (survival and growth), at seven concentration levels (100 per cent, 50 per cent, 25 per cent, 12.5 per cent, 6.25 per cent, 3.12 per cent and 1.6 per cent OSPW). The results showed that no adverse effects on survival of *P. promelas* was observed over the 14-day exposure period. There was an observed adverse effect on growth (biomass) of *P. promelas* over the 14-day exposure period, with an inhibition concentration (IC25). It is estimated to cause a 25 per cent reduction in biomass, occurring at the 75.7 per cent OSPW concentration level. This effect level corresponds to an BE-SPME and total NA concentration of 78 mM and 13,400 ug/L, respectively. These results suggest that *P. promelas* is much less sensitive to effects associated with dissolved organic contaminants in OSPW compared to rainbow trout.

Chronic Toxicity Studies with Early Life Stage Amphibians

We collected egg masses of wild spawning wood frogs **(***Lithobates sylvaticus***)** during spring 2022 in northern Alberta. Using the collected embryos, we conducted a 96-day chronic toxicity assay following OECD Larval Amphibian Growth and Development Assay (LAGDA). Experiments involved exposure to operational OSPW/diluted operational OSPW (80 per cent, 46 per cent, 22 per cent, 10 per cent, 4.6 per cent, 2.2 per cent, one per cent, Controls).

Significant mortality of wood frogs that survived until metamorphosis was observed only in the 80 per cent operational OSPW after 20 to 40 days (Figure 3a). Exposures of wood frogs to 40 and 80 per cent operational OSPW treatments exhibited delayed development of wood frogs in time to metamorphosis with respect to its corresponding hard water control (Figure 3b). Time to hatch was unaffected by OSPW. Frogs at metamorphosis exhibited a higher incidence of severe scoliosis (skeletal deformities) at 20 per cent compared to all other treatments and the control.

The LC50 for the tested operational OSPW in wood frogs was 96.2 BE units (2,3 mM dimethylnaphthalene equivalent), equivalent to a total Orbitrap-MS Total NA concentration of 10.2 mg/L. The apparent LC50 for wood frogs (96.2 BE mM) is higher than the LC50 for early life stage rainbow trout (20 mM). The lowest observable effect concentration (LOEC) related to skeletal deformities was 19.9 mM 2,3, dimethylnaphthalene, equivalent to a total Orbitrap-MS NA concentration of 3.6 mg/L. The apparent LOEC for chronic operational OSPW exposure in early life stage wood frogs is comparable to previously reported threshold effect levels in aquatic organisms (average EC50 values of~ 10 mM), Redman et al. (2018). The results provide important information regarding chronic effects of OSPW in early life stage wood frogs and application of BE-SPME for hazard assessment.

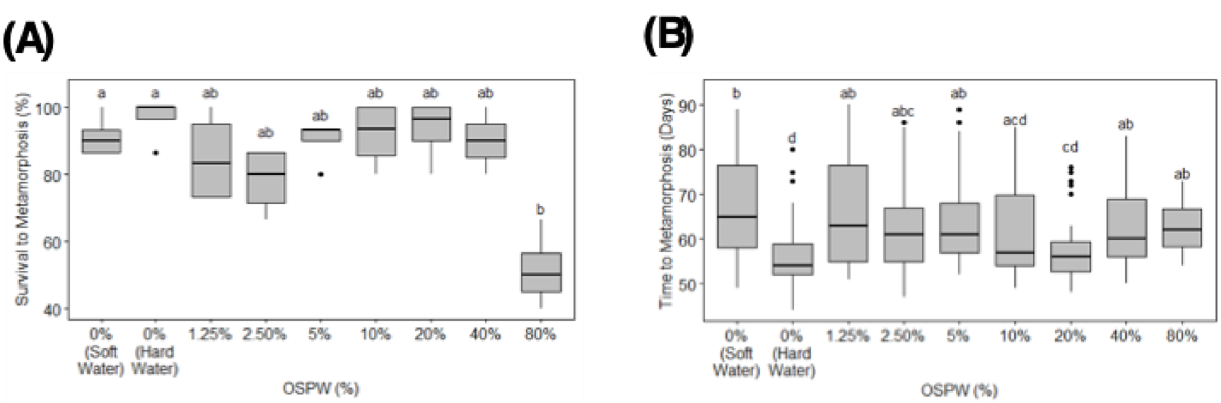


Figure 3: (A) Per cent of early life-stage wood frogs that survived until metamorphosis (Kruskal-Wallis chi squared = 18.1, df = 8, p-value = 0.02, followed by a Dunn's Test for pairwise comparison). (B) Time to metamorphosis in days from the start of the exposure (Kruskal-Wallis chi squared = 37.4, df = 8, p < 0.01, followed by a Dunn's Test for pairwise comparison). Thick horizontal lines represent median values, and the surrounding box represent the lower and upper 25th and 75th percentiles and dotted lines depict the minimum and maximum values with the outliers as

black circles. The replicates for each treatment were as follows: soft water control n=8; hard water and all OSPW treatments n=4. Different letters indicate significant differences between treatment groups.

LESSONS LEARNED

There were several key findings and lessons learned from work conducted during this reporting period. One key finding was we observed a strong positive correlation between measured BE-SPME concentrations via GC-FID and measured total naphthenic acid concentrations via high resolution Orbitrap-MS. This indicates the BE-SPME method is correctly measuring the target dissolved organic compounds in operational OSPW/treated OSPW samples. This is important as a major goal of the developed BE-SPME approach is to provide a simple cost-effective surrogate measure of the potentially toxic dissolved organic substances (i.e., NAs) in OSPW and treated OSPW.

Another key finding from the work completed during this reporting period is the observed concentration-response relationship for rainbow trout chronic operational OSPW exposure was comparable to results previously reported for shorter-term/acute assays using different species. This indicates chronic effect levels are not substantially lower than previously believed, based on the available acute toxicity study results. The BE-SPME based chronic LC50 value observed in the present 30-day exposure studies of rainbow trout (20 mM) is comparable to acute LC50 values observed for short-duration (four-day) operational OSPW exposure in early life-stage zebrafish (Danio rerio), (45.7 mM) and fathead minnow (19.5 mM), (Redman et al. 2018).

Chemical analyses (BE-SPME and speciated NA's) and toxicity testing in treated OSPW (wetland effluent) and aged OSPW showed reduced contamination levels and lower chronic toxicity in early life-stage fish. This is important information, as passive treatment of OSPW via constructed wetlands is viewed as a possible treatment technology for oil sands companies.

There is limited information regarding the toxicity of OSPW in amphibians. The present study provides novel results, which indicate a common amphibian species native to the oil sands region (early life-stage wood frog) is apparently less sensitive to OSPW exposure than early life-stage fish. While low mortality of wood frogs was observed, the data clearly shows exposure to operational OSPW does result in various sublethal effects, including higher incidence of deformities. It is also important to note observations from the wood frog exposure experiments were highly variable, reducing the statistical power to detect significant differences between control and treatment groups. This is common for toxicity experiments using field-collected organisms (wood frog egg masses), due to higher natural variations compared to laboratory-raised test organisms.

Lastly, it is important to note observations of some interlaboratory variability with the BE-SPME measurements. Results of an interlaboratory comparison study for BE-SPME was recently published (Letinski et al., (2022), Environ. Toxicol. Chem. (2022).; https://setac.onlinelibrary.wiley.com/doi/10.1002/etc.5340). The study found relatively high variability between various laboratories analyzing a given OSPW sample. To provide an ongoing assessment of interlaboratory variability in BE-SPME results, we conducted parallel split sample analyses at three laboratories, including InnoTech Alberta, Exxon Mobil and Simon Fraser University. Ongoing accuracy and precision assessments shows high measurement bias. Paired BE-SPME sample analysis indicates BE-SPME results can differ substantially between laboratories, especially for concentrated samples such as raw OSPW, where in some cases, BE-SPME results can differ by up to a factor of two.

Further method standardization is required to limit bias, which will allow pooling of data from different laboratories, comparison of results to existing aquatic toxicity data sets, and the ability to conduct reproducible hazard assessments of waters containing complex petroleum substances. Further collaboration to improve reproducibility across different laboratories will allow for improved accuracy and acceptance of BE-SPME as a routine toxicity screening tool.

Other BE-SPME method parameters currently being investigated include:

1. Differences in instrument calibration protocol using 2,3, dimethylnaphthalene standard.
2. Differences in chromatogram integration and quantification based on 2,3 dimethylnaphthalene calibration curve.
3. Variability associated with the acidification step due to precipitation.
4. Other differences in instrument injector/column/detector behaviour due to types of instruments used by different laboratories or application of the SPME fibre-based method.

We are currently conducting more comprehensive BE-SPME method validation investigations. These involve several participating analytical laboratories and analytical instrument companies.

QA/QC samples are also currently being developed and tested for use as laboratory precision and accuracy related to reporting BE-SPME test method results. Further method validation investigations will provide confidence to a wider group of government, academic and private sector entities to routinely adopt BE-SPME sampling method as a tool for risk.

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Young, R.F., Wismer, W.F., and Fedorak, P.M. 2008. Estimating naphthenic acids concentrations in laboratory-exposed fish and fish from the wild. *Chemosphere 73*: 498–505.

PRESENTATIONS AND PUBLICATIONS

Conferences, presentations, and workshops:

Stenner, K; danis, b.; Bekele, A; Tanna, N.; Drozdowski, B.; Gobas,. Kelly, B.; Marlatt, V. 2022. Toxicity of Oil Sands Process-Affected Water in Early Life Stage Wood frogs (Lithobates sylvaticus). Canadian Ecotoxicity Workshop. Winnipeg, MB, Canada.

Vega, V., Stenner1, K; danis, b.; Bekele, A; Tanna, N.; Drozdowski, B.; Gobas,. Kelly, B.; Marlatt, V. 2022. Chronic Toxicity of Oil Sands Process-Affected Water in Early Life Stage Rainbow Trout (Oncorhynchus mykiss). SETAC North America Annual Meeting. Pittsburgh, PA., USA.

Stenner, K; danis, b.; Bekele, A; Tanna, N.; Drozdowski, B.; Gobas,. Kelly, B.; Marlatt, V. 2022. Chronic Toxicity of Oil Sands Process-Affected Water in Early Life Stage Wood Frogs (Lithobates sylvaticus). SETAC North America Annual Meeting. Pittsburgh, PA., USA.

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RESEARCH TEAM AND COLLABORATORS

Institution: Meta Analytical Inc.

Principal Investigator: Barry C. Kelly

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Dr. Barry Kelly	Meta Analytical Inc.	Research Scientist	-	-
Dr. Frank Gobas	Simon Fraser University	Professor	-	-
Dr. Vicki Marlatt	Simon Fraser University	Professor	-	-
Katelyn Stenner	Simon Fraser University	Masters Student	Sep. 2021	Dec. 2023
Valeria Vega	Simon Fraser University	Masters Student	Sep. 2021	Dec. 2023

PIT LAKES

WJ0091 - Suncor Lake Miwasin Pilot Pit Lake Project

COSIA Project Number: WJ0091

Research Provider: Hatfield Consultants, InnoTech Alberta, University of Alberta, University of Saskatchewan, Athabasca University, and University of Waterloo

Industry Champion: Suncor Energy Inc.

Industry Collaborators: Canadian Natural, Syncrude Canada Ltd.

Status: Year 6 of 6

PROJECT SUMMARY

Lake Miwasin is a scaled-down representation of Suncor's commercial scale pit lake at Dedicated Disposal Area 3 (DDA3, the future Upper Pit Lake (UPL)). It uses the Permanent Aquatic Storage Structure (PASS) process, an inline tailings treatment process of coagulant addition followed by flocculant addition. The goal of the Lake Miwasin pilot project is to monitor and evaluate if the PASS process, when combined with the closure landform design, will lead to a self-sustaining boreal lake ecosystem. Specific objectives of the Research & Monitoring (R&M) Plan are to: (1) test assumptions in the pit lake design; and (2) address critical gaps in the pit lake design. To meet the goal and objectives, research and monitoring activities are planned to take place over a 15-year period (2018-2033).

The Lake Miwasin R&M Plan adopts an Effectiveness Monitoring (EM) design within an adaptive management framework (CEMA 2013). EM is the process of identifying and monitoring key indicators of ecosystem response to evaluate the success of a reclamation initiative or goal. The EM framework is structured on a Goal – Objective – Assumption – Question – Indicator hierarchy. Following the EM design, measurable and obtainable assumptions were selected on the basis of being fundamental to achieving the Lake Miwasin Project goal. Key test questions, hypotheses, and indicators were also identified. The R&M plan identifies three priority monitoring areas to monitor and assess the performance of the Lake Miwasin project: 1) treated tailings deposit; 2) aquatic cover and watershed; and 3) biodiversity. Research questions are identified and grouped into five research priority areas: 1) deposit characteristics; 2) water quality; 3) closure modeling; 4) landform design; and 5) performance trajectories.

The first five-year Lake Miwasin Research and Monitoring program was developed and implemented in 2019 following the overarching R&M Plan. Core monitoring components include water quality, hydrology, hydrogeology (groundwater dynamics and quality), aquatic ecology and biodiversity (including aquatic, riparian and upland vegetation and amphibian communities), air quality, and tailings. The current research programs comprise four studies led by multiple principal investigators and carried out by four universities, focusing on watershed hydrology, long-term fate and transport of CoPCs (e.g. trace elements and organic compounds), and ecotoxicity. An integrated Lake Miwasin modeling program was initiated end of 2019 and is currently ongoing.

The Lake Miwasin pilot project is expected to have four operational and reclamation phases:

- Phase 1: Dewatering and treatment of Fluid Tailings (FT) (Q3 2017 to Q3 2018)
- Phase 2: Placement of the aquatic cover (Q3 2018)

- Phase 3: Controlled water flow through and release (~2019 to current)
- Phase 4: Water release under natural flow (location and timing to be determined)

PROGRESS AND ACHIEVEMENTS

The Lake Miwasin project completed Phases 1 and 2 operations by October 2018 and is currently in Phase 3. The first five-year phase of the R&M program started in March 2019 and continued through 2023. The Lake Miwasin pilot project has provided a comprehensive dataset and insights on the development of the pit lake ecosystem and the performance of the pilot-scale reclamation design. Key results and findings are detailed below:

- The PASS process accelerates tailings dewatering and improves expressed water quality, and thus creates a DDA favorable for aquatic closure. The treated fluid tailings (FT) in Lake Miwasin dewatered at rates that met the PASS technology performance expectations and achieved 90 per cent settlement as a result of consolidation. Mudline settles at much lower rates (i.e. ~0.1 m in 2023) after rapid initial settlement (~2.2m in the first 5 months after initial deposition). Monitoring results showed low turbidity and total suspended solids (TSS) in the water cap throughout the monitoring years, indicating no tailings re-suspension.

- In a longer-term context, the dominant components of the water budget have consistently been inflow, outflow, lake evaporation, and rainfall on the lake. Uncertainties in the calculated water budget tend to be greatest during freshet, when ice effects may affect measured inflows and outflows.

- Lake Miwasin maintains its lake level, even in dry conditions, as inflow from spring freshet has nearly replenished the lake level in all years and losses have remained consistent following this point every year. A regional analysis also revealed the declines in lake level observed at Lake Miwasin between 2021 to 2023 are not uncommon for the region.

- Snow continues to be a significant source of hydrologic input to the Lake Miwasin watershed. Inputs from spring freshet were sufficient to recover the lake levels back to full capacity under varying climate conditions (both following a wet and dry year). Lake contribution magnitude and timing of snowmelt are highly dependent on snowfall amounts and antecedent moisture conditions, especially of the preceding fall. Frozen soil dynamics also affect infiltration, generally encouraging more runoff at the start of the melt period from surficial ice, with the slightly deeper frozen water table from the previous fall determining infiltration capacity of the thawing soil. Snow accumulation is controlled by wind redistribution, with accumulation concentrating in the low-lying vegetated areas (swale and opportunistic wetlands) with minimal accumulation across the rest of the upland. While ongoing vegetation growth will likely help with snow accumulation in other areas, encouraging more of the quick growing pockets throughout the upland would be beneficial.

- Understanding of the physical dynamics of the lake continues to develop. The lake experiences typical patterns of stratification and mixing. The primary controls on water density in Lake Miwasin were temperature rather than total dissolved solids (TDS). Water temperatures in the shallowest three metres responded to periodic precipitation events and wind-generated mixing during the stratified period.

- Like regional natural lakes, near-bottom dissolved oxygen in Lake Miwasin declined to hypoxic levels over winter. Lake Miwasin showed elevated dissolved oxygen conditions in the hypolimnion in the early open-water season of 2022 and 2023, which was likely related to photosynthetic oxygen production. Unlike 2022, the bottom waters did not become anoxic in the open water season.

- Annual sedimentation rates on the lake bottom were ~2 mm. Sampled particle size was typically clay to fine silt and total carbon averaged 4.7 per cent and was mostly composed of organic carbon.
- Concentrations of major nutrients and chlorophyll *a* indicate a low to moderate ("oligo-mesotrophic") level of aquatic productivity in Lake Miwasin.
- Dominant major ions were sodium, calcium, magnesium, bicarbonate, chloride, and sulphate with a mean concentration of TDS of 1,125 mg/L. Concentrations of these major ions show a variety of trends:
    - Sodium, bicarbonate, and chloride concentrations decreased during the first two years of Phase I (i.e., 2019 and 2020) and then were fairly stable;
    - Magnesium and sulphate concentrations increased during the program; and
    - Calcium increased early in the Phase I and then subsequently decreased.
- Surface water quality meets most guidelines for the protection of aquatic life with a few exceptions. Water column mass balances of most ions, metals, and organic compounds decreased during Phase I, with the notable exceptions for sulphate, magnesium, dissolved organic carbon, and zinc. Concentrations of most metals continue to decrease. Several organic compounds typically associated with oil sands process waters were measurable in Lake Miwasin, including naphthenic acids and some heavier hydrocarbon compounds. Most volatile organics, phenolic congeners, and PAH species generally were less than their respective analytical detection limits.
- Lake Miwasin water was not toxic to phytoplankton, invertebrates, or fish in laboratory tests, but remains distinct in its chemistry from regional reference lakes.
- No groundwater interaction with the Wood Creek Sand Channel (WCSC) aquifer has been observed.
- Key components of the terrestrial and aquatic ecology are established in the lake and its watershed. The vegetation community continues to develop, consistent with our understanding of reclaimed terrestrial plant communities.
- The aquatic food web in Lake Miwasin is composed of typical boreal organisms, including multiple groups of phytoplankton, zooplankton, and benthic invertebrates. Key findings include:
    - Phytoplankton and aquatic plants are the primary producers in Lake Miwasin, and their growth follows expected patterns during the growing season.
    - Zooplankton and benthic invertebrates are found throughout in the water column and sediments of the Lake, with substantially higher abundances of benthic invertebrates in the constructed littoral zone.
- There is suitable breeding habitat for three amphibian species: the Canadian toad (a species of provincial concern), wood frog, and boreal chorus frog, all of which were detected.

LESSONS LEARNED

Lake Miwasin is still in an early stage for pit lake development as 2023 was only the sixth year after its construction (including the completion of tailings treatment and the water cap placement). The R&M program to date has provided an extensive dataset and insights to achieve the goal and objectives. Monitoring data and results indicate tailings performance met the expectations of the PASS technology at Lake Miwasin and it is on trajectory towards a functioning boreal lake ecosystem. The PASS process, as demonstrated at the pilot scale, accelerates tailings dewatering and improves expressed water quality, and thus creates a treated FT deposit and DDA favorable for an aquatic closure outcome. The reclaimed watershed provides storage and transport functions fundamental to a lake ecosystem. The closure landform design is deemed sufficient to sustain the lake water balance under various climate conditions, but continued monitoring is required to verify this in long term. Understanding of the physical, chemical and biological processes in the lake and its watershed continues to improve, which will lead to important findings and insights that can inform the planning and design of commercial scale pit lakes.

PRESENTATIONS AND PUBLICATIONS

Journal Publications:

Published

Hansika D. (MSc thesis): Influence of concentrations of V, Ni, and Mo in soil solutions on plant uptake and accumulation by *Hordeum jubatum* L. (granted in 2024)

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Under review

Panigrahi, B., Doig, L. E., Davila-Arenas, C. E., Ezugba, I., & Liber, K. (2024a). Spatio-Temporal Analysis of Water Chemistry and Ecotoxicological Risk Characterisation for a Constructed Pilot-Scale Pit Lake in the Athabasca Oil Sands Region, Canada. Submitted to Chemosphere (under review).

Panigrahi, B., Razavi, S., Doig, L. E., Cordell, B., Gupta, H., & Liber, K. (2024b). On Robustness of the Explanatory Power of Machine Learning Models. Submitted to Water Resources Research (under review).

Bello, A., Arslan, M., Fan, X., and Gamal El-Din, M. 2024. Biogeochemical Processes in Oil Sands Tailings and Capping Water: Insights into Permanent Aquatic Storage Structure Technology. Water Research (Under Review).

Conferences, presentations, and workshops:

Choi S., Cuss C.W., Nagel A.N., Shotyk W., Goss G., Glover C. 2021. An Investigation of Chronic Trace Element Toxicity of Lake Miwasin Water and Sediment to Daphnia magna. 42nd annual meeting, SETAC North America. November 14–18, 2021 (Oral presentation)

Hussain N., Lillico D.M.E., Richardson E., Choo-Yin Y., Hanington P., Stafford J.L. 2021. An immune cell-based assay for detecting and monitoring bioactive constituents within oils sands process-affected waters (OSPW). Presented at Society of Environmental Toxicology and Chemistry (SETAC) North America 42nd Annual Meeting, Portland OR, USA. November 14-18, 2021 (Oral presentation).

Choi S., Cuss C.W., Shotyk W., Glover C.N. 2022. Chronic trace element toxicity of Lake Miwasin water and sediment to *Daphnia magna*. *Faculty of Agriculture, Life, and Environmental Sciences Graduate Student Symposium*, Edmonton, Alberta.

Choi S., Cuss C.W., Glover C.N., Goss G., Shotyk W. 2022. Chronic toxicity and bioaccumulation in daphnids exposed to water and sediment from an oil-sands tailings pit lake. *Canadian Ecotoxicology Workshop*, Winnipeg, Manitoba.

Choi S., Cuss C.W., Glover C.N., Goss G., Shotyk W. 2022. Chronic toxicity and bioaccumulation of trace elements in daphnids exposed to water and sediment from an oil-sands tailings pit lake. *43rd Annual meeting, SETAC North America*, Pittsburgh, Pennsylvania.

Hansika D., Cuss C.W., Du L., Noernberg T., Shotyk W. 2022. Influence of Concentration and Speciation of Trace Elements in Soil Solution on Plant Uptake and Accumulation by *Hordeum Jubatum* L. *Canadian Society of Soil Science annual general meeting*, Edmonton, Alberta.

Hansika D., Cuss C.W., Du L., Noernberg T., Shotyk W. 2022. Influence of Concentration and Speciation of Trace Elements in Soil Solution on Plant Uptake and Accumulation by Hordeum Jubatum L. *Faculty of Agriculture, Life, and Environmental Sciences Graduate Student Symposium*, Edmonton, Alberta.

Hansika D., Cuss C.W., Du L., Dyck M., Shotyk W. 2022. Influence of concentration and speciation of V, Ni and Mo in soil solutions on plant uptake and accumulation by *Hordeum jubatum L. Soil Science Society of America*, Baltimore MD.

Nagel A., Cuss C.W., Shotyk W., Glover C.N. 2022. Understanding the uptake and bioaccumulation of trace metals following exposure of aquatic invertebrate Lumbriculus variegatus to pit lake sediments from the Alberta Oil Sands Region. 43rd Annual meeting, SETAC North America, Pittsburgh, Pennsylvania.

Richardson E., Arslan M., Gamal El-Din M., Hanington P. 2022. Microbiome analysis of tailings reclamation protocols in the Athabasca Oil Sands Region. BioNet Conference, Calgary Alberta.

Hussain N.A.S., Lillico D.M.E., Choo-Yin Y., Qin R., Zuo Tong How, Paul S., Gamal El-Din M, Stafford J.L. 2022. Detection and Tracking of Inflammatory Constituents in Environmental Water Samples Using Immune Cell Lines. Oral presentation. Society of Environmental Toxicology and Chemistry. Pittsburgh, USA.

Hussain, N., I. Sánchez-Montes, M. Gamal El-Din, and J.L. Stafford. 2023. Bioactivity Assessment of Environmental Waters Using Immune Cell Lines. Oral presentation. Society of Environmental Toxicology and Chemistry. Louisville, USA.

Paul, S., D.M.E. Lillico, M.A. Suara, S.O. Ganiyu, M. Gamal El-Din, and J.L. Stafford. 2023. Examination of Acute Exposure Effects of Untreated and AOP-treated OSPW using a Human Immune Cell-Based Bioindicator System. Oral presentation. Society of Environmental Toxicology and Chemistry. Louisville, USA.

Hussain, N., D.M.E. Lillico, Y.Y. Choo-Yin, R. Qin, Z.T. How, S. Paul, M. Gamal El-Din, and J.L. Stafford. 2022. Detection and Tracking of Inflammatory Constituents in Environmental Water Samples Using Immune Cell Lines. Oral presentation. Society of Environmental Toxicology and Chemistry. Pittsburgh, USA.

Panigrahi B., Doig L., Davila A.C., Ezugba I., Liber K. 2022. Application of Machine Learning Algorithms to Predict Key Water Quality Parameters in an Oil Sands Demonstration Pit Lake Based on Real Time Sensor Data. Canadian Ecotoxicity Workshop (CEW), Winnipeg, MB, Oct- 2-5, 2022

Panigrahi B., Doig L., Davila A.C., Ezugba I., Liber K. 2022. Use of Autonomous Sensors to Monitor Spatio-temporal Changes in Water Chemistry in an Oil Sands Demonstration Pit Lake, Alberta. 20th International Symposium on Toxicity Assessment (ISTA 20) Saskatoon, SK, August 15-18, 2022

Davila C.E., Doig L.E., Panigrahi B., Ezugba I., Liber K. 2022. Effects of water from Suncor's Demonstration Pit Lake, Lake Miwasin, on saline-tolerant zooplankton 20th International Symposium on Toxicity Assessment (ISTA 20) Saskatoon, SK, August 15-18, 2022

Ezugba I., Doig L., Panigrahi B., Davila C. E., Liber K. 2022. Toxicity Assessment of bottom-substrate from a Pilot-Scale Pit Lake containing Polymer-Treated Oilsands Tailings. SETAC North America 43rd Annual Meeting, Pittsburgh Convention Center, Pittsburgh, Pennsylvania, USA, November 13–17, 2022

Panigrahi, B., Doig, L., Davila, A.C.; Ezugba, I., Liber, K. 2023. Spatio-temporal analysis of water chemistry and ecotoxicological risk characterization of a pilot-scale pit lake in the Athabasca oil sands region. Canadian Ecotoxicity Workshop (CEW). Ottawa, ON, Oct- 2-5, 2023

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Ezugba, I., Doig, L., Panigrahi, B., Davila, C.E., Liber, K. 2023. Toxicological assessment of bottom substrate (consolidated tailings) from a pilot-scale end-pit lake in the Alberta Oil Sands Region. SETAC PNC Saskatoon, SK, June 18–20, 2023.

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Trembath, T., Ketcheson, S.J., Petrone, R.M. (2023) Importance of Snow Distribution and Melt for a Constructed Pit-lake Watershed. Canadian Geophysical Union Annual Meeting (National level), Canada; 10-May-2023.

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RESEARCH TEAM AND COLLABORATORS

Institution: Multiple consultants and research institutions are involved in this program.

Principal Investigator: Multiple principal investigators are involved in this program.

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
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Dr. Benjamin Beall	Hatfield Consultants	Project Manager		
Jackson Woren	Hatfield Consultants	Physical Limnology Component Lead		
Allison Pottie	Hatfield Consultants	Field Coordinator		
Carina Helm	Hatfield Consultants	Water Budget Component Lead		
Felix Chan	Hatfield Consultants	Field Lead		
Dr. Ted Lewis	Hatfield Consultants	Water Budget and Physical Limnology Technical Lead		
Dr. Lauren Thompson	Hatfield Consultants	Specialist		
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Dr. Matthew Elmes	Hatfield Consultants	Groundwater Technical Specialist		
Dr. Michael Vander Meulen	Hatfield Consultants	Water Quality and Aquatic Ecology Technical Lead		
Dr. Babar Javed	Hatfield Consultants	Water Quality and Aquatic Ecology Specialist		
Zachary Mueller	Hatfield Consultants	Data Management Lead		
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Brenten Vercruysse	Hatfield Consultants	Field Technician		

Cassandra Bruce	Hatfield Consultants	Field Technician		
Nadine Clifton	Black Fly Environmental	Vegetation Lead		
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Rich Petrone	University of Waterloo	Principal Investigator		
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Eric Murray	University of Waterloo	Research Technician		
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Chad W. Cuss	Memorial University of Newfoundland	Assistant Professor		
Chris Glover	Athabasca University	Professor		
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Taylor Bujaczek	University of Alberta	Research Coordinator (part time)		
Sunny Choi	University of Alberta	PHD student	May 2020	April 2025
Parvin Moussavi	University of Alberta	PHD student	Sept. 2020	April 2025
Dulani Hansika	University of Alberta	MSc student	Sept. 2019	April 2024
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Marjan Ghotbizadeh	University of Alberta	Data Specialist (part time)		
Dr. Mohamed Gamal El-Din	University of Alberta	Principal Investigator		
Dr. Muhammad Arslan	University of Alberta	Postdoctoral Fellow		
Dr. Zuo Tong How	University of Alberta	Postdoctoral Fellow		January 2022
Dr. Mohamed Ahmed	University of Alberta	Postdoctoral Fellow	June 2024	May 2025
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Patrick Hanington	University of Alberta	Professor		
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Karsten Liber	University of Saskatchewan	Principal Investigator		
Lorne Doig	University of Saskatchewan	Research Scientist		
Banamali Panigrahi	University of Saskatchewan	PHD student	Sept. 2019	Sept. 2024
Catherine Davila Arenas	University of Saskatchewan	MSC student	Sept. 2019	Sept. 2023
Immanuela Ezugba	University of Saskatchewan	PHD student	Sept. 2019	May 2025

WJ0121 - Base Mine Lake Demonstration

COSIA Project Number: WJ0121

Research Provider: Multiple Researchers and Institutions

Industry Champion: Syncrude Canada Ltd.

Industry Collaborators: Suncor, Canadian Natural

Status: Multi-year project, ongoing

PROJECT SUMMARY

Base Mine Lake (BML) Demonstration is the first, and currently the only full-scale commercial demonstration of the end pit lake technology in the oil sands industry. The demonstration is located in the former West In-Pit (WIP) of the Syncrude Mildred Lake (Base Lease) operation. It consists of a mined-out oil sands pit filled with untreated fluid tailings (FT). Fluid tailings are comprised of silt, clay, process-affected water and residual bitumen. The FT is physically sequestered below a combination of oil sands process-affected water (OSPW) and fresh water. This pit lake configuration is often referred to as Water Capped Tailings Technology (WCTT). Based on previous research and modelling, the prediction for WCTT is that with time, EPL water quality improves and the fluid tailings (or other tailings) will remain sequestered below the water cap.

Freshwater is pumped into Base Mine Lake from the Beaver Creek Reservoir (BCR) and as required, water is pumped out of BML to the tailings recycle water system (RCW) where it is utilized in the bitumen extraction process. The Beaver Creek watershed will connect to BML at closure and the decision was made to connect Beaver Creek to BML Demonstration using active management from operation to closure. This flow-through process dilutes the water cap and active inflow management will be in place until a more substantial upstream surface watershed is reclaimed and connected to BML Demonstration, final inlet design for BML is constructed, and outflow is established to the receiving environment (i.e., Athabasca River). As the tailings continue to dewater over time, the lake water will get deeper.

Placement of fluid tailings began in 1995, was completed in late 2012, and BML was commissioned as of 31 December 2012. No tailings solids were added after this time. During 2013, fresh water and OSPW was added to the existing OSPW upper layer to attain the final water elevation.

The BML Demonstration monitoring and research program began upon commissioning and is ongoing. The initial focus of the monitoring and research program is to support the demonstration of the WCTT and to provide a body of scientific evidence which demonstrates that BML Demonstration is on a trajectory to become integrated into the reclaimed landscape. The outcomes from the BML MRP can be used to inform the design and management of future pit lakes, including those that may contain tailings materials, such as treated or untreated fluid tailings. At the same time, the program establishes a baseline of biophysical data to assess the changes in BML through time, and the state of the lake at certification, including water quality and other lake processes. The monitoring program is designed to track trends in the lake both seasonally and annually. The research program focuses on key scientific questions designed to elucidate the mechanisms and processes that govern the current state of BML, and explain changes detected by the monitoring program. In other words, the monitoring program tracks the trends in the lake through time, and the research program investigates why those changes are occurring.

The specific objective of the BML Monitoring Program is to provide information to support the validation of WCTT as a viable tailings management and reclamation option. In the early stages, the BML Monitoring Program will demonstrate that fluid fine tailing are sequestered and that the water quality in the lake is improving. The monitoring program is designed to do this by tracking the physical, chemical and biological changes in BML (Table 1). The program captures these changes both temporally and spatially, and eventually in the context of regional climate cycles. The monitoring program supports regulatory compliance, but also informs adaptive management of BML. The BML Research Program uses a multi-university, multi- and inter- disciplinary approach that focuses on the analysis and interpretation of monitoring data, hypothesis driven research activities, and integration and collaboration among and between research programs. Research results are integrated with monitoring results on an ongoing basis, with the ultimate goal of identification and quantification of the processes and properties in BML that are responsible for the trends observed in the Monitoring Program. The various components comprising the BML Monitoring and Research Program are closely linked.

Table 1: Base Mine Lake Monitoring Program Components

Physical	Chemical	Biological
FFT Settlement	Water Balance Assessment	Aquatic Biology Assessment
FFT Geochemistry Assessment	Surface Water Quality Assessment	Surface Water Toxicity
Physical Limnology Assessment	Groundwater Assessment	Sediment Toxicity
Meteorological Monitoring	Chemical Mass Balance	
FFT Physical Assessment		

The current focus of the Research Program is to support the demonstration of the Water Capped Tailings Technology (WCTT). The program also provides supporting information about key processes fundamental to the progression of BML towards a functional component of the closure landscape. The current research programs were focused on key parameters influencing early BML development. The program focus is to validate WCTT. Several research programs will determine the potential fluxes from the FFT to the water column, including chemical, geochemical, mineral, gases and heat and bitumen. Physical, biological and chemical mechanisms are being investigated (Table 2).

Table 2: Current Base Mine Lake Research Programs

Research Component	Primary Objective	University	Researchers (PIs)
Physical limnology of BML and the potential for meromixis	To understand the circulation of BML and its potential for meromixis	University of British Columbia	Greg Lawrence / Ted Tedford / Roger Pieters
Characterization of controls on mass loading to an oil sands end pit lake	To define mass loading to Base Mine Lake by characterizing the mechanisms and distribution of heat and mass transfer from the tailings column to the overlying water column.	University of Saskatchewan	Lee Barbour / Matt Lindsay
Field investigation of BML water cap oxygen concentrations, consumption rates and key BOD/COD constituents affecting oxic zone development.	To establish temporal and spatial variability in in situ BML water cap oxygen concentrations, oxygen consumption rates and identify the biogeochemical processes linked to its consumption from the FFT-water interface to the BML water surface	University of Toronto / McMaster University	Lesley Warren / Greg Slater
Microbial communities and methane oxidation processes in Base Mine Lake	i) To study Biological Oxygen Demand (BOD) in the lake, ii) to examine a potential role of methanotrophs in the degradation of naphthenic acids (NAs), and iii) to examine the microbial community in BML, how the community changes over time with changes in lake chemistry, and the potential use of community analyses as an indicator of reclamation	University of Calgary	Peter Dunfield
Understanding Air-Water Exchanges and the long-term hydrological viability of Base Mine Lake	To measure and improve the understanding of the physical mechanisms controlling CH_4 and CO_2 fluxes across the air-water interface, to determine the factors that control evaporation from BML and to understand the long-term water balance of BML	McMaster University / Carleton University	Sean Carey / Elyn Humphreys
Characterization of Organic Compounds and Naphthenic Acids in Base Mine Lake: Implications for	To understand methane production and release, the sources of naphthenic acids and petroleum hydrocarbons to the BML water cap,	McMaster University	Greg Slater

methane production, transport, oxygen consumption, and NA persistence	and the role of ebullition in transporting FFT constituents into the water cap		

PROGRESS AND ACHIEVEMENTS

The two key desired outcomes for Base Mine Lake that are important for the validation of the Water-Capped Tailings Technology are the physical sequestration of the fine tailings solids below the water cap and water quality improvements over time. Demonstrating the physical isolation of fines beneath the water cap of BML is a key performance outcome related to the validation of Water Capped Tailings Technology. Results so far indicate that the FT are settling as expected by model predictions, the mudline is declining in elevation year over year, the water cap is increasing in depth, and although the turbidity in the water cap fluctuates seasonally, there is generally a decrease in the suspended solids concentration over time, especially in the upper layers of water. Surface water quality has been improving with time in Base Mine Lake, as expected to demonstrate Water Capped Tailings Technology. The lake water is not acutely toxic. Except for F2 hydrocarbons all parameters measured are below Alberta Surface Water Quality short term guidelines for the Protection of Aquatic Life.

LESSONS LEARNED

Lessons learned and key results are reported annually to the Alberta Energy Regulator and are publicly available here: Syncrude Canada Ltd. Reports

The most recent (2024) report can be found here: Syncrude 2024 Pit Lake Monitoring and Research Report

PRESENTATIONS AND PUBLICATIONS

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RESEARCH TEAM AND COLLABORATORS

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Jared Robertson	University of Saskatchewan	Post Doc Fellow	2017	2018
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Emad Albakistani	University of Calgary	M.Sc.	2015	2018
Sam Rawluck	University of Calgary	M.Sc.	2016	2017
Angela Smirnova	University of Calgary	Research Associate		
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Dr. Ted Tedford	University of British Columbia	Research Associate		
Dr. Roger Pieters	University of British Columbia	Research Associate		
Dr. Jason Olsthoorn	University of British Columbia	Post-doctoral		
Dr. Marjan Zare (50% time)	University of British Columbia	Post-doctoral		
David Hurley	University of British Columbia	Master's student	2015	2017
Tomy Doda	EPFL	Master's student	2016	2017

WJ0192 - Mesocosm Research in Support of Pit Lakes

COSIA Project Number: WJ0192

Research Provider: InnoTech Alberta

Industry Champion: Canadian Natural

Industry Collaborators: Imperial Oil Resoures Ltd., Teck Resources Limited, Kilgour Associates, WaterSMART Solutions Ltd.

Status: Year 6/7 of 8

PROJECT SUMMARY

To better understand modeled results based on laboratory studies, an array of 30 outdoor 15,000-litre mesocosms was used in a study that examined chemical changes, as well as biological and ecological responses, in model wetland ecosystems with various mine waters added to them. This work is meant to scale up laboratory studies, to ensure planned pit lakes are designed to be ecologically self-sustaining multi-use landscape features.

Since 2017, the Demonstration Pit Lake (DPL) Joint Industry Project (JIP) has examined the effects of different source materials and mining byproducts (including different tailings materials and process affected water) on the chemical, biological and ecological properties of replicated model wetland ecosystems. The 2022-2023 aquatic mesocosm study attempts to disentangle the effects of salinity and naphthenic acids (NAs).

The following objectives were conceived based on the previous mesocosm research, subsequent data and gap analysis, operator-specific objectives, and feedback from relevant parties and Indigenous communities.

- Objective #1: Evaluate the individual and interactive effects of salinity, NAs, and other constituents of concern (COCs) in oil sands saline groundwater and process water on water quality and aquatic biota to advance our understanding of potential in-pit lake performance with respect to these variables.
- Objective #2: Compare toxicity test results with both conventional and unconventional test species from this study to the Canadian Council of Ministers of the Environment (CCME) toxicity sensitivity distribution curve.
- Objective #3: Compare toxicity endpoints of standard test species to locally relevant non-standard test species to better understand how locally relevant native aquatic species respond to salinity and NAs relative to the standard test species and how feasible it is to use non-standard test species in toxicity testing.
- Objective #4: Compare modeling assumptions and screening criteria made specifically in Canadian Natural's pit lake planning process to trajectories observed in aquatic mesocosms with respect to water quality and ecological health.
- Objective #5: Share the research and outcomes publicly with relevant parties and Indigenous community members in a manner that is accessible and practical.

The experimental design was comprised of 30 aquatic mesocosms that contained homogenized Athabasca River water, including a mix of native regionally relevant biota. The experimental design (Table 1) was devised to evaluate how receptors would respond to fixed concentrations and combinations of two chloride (Cl) source waters and one NAs source water. Each water type was evaluated individually. Each saline water was evaluated in combination with the NAs water type. Levels were set as low, medium, and high concentrations for each source. In all cases, the low level is the ambient concentration found in Athabasca River water. This value is viewed as the 'control' or 'reference' group for the experiment (i.e., 1-LL in Table 1). Medium and high concentrations correspond to proposed guideline values (i.e., 120 and 640 mg/L for Cl), and 10 and 25 mg/L for NAs. Given the interest in understanding the interactive effects of Cl and NAs, two mesocosms were allocated to each combination of Cl and NA (i.e., the number 2 in each of the rectangles in Table 1). For the 2022/2023 study, each groundwater and the NAs source water were installed at "low (L)", "medium (M)", and "high (H)" concentrations as outlined in Table 1. Each experimental group had two replicates. The study ran continuously from the spring of 2022 (including overwinter), through the fall of 2023.

Table 1. Mixtures for source waters to derive the 15 treatment combinations

TRT	Target Concentration (mg/L)		TRT	Target Concentration (mg/L)	
[Cl]-[NA]	**Chloride**	**NAs**	**[Cl]-[NA]**	**Chloride**	**NAs**
1 – LL	10	0	1 – LL	10	0
2 – LM	45	11	2 – LM	45	11
3 – LH	87	24	3 – LH	87	24
4 – ML	120	0	10 – ML'	121	0
5 – MM	120	12	11 – MM'	121	11
6 – MH	120	23	12 – MH'	120	23
7 – HL	643	0	13 – HL'	641	0
8 – HM	643	12	14 – HM'	645	11
9 - HH	642	24	15 – HH'	641	23

Notes: The fraction of each saline water source was calculated based on a preliminary investigation in 2021. HBW: Horizon basal water; AC2AW: Albian Cell 2A water; ICP 3: Inpit Cell 3; ARW: Athabasca River water; NA: naphthenic acid; TRT: Treatment; L: low; M: medium; H: high. Apostrophe (') represents the groundwater source of AC2AW.

PROGRESS AND ACHIEVEMENTS

The first aquatic mesocosm study was led by Suncor and occurred from May 2017 to September 2018.

The second mesocosm study was led by Imperial and carried out from May 2019 to October 2021.

A statistical analysis of the fully integrated dataset obtained from the first four years of DPL research was performed in 2021 by Kilgour & Associates Ltd. (KAL). The findings were summarized and informed the gap analysis, which was used to evaluate and prioritize remaining and emergent research questions. A literature review was also completed to inform the next phase of research. Feedback was incorporated from external partners and Indigenous community members to use additional native aquatic biota in the research plan and assess the feasibility of including non-standard test species in the toxicological testing program.

The literature review indicated limited toxicological information on the interaction between salts and organic compounds (such as NAs), and no studies have investigated the effects of long-term exposure to combinations of salinity and NAs prior to November 2021. A preliminary range-finding set of toxicity tests was conducted to inform the design of the 2022/23 mesocosm trials in 2021. Trial toxicity testing of two non-standard test species, walleye (Sander vitreus) and fatmucket freshwater mussels (Lampsilis siliquoidea), were conducted to ascertain the feasibility of using native aquatic biota as a test organism.

Preliminary analyses indicate specific conductivity and dissolved oxygen remained relatively stable. Turbidity decreased first, followed by a plateau. pH was also in the neutral to alkaline range. In laboratory water chemistry results, total NAs concentrations decreased with time, as observed previously. Concentrations of dissolved chloride and other inorganics remained stable, even with a slight increase in some treatments. COD and dissolved sulphate were either unchanged or significantly higher by the end of 2022 and 2023 than at the beginning of 2022. Saline groundwater sources did not influence the total or degradation rate of NAs concentrations. However, the dissolved chloride levels in HBW treatments were significantly higher than in AC2AW treatment, mainly due to logistics challenges.

Preliminary analysis indicates the HBW+IPC3W mixture had higher hardness and concentrations of total Boron, Lithium, Magnesium, Potassium, and Sodium, and, the AC2AW+IPC3W mixture had higher hardness and concentrations of Calcium, Magnesium, Sodium, and dissolved sulphate compared to the control group.

Preliminary results from toxicity testing indicated no adverse effects were observed on the survival of walleye for the acute 96-h test. Observed levels of toxicity in Ceriodaphnia dubia for survival (LC50, per cent v/v) and reproduction (IC25, per cent v/v) were low (>100) in both years. Sublethal testing results in all samples collected in both 2022 and 2023 were reported to have an LC50 >100 (per cent v/v) for fathead minnow. Preliminary analysis indicated a significant negative relationship between the 24/48-hour viability of fatmucket mussel glochidia and dissolved chloride concentrations in both years. No significant relationship was observed between mussels and the tested NAs concentrations.

Biomimetic extraction via solid-phase microextraction (BE-SPME) values were correlated with the NAs concentrations, adding to the database for this method. There was no apparent growth inhibition of installed emergent plants over the course of the study, although growth inhibition of floating plants (hornwort) was observed in mesocosms with process water.

LESSONS LEARNED

For most COCs, concentrations remained stable or significantly lower at the end of 2022 and 2023 compared to the beginning of the study.

Stratification and a chemocline were observed in 2023, indicating the mesocosms were not always well mixed.

The sensitivity of walleye is somewhat lower than that of fathead minnow. However, caution should be noted when interpreting the results due to the different life stages of the fish tested and the test duration. Non-standard test species are a viable option, but the seasonality of these test species remains a challenge.

PRESENTATIONS AND PUBLICATIONS

Conferences, presentations, and workshops:

Kilgour, B., R. Melnichuk, Z. Chen. Mesocosms as small-scale models of pit lakes: integration, analysis and interpretation of multiple years of data. COSIA Mine Water Management Workshop. Virtual. Invited Speaker. 2021.

Melnichuk, R., Z. Chen. In-ground and above-ground aquatic mesocosms as tools to understand short-term and multi-year to biological, ecological and chemical effects of reclamation technologies. RemTech. Banff, AB. Oral Presentation. 2021

Melnichuk, R. Using aquatic mesocosms to inform pit-lake design. COSIA Mine Water Release Workshop. Virtual. Invited Speaker. 2020

Melnichuk, R. Using aquatic mesocosms to investigate biological, chemical and ecological community responses to oil sands process-affected water and tailings to inform pit-lake design. COSIA Mine Water Release Workshop. Edmonton, AB. Invited Speaker. 2019.

Melnichuk, R., J. Davies, M. Hiltz, B. Eaton and C. Aumann. Using aquatic mesocosms to investigate biological, chemical and ecological community responses to oil sands process-affected water and tailings to inform pit-lake design: a 2-year study. Oil Sands Innovation Summit (OSIS). Calgary, AB. Oral Presentation. 2019.

Melnichuk, R. Using aquatic mesocosms to inform pit lake design: Toxicology study. BML Research and Monitoring Technical Update. Edmonton, AB. Oral Presentation. 2019.

Melnichuk, R. Using aquatic mesocosms to inform pit lake design: Chemical responses to oil sands by-products. BML Research and Monitoring Technical Update. Edmonton, AB. Oral Presentation. 2019.

Melnichuk, R., J. Davies, M. Hiltz, B. Eaton and C. Aumann. Using aquatic mesocosms to inform pit lake design: Ecological responses to oil-sands by-products. COSIA Pit Lake. Workshop. Edmonton, AB. Invited Speaker. 2018.

Melnichuk, R., J. Davies, C. Aumann, M. Hiltz and B. Eaton. Using aquatic mesocosms to examine potential ecological responses to oil sands water and tailings to inform pit lake adaptation in Alberta's oil sands. Oil Sands Innovation Summit (OSIS). Calgary, AB. Oral Presentation. 2018.

Reports:

Chen, Z., Melnichuk, R. (2022). A Mesocosm - Scale Study of Chemical and Ecological Response to Different Types of Oil Sands Tailings and Process Water (2019-2021). https://cosia.ca/sites/default/files/attachments/2019-21 Mesocosm Research Report.pdf

Melnichuk, R. (2020). Densified fluid fine tails and oil sands process water - an extension of the 2017 study. https://cosia.ca/sites/default/files/attachments/2018 Mesocosm Research Report.pdf

Davies, J. (2018). Densified Fluid Fine Tails and Oil Sands Process Water: a Screening Study. https://cosia.ca/sites/default/files/attachments/2017 Mesocosm Research Report.pdf

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Principal Investigator: Zhongzhi Chen (2022) and Ryan Melnichuk (2023)

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Ryan Melnichuk	InnoTech Alberta	Research Scientist		
Jim Davies	InnoTech Alberta	Researcher		
Brian Eaton	InnoTech Alberta	Manager		
Bruce Kilgour	Kilgour & Associates Ltd.	President		
Sawyer Stoyanovich	Kilgour & Associates Ltd.	Scientist		
Robert Hough	WaterSMART Solutions Ltd.	Scientist		

WATER TREATMENT

WE0025 - Industrial Research Chair in Oil Sands Tailings Water Treatment - Second Term

COSIA Project Number: WE0025

Research Provider: University of Alberta

Industry Champion: Syncrude Canada Ltd.

Industry Collaborators: Canadian Natural, Imperial Oil Resources Ltd., Suncor Energy Inc., Teck Resources Limited

Status: Year 7 of 8

PROJECT SUMMARY

Project Scope and Objectives

The NSERC IRC Program - Second Term (July 2017 to February 2025) focused on developing and assessing innovative water treatment/reclamation technologies and strategies. The program reviewed a combination of passive (low-energy) and semi-passive treatment approaches to help promote and protect both the environment and public health.

The short-term objectives of the NSERC IRC Program - Second Term were:

- Understand the fundamentals of semi-passive and engineered passive treatment processes.
- Conduct life-cycle assessments and cost analyses of different treatment approaches.
- Assess the performance of selected treatment processes at the pilot-scale level.
- Assess the performance of large field pilots on active mine sites.

The long-term objectives, including those beyond the period covered by this program, are:

- Train highly qualified personnel with the skills necessary to promote and protect environmental and public health.
- Support current research programs focused on the treatment/reclamation of Oil Sands Process Affected Water (OSPW) by facilitating the transfer of knowledge and new discoveries.
- Integrate the knowledge gained into actual water management options by the oil sands industry.

Significance of the Research to the Industry

The research aims to assess various types of low-energy OSPW treatment processes, including semi-passive and engineered passive approaches. This will help in understanding how treated or reclaimed OSPW can be safely discharged into the environment. The program involves a comprehensive characterization of OSPW before and after treatment, a dose-response analysis of toxic effects induced by different OSPW fractions, and the use of different treatment processes for OSPW. These findings will contribute to the development of reclamation strategies for the safe release of OSPW into the environment.

Methodology

To achieve the objectives of the NSERC IRC Program – Second Term, 29 projects were established. The projects were grouped into seven research areas: water and tailings quality, advanced oxidation processes, electro-oxidation processes, biological treatments, material development, piloting tests, and cost assessment (see Table 1).

Table 1: Projects conducted during NSERC IRC Program – Second Term

Project ID #	Research Area	Title	Status
1	Water and Tailings Quality	Long-Term Assessment of OSPW Quality Due to Self-Attenuation	Completed
2a	Advanced Oxidation Processes	Solar Photocatalytic Treatment of OSPW Using Bismuth Tungstate Based Photocatalysts	Completed
2b	Advanced Oxidation Processes	Assessing the Catalytic Potential of the OSPW Inorganic Matrix on Advanced Oxidation Process	Completed
2c	Advanced Oxidation Processes	Application of Persulfate-Based Advanced Oxidation Processes for OSPW Treatment	Completed
2d	Advanced Oxidation Processes	Comparison of Catalytic Ozone, UV/H_2O_2, UV/ Peroxymonosulfate and UV/Fenton in Degrading the NAs in OSPW	Completed
2e	Advanced Oxidation Processes	Treatment of OSPW by Ferric Citrate under Visible Light Irradiation	Completed
2f	Advanced Oxidation Processes	Solar-Based Advanced Oxidation Processes for OSPW Treatment Using Zinc Oxide as Catalyst	Complete
2g	Advanced Oxidation Processes	Treatment of NAs in OSPW Using Low-Dose CaO_2 as an Additive under Sunlight Irradiation	Completed
3	Advanced Oxidation Processes	In-Situ Generation of Reactive Oxygen Species Using Biochar as a Catalyst	Complete
4	Biological Treatments	Understanding of Engineered Passive Processes for OSPW Treatment Using Biofiltration Columns	Ongoing
5a	Electro-Oxidation Processes	Application of Electro-Oxidation for the Degradation of Organics in OSPW	Completed
5b	Electro-Oxidation Processes	Treatment of OSPW Using Electro-Oxidation and Electrochemically Activated Reactive Sulfate Species Using Boron Doped Diamond Electrode	Completed
5c	Electro-Oxidation Processes	Treatment of OSPW by Packed Bed Electrode Reactor	Completed
5d	Electro-Oxidation Processes	Electro-Oxidation of NAs in OSPW by Polyaniline Modified Biochar/Graphene Electrode	Completed
6	Biological Treatments	Remediation of OSPW Using Deep Biofilters – From Bench to Scale-up Tests	Completed

7	Electro-Oxidation Processes	Degradation of NAs and Real OSPW Using Combined Electro-Oxidation and Chemically Activated Peroxymonosulfate (PMS)	Completed
8a	Material Development	Adsorption Using Carbon Xerogel	Completed
8b	Material Development	Applications of Cellulose Nanofibers for Process Water Remediation	Completed
8c	Material Development	Application of Sludge-Based Materials for Adsorption Treatment	Completed
8d	Material Development	Preparation of Biochar-Chitosan Composite and its Application for Metals Removal from OSPW	Completed
8e	Material Development	Evaluation of Adsorption-Desorption of Contaminants of Potential Concern (COCs) in OSPW onto Different Types of Reclamation Materials	Completed
9	Piloting Tests	Coke-Treatment Piloting	Postponed
10	Piloting Tests	Wetland Piloting	Postponed
11	Piloting Tests	Vegreville Mesocosm Piloting	Completed
12	Piloting Tests	Suncor Demonstration Pit Lake (DPL) Piloting	Ongoing
13	Cost Assessment	Economic Analysis and Policy Options	Ongoing
14	Water and Tailings Quality	Application of biomimetic solid phase micro-extraction (BE-SPME) Method as a Screening Tool	Completed
15	Water and Tailings Quality	Assessing the Effects of Polymers and Polymer Degradation on Water Chemistry and the Quality of the Tailings	Completed
16	Water and Tailings Quality	Development of Mass Spectrometry-Based Analytical Methods for the Detection of Multiple NAs and Identification of Byproducts	Completed

PROGRESS AND ACHIEVEMENTS

The NSERC IRC Program - Second Term successfully achieved several short- and long-term goals. As far as water and tailings quality is concerned, we have assessed the quality of OSPW due to self-attenuation and analyzed the stability and degradation of anionic polyacrylamides (A-PAM) in oil sands tailings. Our findings indicate that A-PAM undergoes hydrolysis of amide groups through amidase enzymes, releasing ammonia and smaller molecules such as organic acids. We have used Biomimetic Extraction (BE) coupled with SPME and gas chromatography with a flame ionization detector (GC-FID) to quantify bioavailable organics. This approach, developed by Imperial, shows promise as a benchmark technology for rapidly assessing the toxicity of dissolved organics in various treatment processes and natural environments.

Research conducted under the NSERC IRC Program has highlighted the significant role of advanced oxidation processes in enhancing the remediation of OSPW by accelerating the degradation of naphthenic acids (NAs) and other organic compounds.

Using inexpensive electrode materials such as graphite under low voltage conditions can selectively degrade NAs, enhancing OSPW biodegradability and reducing toxicity. Electro-oxidation with boron-doped diamond (BDD) electrodes proved effective in achieving complete degradation of NAs within short timeframes at the bench scale, approximately 1L), and may be a cost-effective options for OSPW treatment.

A new photocatalyst, Bi_2WO_6/NiO/Ag, has been tested at the bench scale, and is showing promise. It has a hierarchical flower-like Z-scheme heterojunction. After six hours of photocatalytic treatment, complete removal of classical naphthenic acids (NAs), and heteroatomic NAs, was observed. Similarly, after four hours of treatment, more than 99 per cent removal of NAs was achieved, while virtually all fluorophore organic compounds were oxidized within the same reaction time using solar-activated zinc oxide (ZnO) photocatalysis (at one g/L) under simulated solar radiation with a steady irradiance of approximately 278 W/m^2. The next step is scaling up the technology, testing it at larger scales in incremental steps, the next step being approximately 1 m3. All water treatment technologies go through this process.

We have made significant progress in material development, including the development of carbon xerogels, biodegradable cellulose nanofibers, and sludge-based biochar for adsorption treatment. We have found using zinc-chloride-activated biochar for adsorption treatment can effectively reduce the overall organic matter, some metals, and acute toxicity indicators found in OSPW. This method can be combined with passive treatment technologies. We also found the sludge-based biochar/iron oxide composite is a highly efficient peroxymonosulfate catalyst for the degradation of NAs, and need to be scaled up to determine their commercial performance.

Approaches such as solar-activated sulfate radical-based advanced oxidation processes (SR-AOPs) combined with biofiltration have been found to be an effective method for degrading dissolved organics in OSPW at the bench scale.

Electrocatalytic peroxomonosulfate activation (EC-PMS) has also been investigated for enhanced degradation of organics in OSPW. EC-PMS synergistically couples an early-stage PMS electro-activation (E-PMS) with subsequent heterogeneous electro-Fenton oxidation (HEF) catalyzed by Fe-modified biochar (BC-Fe). The EC-PMS has excellent reusability and is effective in treating real OSPW. It achieves complete degradation of real NAs in OSPW and relatively good mineralization of the water.

As with all these technologies which have been tested at the bench scale, which have shown promise, the next step in to scale up these technologies testing them incrementally at larger scales. Term 3 of the program is dedicated to scaling to the technologies which have shown promise at the bench scale.

LESSONS LEARNED

The following are the key outcomes achieved so far:

1. The characterization and treatment of OSPW presents challenges, including the presence of dissolved organic compounds such as NAs, other organic acids, total suspended solids, salinity, and various dissolved organic and inorganic compounds. Comprehensive water characterization and toxicity assessment of both untreated and treated OSPW are essential for gaining a thorough understanding of the potential environmental impacts of treated OSPW.

2. Employing sewage sludge as a precursor for producing sewage sludge-based materials (sludge-based biochar) offers several advantages. It can effectively adsorb organic compounds from OSPW

and serve as catalysts for advanced oxidation processes, contributing to OSPW remediation efforts.

3. Low-current electro-oxidation emerges as a promising pre-treatment option for OSPW prior to discharge into pit lakes or wetlands, enhancing biodegradability and reducing toxicity of OSPW organics. This process, facilitated by low-cost graphite electrodes and lower voltage requirements, can be powered by solar energy or implemented for in-pipe treatment.

4. In situ catalytic oxidation holds significant potential in enhancing OSPW remediation by accelerating the degradation of NAs and other organics. Applied as a pre-treatment step, it can effectively prepare OSPW for subsequent remediation processes.

5. Solar-based advanced oxidation processes using photo-active materials either in suspension or on a floating support media present viable options at the bench scale for targeting recalcitrant organics in pit lakes and wetland systems. These need to be scaled up to determine their commercial scale technical and economic viability.

6. Offering advanced multi-barrier treatment methods and water recycling options will safeguard public health, improve water quality, and support cost-effective development of Alberta oil sands resources.

PRESENTATIONS AND PUBLICATIONS

Since 2017, there have been 82 publications in peer-reviewed journals and 126 presentations at conferences and workshops.

Journal Publications

Published

Ganiyu, S.O., N.A.S. Hussain, J.L. Stafford, and M. Gamal El-Din. 2024. Electrocatalytic activation of peroxomonosulfate (PMS) under aerobic condition for the remediation of oil sands process water: insight into one-pot synergistic coupling of PMS electro-activation and heterogeneous electro-Fenton processes. Chem. Eng. J., 480, 147737.

Medeiros, D., P. Chelme-Ayala, and M. Gamal El-Din. 2023. Sludge-based activated biochar for adsorption treatment of real oil sands process water: selectivity of naphthenic acids, reusability of spent biochar, leaching potential, and acute toxicity removal. Chem. Eng. J., 463, 142329.

Meng, L., Z.T. How, P. Chelme-Ayala, C. Benally, and M. Gamal El-Din. 2023. Z-Scheme plasmonic Ag decorated Bi_2WO_6/NiO hybrids for enhanced photocatalytic treatment of naphthenic acids in real oil sands process water under simulated solar irradiation. J. Hazard. Mater., 454, 131441.

Sánchez-Montes, I., H. Mokarizadeh, S. Paul, K. Moghrabi, N. Hussain, P. Chelme-Ayala, J.L. Stafford, M.R.V. Lanza, and M. Gamal El-Din. 2024. UVA LED-assisted breakdown of persulfate oxidants for the treatment of real oil sands process water: removal of naphthenic acids and evaluation of residual toxicity. Chem. Eng. J., 481, 148631.

Paul, S., N.A.S. Hussain, D.M.E. Lillico, M.A. Suara, S.O. Ganiyu, M. Gamal El-Din, and J.L. Stafford. 2023. Examining the immunotoxicity of oil sands process affected waters using a human macrophage cell line. Toxicol., 500, 153680.

RESEARCH TEAM AND COLLABORATORS

Institution: University of Alberta

Principal Investigator: Mohamed Gamal El-Din (Professor, Department of Civil and Environmental Engineering)

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Dr. Mohamed Gamal El-Din	University of Alberta	Professor		
Rongfu Huang	University of Alberta	Research Associate		2019 (completed)
Pamela Chelme-Ayala	University of Alberta	Research Associate		
Lingling Yang	University of Alberta	Research Associate		
Selamawit Messele	University of Alberta	Postdoctoral Fellow		2020 (completed)
Mingyu Li	University of Alberta	Postdoctoral Fellow		2020 (completed)
Shailesh Sable	University of Alberta	Postdoctoral Fellow		2020 (completed)
Zou Tong How	University of Alberta	Postdoctoral Fellow		2022 (completed)
Ming Zheng	University of Alberta	Postdoctoral Fellow		2023 (completed)
Soliu Ganiyu	University of Alberta	Postdoctoral Fellow		
Muhammad Arslan	University of Alberta	Postdoctoral Fellow		
Muhammad Usman	University of Alberta	Postdoctoral Fellow		
Isaac Sanchez	University of Alberta	Postdoctoral Fellow		
Zhijun Luo	University of Alberta	Visiting Professor		2019 (completed)
Abdallatif Abdalrhman	University of Alberta	PHD Student	2014	2019 (completed)
Rui Qin	University of Alberta	PHD Student	2014	2019 (completed)
Lei Zhang	University of Alberta	PHD Student	2014	2018 (completed)
Lingjun Meng	University of Alberta	PHD Student	2017	2022 (completed)
Chelsea Benally	University of Alberta	PHD Student	2012	2018 (completed)
Jia Li	University of Alberta	PHD Student	2019	2023 (completed)
Monsuru Suara	University of Alberta	PHD Student	2019	2024 (completed)

Zhexuan An	University of Alberta	PHD Student	2019	2024 (completed)
Foroogh Mehravaran	University of Alberta	PHD Student	2019	2024 (completed)
Deborah Medeiros	University of Alberta	PHD Student	2019	2023 (completed)
Akeen Bello	University of Alberta	PHD Student	2019	2024
Jerico Fiestas Flores	University of Alberta	PHD Student	2020	2024
Hadi Mokarizadeh	University of Alberta	PHD Student	2021	2025
Md Rashid Al-Mamun	University of Alberta	PHD Student	2022	2026
Zhi Fang	University of Alberta	Visiting PHD Student	2017	2017 (completed)
Hande Demir	University of Alberta	Visiting PHD Student	2019	2019 (completed)
Junying Song	University of Alberta	Visiting PHD Student	2019	2019 (completed)
Yue Ju	University of Alberta	Visiting PHD Student	2019	2021 (completed)
Qi Feng	University of Alberta	Visiting PHD Student	2021	2022 (completed)
Adriana Vasquez	University of Alberta	Master Student	2021	2023 (completed)
Ali Abdelrahman	University of Alberta	Master Student	2019	2021 (completed)
Jia Li	University of Alberta	Master Student	2017	2018 (completed)
Sanya Mehta	University of Alberta	Research Assistant	2020	2021 (completed)
Lekha Patil	University of Alberta	Research Assistant	2019	2022 (completed)
Ali Abdelrahman	University of Alberta	Research Assistant	2021	2022 (completed)
Alice Da Silva	University of Alberta	Research Assistant		2018 (completed)
Shimiao Dong	University of Alberta	Research Assistant		2018 (completed)
Yanlin Chen	University of Alberta	Research Assistant		2019 (completed)

Research Collaborators:

- Dr. James Stafford, Professor, Department of Biological Sciences, University of Alberta.
- Dr. Patrick Hanington, Associate Professor, School of Public Health, University of Alberta.
- Dr. Yaman Boluk, Professor, Nanofibre Chair in Forest Products Engineering, Department of Civil and Environmental Engineering, University of Alberta.
- Dr. Dev Jennings, Professor, Alberta School of Business - Department of Strategy, Entrepreneurship and Management.
- Dr. M. Anne Naeth, Professor, Faculty of Agricultural, Life and Environmental Sci - Renewable Resources Department, Director, Future Energy Systems, Vice-President Research Innovation - Future Energy Systems, Director, Land Reclamation International Graduate School, University of Alberta.
- Dr. Vic Adamowicz, Professor and Vice Dean, Faculty of Agricultural, Life and Environmental Science, University of Alberta.
- Dr. Xuehua Zhang, Professor, Department of Chemical & Materials Engineering, University of Alberta.

Non-Pathways Alliance Collaborators:

- EPCOR Water Services
- Alberta Innovates
- Alberta Environment and Protected Areas

WE0089 - Initial Assessment of the Feasibility of Sequestering Highly Saline Groundwater in Tailings Deposits

COSIA Project Number: WE0089

Research Provider: Barr Engineering and Environmental Science Canada Ltd.

Industry Champion: Canadian Natural

Industry Collaborators: Suncor Energy Inc., Syncrude Canada Ltd., Imperial Oil Resources Ltd.

Status: Complete

PROJECT SUMMARY

The oil sands mining industry is exploring the feasibility of sequestering highly saline mine depressurization (DP) water into tailings impoundments that have begun the remediation/reclamation process and are no longer part of the water recycle circuit. DP water is generated during depressurization of the deeper aquifers beneath the oil sands ore and is an essential component of maintaining safe mining conditions. The DP water could be highly saline and must be managed separately from other process and wastewater streams. The study aimed to determine the conceptual feasibility of sequestering highly saline DP water into an in-pit tailings impoundment capped by water. The study comprised two phases:

- Phase 1 consisted of a literature review focused on the sequestration of highly saline waters in tailings impoundments in other mining sectors worldwide. The review focused on approaches to sequester highly saline water and the potential changes in the water quality within the shallow tailings of the deposit.

- Phase 2 used a numerical groundwater model to assess the feasibility of successfully sequestering DP water into fines and sand-dominated tailings deposits in mined-out pits. The modeling included a rigorous stochastic analysis to evaluate the relationship between the characteristics of various tailings deposits and the sequestration of the DP water.

PROGRESS AND ACHIEVEMENTS

The Phase 1 literature review indicated numerous methods have been used for storing and managing brine related wastewater, including:

- Using large brine storage ponds

- Installing a hydraulic barrier, such as a slurry wall, pressure relief network of wells and/or trench, drainage system, or impermeable liner

- Using brine containment wells, such as pumping wells

- Actively treating wastewater (reverse osmosis, ion exchange, chemical precipitation)

- Creating a density-stratified lake within a tailings pit

- Alternative techniques include capping tailings to isolate them from the environment, dissolving salt tailings and injecting them into deep wells, disposing of waste underground, adopting dry stacking methods, and burying salt waste on the surface.

Selecting an appropriate approach for brine management depends on a variety of factors, including the economics of the mining operation, the characteristics of the tailings, the volume of saline water, the hydrogeology and topography of the mine site, and the environmental regulations. Industries employing brine management methods included potash mining and nickel and copper mining.

Phase 2 included development of a generalized conceptual model of the injected DP water, the tailings deposits, and the surrounding groundwater flow system to assess the feasibility of an injection scheme. The conceptual model was a generalization of a typical Athabasca oil sands in-pit tailings impoundment and did not represent any specific site. The conceptual tailings impoundment considered represented an in-pit tailings impoundment that is full and no longer part of the extraction water recycle circuit. The tailings within the impoundment were varied between sand-dominated (>3.5:1 sand to fines (<44 µm) ratio) and fines-dominated (<2:1 sand to fines ratio). The conceptual model assumed the DP water is placed at the bottom of the tailings impoundment and did not consider the specific methodology used to place the DP water at depth. Various technical considerations surrounding the injection of DP water into the tailings were identified. These included injection, extraction, and monitoring wells. The injection infrastructure scheme is likely to be very complex and will require thoughtful planning during any subsequent engineering assessments.

A groundwater numerical model was compiled with numerous model runs varying distributions of model inputs stochastically. The generalized model selected comprised a rectangular active domain 4.2 km in width and 5.0 km in length, covering 21 km2 discretized in plan view using regular 50 by 50 m cells. Vertically, the model was refined into 34 flat layers resulting in 285,600 model cells.

Parameters that were stochastically analyzed using Monte Carlo simulations included:

- Layer thickness – Hydrostratigraphic Units
- Hydraulic conductivity
- Specific storage and specific yield
- Effective porosity
- Diffusion and Dispersivity
- DP Water Total Dissolved Solids (TDS) Concentration (range of 15,000 to 200,000 mg/L)
- DP Water Injection Head (range of 325 m to 1325 m)
- Variation in Regional Hydraulic Gradient
- Recharge

Approximately 2,000 model simulations were completed for both fines and sand-dominated tailings deposits. Simulations in which the TDS concentration in the uppermost one meter of saturated tailings within the impoundment were less than 1000 mg/L after 100 years were considered successful (i.e., saline water was sequestered). Most of the fines-dominated tailings simulations were successful, while a minority of the sand-dominated tailings scenarios were successful. The evaluation of the stochastic groundwater modeling results indicated successful sequestration of brine within the impoundments is not solely determined by a single parameter. It is influenced by the complex interplay between various characteristics of the tailings deposits and groundwater system.

Based on the stochastic groundwater modeling results, the following parameters or conditions can play a role in determining if the sequestration of DP water is feasible within the tailings impoundment:

- The hydraulic properties of tailings, such as horizontal and vertical hydraulic conductivity and effective porosity: the placement of DP water within tailings with low hydraulic conductivity and high effective porosity increases the probability of successful sequestration. The probability of successful sequestration of DP water is higher in fines-dominated tailings than in sand-dominated tailings.
- The TDS concentration of DP water and the depth to the DP water: deeper placement of the DP water increases the probability of successful sequestration in both sand- and fines-dominated tailings.
- Hydrogeology of surrounding aquifers: the impact of the hydraulic properties of surrounding aquifers on sequestrating DP water within the impoundments is more important for the sand-dominated tailings than in fines-dominated tailings. For sand-dominated tailings impoundments, lower hydraulic conductivity of the Upper and Middle McMurray increases the probability of successful sequestration of DP water.
- The dispersion of DP water within the tailings: the upward migration of DP water in tailings is exacerbated by dispersion in both sand and fines dominate tailings.

LESSONS LEARNED

An important finding of this study is the conditions that affect and lead to successful sequestration are principally related to the tailings rather than the natural environment. This suggests that appropriate engineering of the tailings impoundment and sequestration methodology would play an important role in successfully sequestrating DP water within tailings impoundment.

The study conceptually explored the feasibility of sequestering DP water in an oil sands tailings impoundment. The modeling approach included many simplifying assumptions. The results cannot be directly extended to real-world tailings impoundments without considering site-specific conditions. Certain processes and characteristics were also not explicitly simulated, which may be influential in determining successful or unsuccessful sequestration of DP water.

PRESENTATIONS AND PUBLICATIONS

Conferences, presentations, and workshops:

Presentation - 2023 COSIA Mine Water Management Workshop, Edmonton, Alberta.

RESEARCH TEAM AND COLLABORATORS

Institution: Barr Engineering & Environmental Science Canada Ltd

Principal Investigator: Nav Dhadli

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Ryan Conway	Barr Engineering	Hydrogeologist		
Amir Safi	Barr Engineering	Senior Water Resources Engineer		
Jacques Groenewald	Barr Engineering	Senior Hydrogeologist		
Nav Dhadli	Barr Engineering	Vice President – Senior Chemical Engineer		

WE0097 - Geomorphic Basis for Replicating Natural Vegetated Waterways

COSIA Project Number: WE0097

Research Provider: Les Sawatsky, Principal Investigator – Teleo Engineering Ltd

Industry Champion: Imperial Oil Resources Ltd.

Industry Collaborators: Canadian Natural, Syncrude Canada Ltd., Suncor Energy Inc.

Status: In progress

PROJECT SUMMARY

This is the second of a three-phase project to develop a best practices manual for design of vegetated waterways based on the geomorphic approach. Phase 2 commenced at the end of November 2023 and builds on the key learnings of Phase 1. Phase 1 involved extensive interviews with private sector and mining industry specialists, and field inspection of constructed vegetated waterways. Phase 2 extends the GIS analysis of LiDAR DEMs undertaken during Phase 1. The two main deliverables of Phase 2 include a comprehensive geomorphic field survey of natural vegetated waterways summer (2024) and preparation of a two-volume design best practices manual, which will be issued at the end of Phase 2.

PROGRESS AND ACHIEVEMENTS

The progress and achievements of Phase 2 during the first four months of the project include:

- The first task of Phase 2 was to address the issue of non-vegetated conditions in the LiDAR DEMs so the results of the Phase 1 GIS analysis could be used to determine reliable thresholds for flow path lengths and drainage area of vegetated waterways. This work has been completed, resulting in threshold curves for maximum overland flow path lengths that can now be used by the oil sands mining industry for shaping landforms and configuring drainage systems.

- Current work in Phase 2 includes selection of natural analogue candidate survey sites at multiple natural landforms in the oil sands region, and preparation of a detailed plan and specific work instructions (SWIs) for conducting the field survey of natural analogue vegetated waterways. This field survey planning task will be completed by mid-June so the field staff, including the student, can be trained to undertake this work and the field program can commence in July 2024.

- Work has also begun on developing hydrology and tractive force charts that can be used to compare the results of the geomorphic approach with traditional (risk-based) methods of designing vegetated waterways.

- Work on preparing the best practices manual for design of vegetated waterways based on the geomorphic approach is well underway. A comprehensive table of contents complete with content itemization has been prepared and sent out for review to all reviewers and stakeholders.

LESSONS LEARNED

Work on Phase 1 and initial work on Phase 2 has afforded the project team with the following valued learnings.

The most efficient method for eliminating non-vegetated conditions (overland flow path lengths and vegetated waterways) is to constrain the hill slopes and waterway gradients to avoid slopes and gradients where non-vegetated conditions exist in the natural environment. Accordingly, hill slopes of five per cent to 40 per cent were selected for overland flow path lengths and waterway gradients of five per cent to 30 per cent were selected for vegetated waterways. These constraints were deemed to be acceptable because they do not affect usage of the resulting thresholds by designers of steep mine closure landforms in the oil sands region. These constraints do affect usage by designers of low sloped hill slopes and low sloped vegetated waterway conditions, common at the crown and plateau areas of landforms, and at the toe of steep landforms. Further work on low sloped terrain and shallow waterway gradients was deferred to the future in Phase 2.

Density plots of the resulting data show a wide range of natural slope/gradient variability, particularly for steeper slopes/gradients.

Exceedance curve plots show a significant difference between maximum overland flow path lengths at natural landforms composed of high erodibility materials compared to landforms composed of low erodibility materials. Maximum overland flow path lengths at landforms composed of low erodibility materials are upwards of 20 per cent higher than flow path lengths at landforms composed of high erodibility materials.

Exceedance curve plots show an insignificant difference between catchment areas of vegetated waterways at natural landforms composed of high erodibility materials compared to landforms composed of low erodibility materials.

Tentative threshold exceedance curves for overland flow (sheet flow) and vegetated waterway designs are indicated below.

Table 1. Threshold exceedance curves.

Facility	**High Erodible Material (CST)**	**High Erodible Material Covered with LOS**	**Low Erodible Material**
	Recommended Threshold Curve for Design		
MFPL Sheet Flow*	90-percentile	95-percentile	95 or even 98-percentile
Vegetated Waterway*	Never on steep slopes	90-percentile	95-percentile

*These recommended threshold curves are subject to change in the future after collaboration with industry representatives and after continued Phase 2 investigations, such as the upcoming geomorphic field survey of natural analogues.

Proposed threshold curves based on best-fit lines are given below for overland flow path lengths (Figure 1).

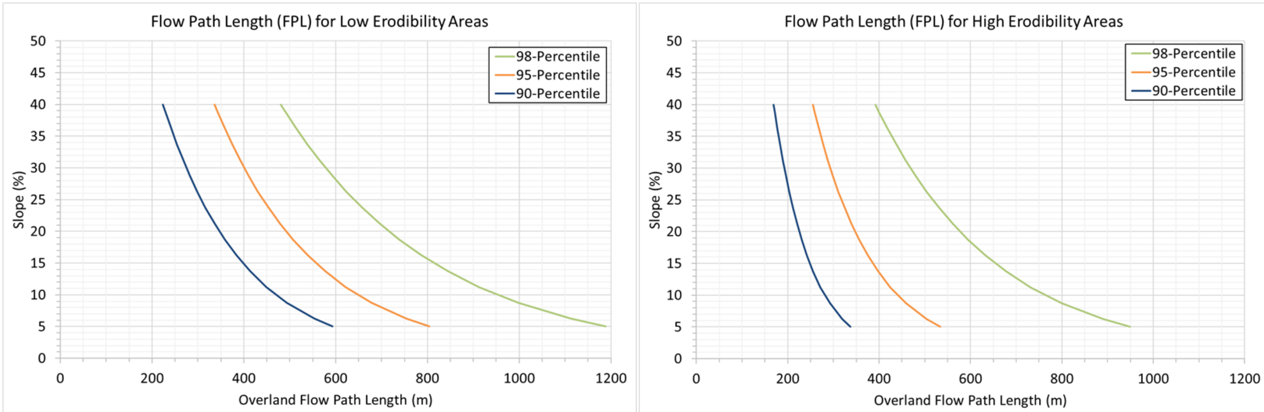

Fig. 1: Proposed threshold curves based on best-fit lines are given below for overland flow path lengths.

PRESENTATIONS AND PUBLICATIONS

Conferences, presentations, and workshops:

Presentations to Kearl Closure Review Board and to CNUL Geotechnical Review Board

Presentation to CNUL Albian Mine Geotechnical Review Board

RESEARCH TEAM AND COLLABORATORS

Institution: University of Saskatchewan (Adjunct Professor - Dirk de Boer, Geomorphologist)

Main subcontractor: WSP

Principal Investigator: Les Sawatsky, Principal Investigator – Teleo Engineering Ltd

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Lanie Guimond	Carleton University	PHD Student	2021	2026

WJ0046 - Wetland Treatment of Oil Sands Process-Affected Water

COSIA Project Number: WJ0046

Research Provider: Simon Fraser University (Frank Gobas) with financial support from NSERC and Imperial Oil Resources Ltd.

Industry Champion: Imperial Oil Resources Ltd.

Industry Collaborators: None

Status: Complete

PROJECT SUMMARY

Large volumes of oil sands process-affected water (OSPW) have been generated through mining operations and bitumen extraction in the Canadian oil sands. Oil sands operators have successfully reduced freshwater requirements during bitumen extraction, but have not released what, as policy does not exist to allow release, Treatment technologies are being evaluated to reduce the ecological footprint and enable release of treated OSPW to the Athabasca River. Ongoing efforts to find feasible treatment solutions have identified treatment wetlands as a potential treatment technology to improve water quality of OSPW. To investigate the application of treatment wetlands in the oil sands mining sector, a one-hectare surface-flow wetland was constructed on Imperial's Kearl Oil Sands site in 2013.

The study's overall goal is to improve the science of treatment wetland technology in Canada's oil sands. Using a combination of passive samplers and aqueous grab sampling, wetland treatment efficiency was evaluated at the Kearl Treatment Wetland for polycyclic aromatic hydrocarbons (PAHs) and naphthenic acids (O2-NAs). This data was used to test and evaluate a contaminant-fate model for both neutral and polar organic contaminants to determine which contaminants can be removed via wetland treatment.

PROGRESS AND ACHIEVEMENTS

In previous years, the concentration-reduction and mass-removal of both PAHs and O2-NAs in the Kearl Treatment Wetland was demonstrated by employing both passive sampling and aqueous grab sampling techniques. This data was used to test and evaluate a contaminant-fate model of the Kearl Treatment Wetland (Cancelli and Gobas, 2024). The final phase of this work was to disseminate the model and supporting data for use by the industry and the scientific community. The model was programmed into Microsoft Excel using Visual Basic for Applications to provide a user-friendly model interface. The model is fully adaptable so it may provide a tool for assessing trade-offs in the design and operation of future treatment wetland projects in Canada. Industry practitioners may use the model to determine the appropriate size of the wetland, optimal flow rates and hydraulic retention time needed to reduce contaminant concentrations to meet water quality guidelines. The model is presented through the Simon Fraser University - Environmental Toxicology Research Group webpage (https://www.sfu.ca/rem/wetlandmodel.html). Our project publications and additional resources regarding model function and application are also available.

LESSONS LEARNED

This research has advanced our understanding of treatment wetlands as a pollution remediation technology. The findings of this research can help support the implementation of phytoremediation remediation technology across other industries in Canada and world-wide.

Knowledge transfer is an important component to this research project to help ensure the findings can be applied throughout the oil sands industry, and to other industries in Canada in need of cost-effective and efficient wastewater treatment options. Therefore, our findings are made readily accessible to the scientific community and industry operators.

PRESENTATIONS AND PUBLICATIONS

Journal Publications:

Published

Cancelli, A. M., & Gobas, F. A. P. C. (2024). Development and testing of a mechanistic model for wetland treatment of neutral and polar organic contaminants in oil sands process-affected water. Ecological Engineering, 198, 107145.

Cancelli, A.M.; Borkenhagen, A.K.; Bekele, A. A Vegetation Assessment of the Kearl Treatment Wetland following Exposure to Oil Sands Process-Affected Water. Water 2022, 14,3686.

Cancelli, A.M.; Gobas, F.A.P.C. 2022. Treatment of naphthenic acids in Oil Sands Process-Affected Waters with a Surface Flow Treatment Wetland. Environmental Research, 213.

Cancelli, A.M.; Gobas, F.A.P.C. 2020. Treatment of Polycyclic Aromatic Hydrocarbons in Oil Sands Process-Affected Water with a Surface Flow Treatment Wetland. Environments, 7, 64.

Conferences, presentations, and workshops:

Cancelli, A. M., Gobas, F.A.P.C. November 30-December 1, 2021. Treatment of OSPW in the Kearl Treatment Wetland. Canadian Oil Sands Innovation Alliance, Mine Water Management Workshop 2021, *virtual.*

Cancelli, A. M., Gobas, F.A.P.C. November 3-7, 2019. The treatment of oil sands process-affected water with the Kearl Treatment Wetland. Society of Environmental Toxicology and Chemistry, 40th North American Annual Meeting, Toronto, ON.

Cancelli, A. M., Gobas, F.A.P.C., Bekele, A. June 3-4, 2019. The removal of organic contaminants from OSPW in the Kearl Treatment Wetland. Canadian Oil Sands Innovation Alliance, 2019 Oil Sands Innovation Summit, Calgary, AB.

Cancelli, A. M., Gobas, F.A.P.C., Bekele, A. May 10, 2019. The removal of organic contaminants from OSPW in the Kearl Treatment Wetland. 11th Western Symposium on Water Quality Research, Edmonton, AB.

Cancelli, A. M., Gobas, F.A.P.C. November 4-8, 2018. A model of contaminant removal from oil sands process-affected waters in the Kearl Treatment Wetland. Society of Environmental Toxicology and Chemistry, 39th North American Annual Meeting, Sacramento, CA.

Cancelli, A. M., Gobas, F.A.P.C. June 7-8, 2018. Quantifying the removal of polycyclic aromatic hydrocarbons in the Kearl Treatment Wetland. Canadian Oil Sands Innovation Alliance, Oil Sands Innovation Summit, Calgary, AB.

Cancelli, A. M., Gobas, F.A.P.C. Sept 6-7, 2018. Model performance evaluation using passive samplers at the Kearl Treatment Wetland. Canadian Oil Sands Innovation Alliance, Science Workshop: Oil Sands Process Wastewater Characterization, Identification, and Treatment, Calgary, AB.

Brueggeman, J., Gobas, F.A.P.C., Cancelli, A.M. November 13 – 17, 2022. Application of Biomimetic Extraction to Measure Toxicity Reduction in Oil Sands Process-Affected Water After Wetland Treatment. Society of Environmental Toxicology and Chemistry, 43rd North American Annual Meeting, Pittsburgh, PA.

RESEARCH TEAM AND COLLABORATORS

Institution: Simon Fraser University

Principal Investigator: Frank A.P.C. Gobas

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Prof. Frank A.P.C. Gobas	Simon Fraser University	Professor		
Alexander M. Cancelli	Simon Fraser University	Postdoctoral Fellow		
Nina Piggott	Simon Fraser University	Master's student	2018	2022
Julia Brueggeman	Simon Fraser University	Master's student	2019	2023

WJ0139 - Carbonix Activated Carbon Project

COSIA Project Number: WJ0139

Research Provider: Ashkan Zolfaghari

Industry Champion: Suncor Energy Inc.

Industry Collaborators: Pathways Alliance

Status: Year 3 of 3

PROJECT SUMMARY

This project focuses on converting petroleum coke (petcoke), a byproduct of oil sands extraction, into activated carbon through chemical and thermal activation methods. The objective is to evaluate the activated carbon's efficiency, yield, and surface properties for use in environmental remediation, water treatment, and tailings management. The project broadly addresses Oil Sands Process-affected Water (OSPW) management from multiple angles.

- ***Modified petcoke as an adsorbent:*** One of the project's objectives is to explore modifying petcoke to improve its ability to remove pollutants from OSPW. By enhancing its adsorption capacity for organic contaminants such as naphthenic acids and toxic metals, the modified petcoke could contribute to more effective tailings and petcoke management while supporting regulatory compliance.

For Suncor's petcoke, potassium hydroxide (KOH) proved the most effective activation method, producing large surface areas and ideal pore structures for adsorption. The optimized KOH method enhanced mesoporosity, improving water treatment performance. This project also assessed activated petcoke's ability to remove organic pollutants such as naphthenic acids from OSPW and adsorb toxic metals such as arsenic, chromium, and selenium.

- ***Modified petcoke as a flocculant aid:*** Another project objective is to evaluate modifying petcoke to enhance flocculation in the PASS (Permanent Aquatic Storage Structure) process. The developed flocculant aid can potentially improve the dewatering process, reduce chemical consumption, streamline petcoke management, and lower overall process costs. Preliminary results indicate petcoke can be modified by grafting polymeric chains onto its surface, enhancing dewatering performance.

PROGRESS AND ACHIEVEMENTS

The project's initial phase involved converting petcoke into activated carbon using various activation methods. Among these, KOH activation proved most effective. This method produced activated petcoke with a surface area ranging from 900 to 2,200 m^2/g, depending on the KOH ratio and heat cycles applied. The yield was higher (60–75 per cent) compared to methods using steam or sodium hydroxide. The carbon's pore structure was predominantly microporous, with mesoporosity increasing with additional heat cycles.

Subsequent efforts focused on optimizing the pore structure to enhance adsorption capacity. Increasing the number of heat cycles significantly improved mesoporosity, raising it from 25 per cent to 63 per cent. This adjustment resulted in a surface area of 1,800–2,200 m^2/g and a yield exceeding 50 per cent, achieving a balance between pore enhancement and carbon retention. The effectiveness of the activated petcoke in removing organic contaminants, particularly naphthenic acids. The modified petcoke demonstrated a high adsorption capacity, ranging from 70 to 90 mg/g, with a removal efficiency of up to 95 per cent. The research also extended to the adsorption of inorganic contaminants, including metals and ions. The modified petcoke exhibited promising performance in adsorbing arsenic, chromium, and selenium, with capacities of 75–90 mg/g, 60–85 mg/g, and 50–70 mg/g, respectively. Ion exchange efficiencies were also notable, with chloride and sodium ions removed at rates of 80 per cent and 85 per cent.

The project's second phase focuses on modifying petcoke to serve as a flocculant aid for the PASS process. Preliminary results indicate polymers can be successfully grafted onto the surface of the modified petcoke. As a flocculant aid, the modified petcoke has demonstrated promising potential, with settlement rates increasing by more than 30 per cent. Ongoing efforts aim to further enhance the performance and cost-effectiveness of the modified petcoke.

LESSONS LEARNED

This project focuses on modifying petcoke into high-adsorption activated carbon, to addresses pollutants such as naphthenic acids and toxic metals in oil sands process-affected water (OSPW). It also promotes water recycling and waste reduction while aligning with future environmental regulations for tailings management. The modified petcoke has demonstrated potential for various applications. These include use as an adsorbent for improved removal of harmful contaminants in water treatment and as a substrate for polymer grafting to accelerate dewatering during OSPW treatment, transforming a waste byproduct into a valuable resource.

PRESENTATIONS AND PUBLICATIONS

Journal articles

Published

T.M. Roy, E. Nazari, O.K.L. Strong, P.R. Pede, A.J. Vreugdenhil. The Effect of Adsorbent Textural and Functional Properties on Model Naphthenic Acid Adsorption. *J. Env. Sciences* January *J. Env. Sciences* January, 148, 27-37 (2025). https://doi.org/10.1016/j.jes.2024.01.003

S. J. Bégin, K.M. Scotland, P.R. Pede, A.J. Vreugdenhil. Polyacrylamide Grafted Activated Carbon by Surface-Initiated AGET ATRP for the Flocculation of MFT., Macromolecular Chemistry and Physics. 2300223. (2023). https://doi.org/10.1002/macp.202300223

K.S. Fisher, A.J. Vreugdenhil. Metal-Impregnated Petroleum Coke-Derived Activated Carbon for the Adsorption of Arsenic in Acidic Waters., ACS Omega. 8(32) 29083-29100 (2023). https://doi.org/10.1021/acsomega.3c02078

K.M. Scotland, S. J.Bégin, O.K.L. Strong, P.R.Pede, A.J. Vreugdenhil. The development of a novel non-leaching flocculant, derived from activated carbon and polyacrylamide. Can J. Chem Eng. 1-9. (2023). https://doi.org/10.1002/cjce.25040

O.K.L. Strong, E. Nazari, T. Roy, K.M. Scotland, P.R. Pede, A.J. Vreugdenhil. (2023). Transforming micropores to mesopores by heat cycling KOH activated petcoke for improved kinetics of adsorption of naphthenic acids. Heliyon. 9 (2) e13500 (2023). https://doi.org/10.1016/j.heliyon.2023.e13500

K.S. Fisher, A.J. Vreugdenhil. (2022) Adsorption of Chromium (VI) Using an Activated Carbon Derived from Petroleum Coke Feedstock. International Journal of Molecular Sciences 23 (24), 16172 (2022). https://doi.org/10.3390/ijms232416172

RESEARCH TEAM AND COLLABORATORS

Institution: Carbonix

Principal Investigator: Paul Pede

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TBD (Anjali Leal)	Trent University	Post Doctoral Fellow (Fall 2024)		
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Kyle Reyes	Trent University	M.Sc.	09/2022	12/2024
Teagan Carr	Trent University	M.Sc.	09/2023	12/2025
Nethma Dissanayke	Trent University	M.Sc.	09/2023	12/2025
Sogol Hajifathali	Trent University	M.Sc.	01/2025	04/2027

WJ0188 - Optimizing OSPW Treatment in Constructed Wetland Systems with Genomic-Based Tools

COSIA Project Number: WJ0188

Research Provider: University of Calgary and Natural Resources Canada

Industry Champion: Imperial Oil Resources Ltd.

Industry Collaborators: None

Status: Year 3 of 4

PROJECT SUMMARY

A broad family of organic compounds called naphthenic acid fraction compounds (NAFCs) are constituents of oil sands process-affected water (OSPW) and may contribute to its toxicity. Constructed wetland treatment systems (CWTS) is a scalable and cost-effective method being considered for the treatment of OSPW. The optimal conditions required to establish specialized wetland biological communities able to degrade NAFCs, as well as the specific degradation pathways involved in these processes, are currently not well understood. This research project aims to apply genomic tools to better understand NAFC biodegradation processes in CWTS and provide insight on approaches to enhance the efficacy of CWTS for OSPW treatment. Using mesocosm-scale greenhouse experiments and a pilot-scale CWTS on Imperial's Kearl Oil Sands site as experimental systems, this project will:

1. Assess the dynamics and efficacy of CWTS for the treatment of OSPW under varying conditions;
2. Identify key biological components (microbes, plants, genes) that operate in reducing OSPW toxicity and NAFC biotransformation;
3. Examine the fate of NAFCs from biodegradation;
4. Advance the development of passive samplers and biosensors for NAFC toxicity and quantification;
5. Develop contaminant fate models for the optimization of CWTS design;
6. Use advanced social science methods to provide technical recommendations and social perspectives related to the use of genomics for improving water treatment with CWTS.

This transdisciplinary project is funded by Genome Canada as part of the Large-Scale Applied Research Project (LSARP) Program and involves 16 research groups from universities and federal institutions across Canada. While this project is focused on the remediation of NAFCs, the approaches and outcomes are expected to contribute to the know-how and application of CWTS treatment of other contaminants in various industrial and municipal wastewater.

PROGRESS AND ACHIEVEMENTS

This research project consists of five integrated research activities that have all been progressing in parallel.

Activity 1 – Optimize the rate of NAFC remediation using CWTS mesocosm systems

In this activity, replicated surface-flow greenhouse mesocosm experiments are conducted to determine the impact of various parameters, such as plant species and temperature, on microbial community structure and the remediation of OSPW. While providing valuable insight for the optimization of future CWTS, these experiments contribute rhizosphere/root samples for metagenomics analyses (Activity 2) as well as data to construct predictive models (Activity 4). Three experiments were completed so far using different plant species, which included Carex aquatilis in Experiment #1, Triglochin maritima and Scirpus microcarpus in Experiment #2, and Typha latifolia and Juncus balticus in Experiment #3.

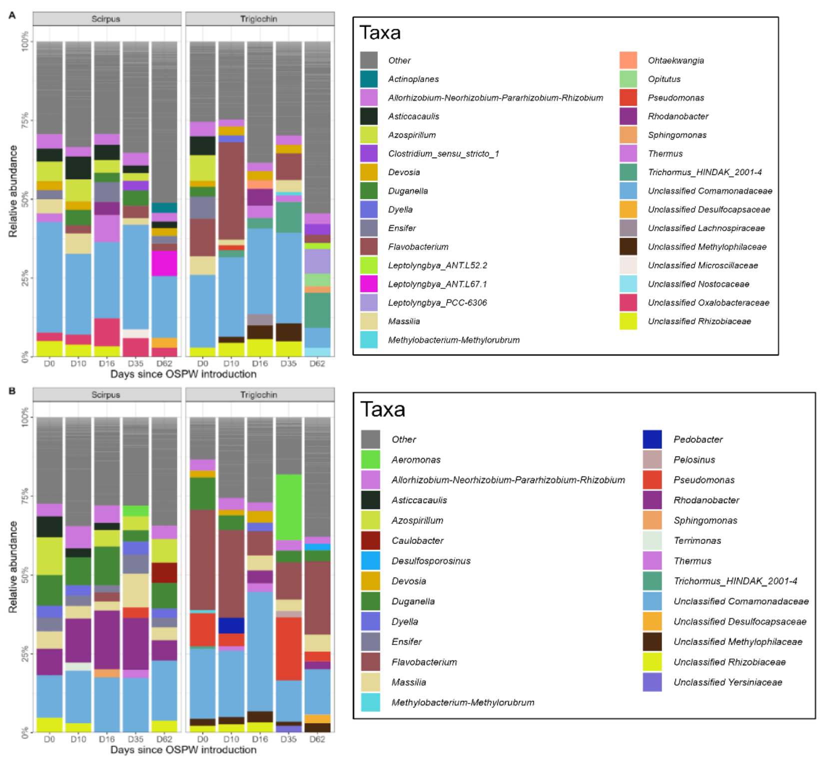

Figure 1. Relative abundance of the top 10 most abundant bacterial genera in the roots of S. microcarpus and T. maritima for each sampling date A) 20°C day, 10°C night mesocosms and B) 10°C day, 5°C night mesocosms. The remaining genera were pooled in the "Other" category.

One manuscript summarizing the results from Experiment #1, which showed an improved remediation of NAFCs in mesocosms planted with C. aquatilis when compared to unplanted controls, is now published (Trepanier et al. 2023). A second manuscript describing plant growth, microbial communities, and NAFC degradation under two temperature regimes (20°C day, 10°C night vs 10°C day, 5°C night) in mesocosms planted with either T. maritima or S. microcarpus (Experiment #2) is in preparation. Although the various treatments led to changes in plant growth and health as well as microbial community composition (Fig. 1), the NAFC degradation rate was lower than in experiment #1 and not significantly impacted by the treatments in this experiment, indicating that other factors, such as nutrient availability, may have been limiting the degradation process.

Compilation and analysis of results from mesocosm Experiment #3, which aimed at characterizing the efficacy of two other plant species, *Typha latifolia* and *Juncus balticus*, to remediate OSPW in CWTS, continued to progress in the past six months. Beside the use of different plant species, this third experiment differed from the previous ones regarding 1) the addition of fertilizers to the mesocosms to avoid the nutrient deficiency observed in Experiment #2 and 2) the addition of control mesocosms filled with reverse osmosis (RO) water ran in parallel with the OSPW mesocosms to better assess the direct impact of OSPW on plant growth and microbial associations.

Activity 2. Deepen the understanding of the mechanisms of NAFC metabolism and enrich for microorganisms with enhanced NAFC degrading ability

Activity 2 aims to enhance our understanding of genes and pathways involved in NAFC degradation and toxicity reduction in plants and microorganisms through the metagenomics and metatranscriptomics analysis of samples from Activity 1, the enrichment and isolation of NA degrading bacteria and algae from samples collected in activity 3, and the implementation of plant laboratory experiments. An important first step for this activity has been to review and summarize the literature on microorganisms and genes currently known to be involved in NA degradation, which is now published (Reis et al. 2023). The list of NA degradation genes identified was used in the past year to screen the metagenomes and metatranscriptomes of sediment and rhizosphere samples collected from mesocosm experiments and the Kearl wetland, allowing to identify several genes that could be involved in the remediation of NAFCs in these systems.

Assessment of the contribution of resident bacterial and algal communities and isolates to NAFC degradation and toxicity reduction is also ongoing. Previous bacterial and algal isolations from water samples from Mesocosm experiments #1 and #2 and the Kearl wetland revealed four bacterial isolates and two algal isolates that appeared to be tolerant of naphthenic acids. These isolates were then tested in liquid culture for their ability to biodegrade CHCA (cyclohexane-1-carboxylic acid) and AdCA (1-adamantane carboxylic acid). The promising bacterial isolates tested were identified as being members of the genera *Exiguobacter*, *Peribacillus*, *Chania*, and *Rhodococcus*. All isolates showed NA degradation to different extents. *Exiguobacter*, *Peribacillus* and *Chania* almost fully consumed CHCA within seven days of incubation, while *Peribacillus* and *Chania* also consumed approximately 90 per cent of the added AdCA within 72 days of incubation. Similarly, several NA-tolerant isolates were obtained from sediment, rhizosphere and root samples from the Kearl wetland. Fourteen of these isolates, mostly belonging to the *Pseudomonas genus*, were tested for NA degradation in growth medium supplemented with NA as the only carbon source or in the presence of an additional carbon source (peptone) in a two-timepoint test. Out of the 14 isolates, 10 showed degradation of CHCA and 6 of AdCA without the addition of peptone. These numbers increased to 13 for CHCA and 12 for AdCA when peptone was added. The genomes of the most promising isolates recovered from water and from sediment, rhizosphere and root samples have been sequenced and are being screened for NA degradation genes.

A subset of bacterial isolates with or without NA tolerance and/or plant growth-promoting potential were transformed separately with Green and Red Fluorescent Protein expression vectors to allow for visualization of colonization and localization patterns in plants using epi-fluorescence and confocal microscopy (Fig. 2). Various germinating seed and seedling inoculation procedures are being tested under controlled conditions, and imaging is well underway to determine colonization and stability of the strains within and on the surface of roots. These strains will later be inoculated into plant systems exposed to OSPW to determine how environmental stressors may impact isolate persistence and localization in soil environments.

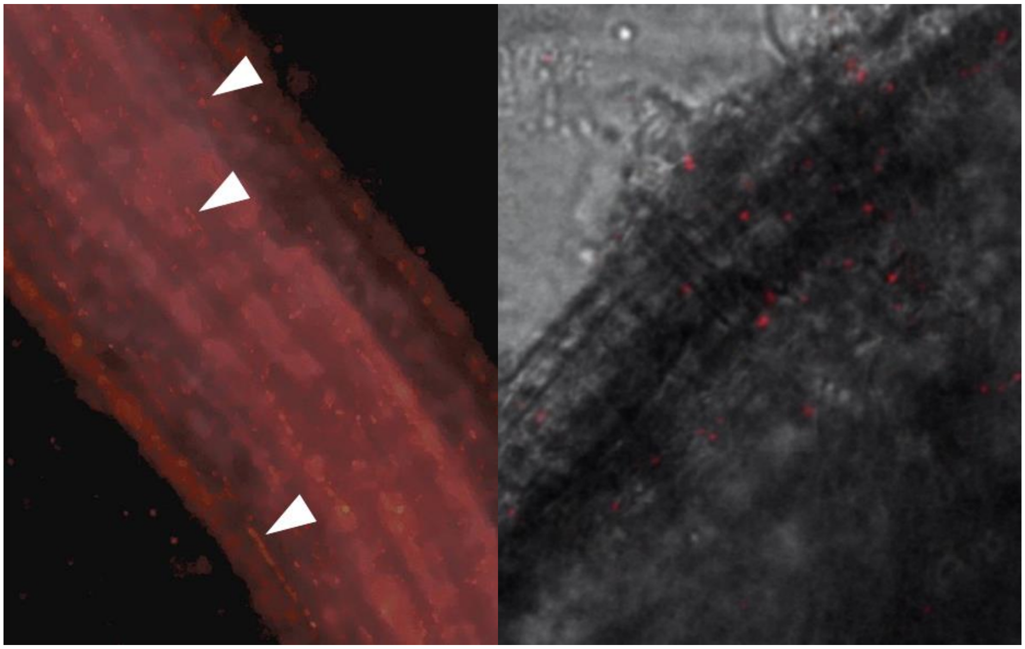

Figure 2. Epifluorescence images of selected red fluorescent protein (RFP)-expressing bacterial isolates inoculated into root tissue of cattail (T. latifolia). Left panel, epi-fluorescence image of a root showing intercellular colonization (arrows) of an isolate of RFP-expressing Rahnella aquatilis (an NA tolerant and growth promoting isolate) 18 days after seedling inoculation. Right panel, mid-focal plane confocal image through a cattail germinated seed tissue five-days post-inoculation with RFP-expressing Pseudomonas sp. J0f29, an NA tolerant non-growth promoting isolate. This image is overlaid onto the brightfield image to show the details of endophytic root colonization of the red fluorescing Pseudomonas cells.

Work aiming at further characterizing the uptake/degradation of NAs by plants and identify potential genes involved in this process has also been progressing in the past year. In a previous publication (Alberts et al., 2021 Sci. Total Environ.), we demonstrated upland plants (sandbar willow and slender wheatgrass) were able to take up five ^{14}C-NA (radioactive) species, ranging from labile to recalcitrant (HA, DA, CHCA, CPCA and AdCA). This work showed plants can take up each of these NAs into the vascular tissue and translocate the carbon to rapidly dividing cells in root and shoot tissues. To determine if wetland plant species can also take up NAs into root and shoot tissue, a radiolabelling experiment was conducted using one of the wetland plant species, Baltic rush (*Juncus balticus*). Plants were exposed to ^{14}C-cyclohexanepentanoic acid (^{14}C-CPCA) and ^{14}C-adamantanecarboxylic acid (^{14}C-AdCA) hydroponically for 24 hours to determine if the radiolabelled ^{14}C-NAs could be taken up by this species. *J. balticus* roots removed 95 per cent and 69 per cent of the ^{14}C-CPCA and ^{14}C-AdCA from the solution, respectively, compared to no-plant controls that had negligible ^{14}C-NA removal. Phosphorimaging (Fig. 3) showed that there was uptake of both naphthenic acids into the root tissue and movement of the radiolabel into the shoot tissue with more ^{14}C-CPCA radiolabel translocated to shoot tissue than ^{14}C-AdCA.

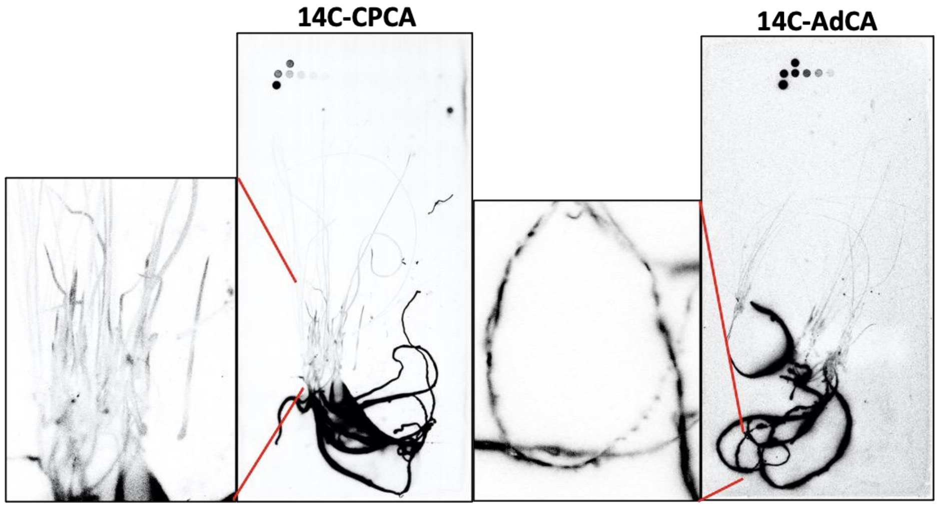

Figure 3. Whole plant radiolabeling of Juncus (baltic rush) with ^{14}C-CPCA and ^{14}C-AdCA. Images collected after a 24-hour pulse label and 24-hour chase period. Shoots are highlighted in the left panel and roots in the right panel.

Finally, a genetic screen using a model plant species is also progressing with the identification of several plant lines having growth tolerance to high NA concentration treatments. A total number of 14 confirmed NA-tolerant lines have been identified so far using this approach. To locate the T-DNA insertion site(s) within each of the NA-tolerant lines, whole genome sequencing (~135 Mb Arabidopsis genome) was performed on the first eight lines. The initial analysis resulted in the identification of T-DNA insertion sites in four of the eight lines.

Activity 3. Analyze the biological dynamics and bioremediation ability of a pilot CWTS

The Kearl CWTS is a one-hectare recirculating, horizontal surface flow wetland that currently operates with a 14-day water retention time and 400 m^3 outflow per day. The wetland has been operational since 2013. OSPW was first introduced into the system in 2021. Sampling of the wetland in 2022 was comprehensive, with more than 1000 samples collected throughout the field season (from May to Sept. 2022), including water samples, sediments, and plant tissues (*C. aquatilis* and *T. latifolia*) for physico-chemical, microbiological, and genomics analyses. Analysis of these samples was mostly completed in 2023, improving our understanding of the system. NAFC attenuation (Fig. 4) and O2 class dynamics (Fig. 5) were observed using Orbitrap MS and correlated in an almost complete reduction of toxicity (95 per cent), as indicated by an early-life stage rainbow trout mortality test after 15 days of treatment in the Kearl CWTS.

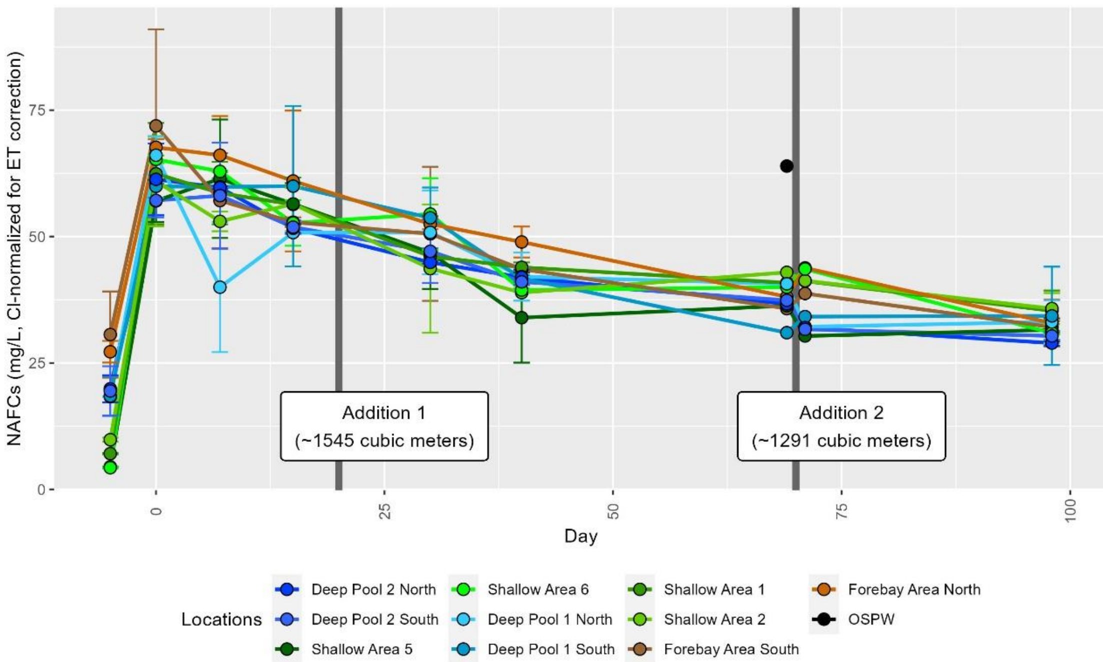

Figure 4. NAFC concentrations in the Kearl wetland water in the 2022 season as determined by Orbitrap MS. Additional OSPW transfer events to compensate for water loss through evapotranspiration are indicated by dark gray vertical bars on the graph.

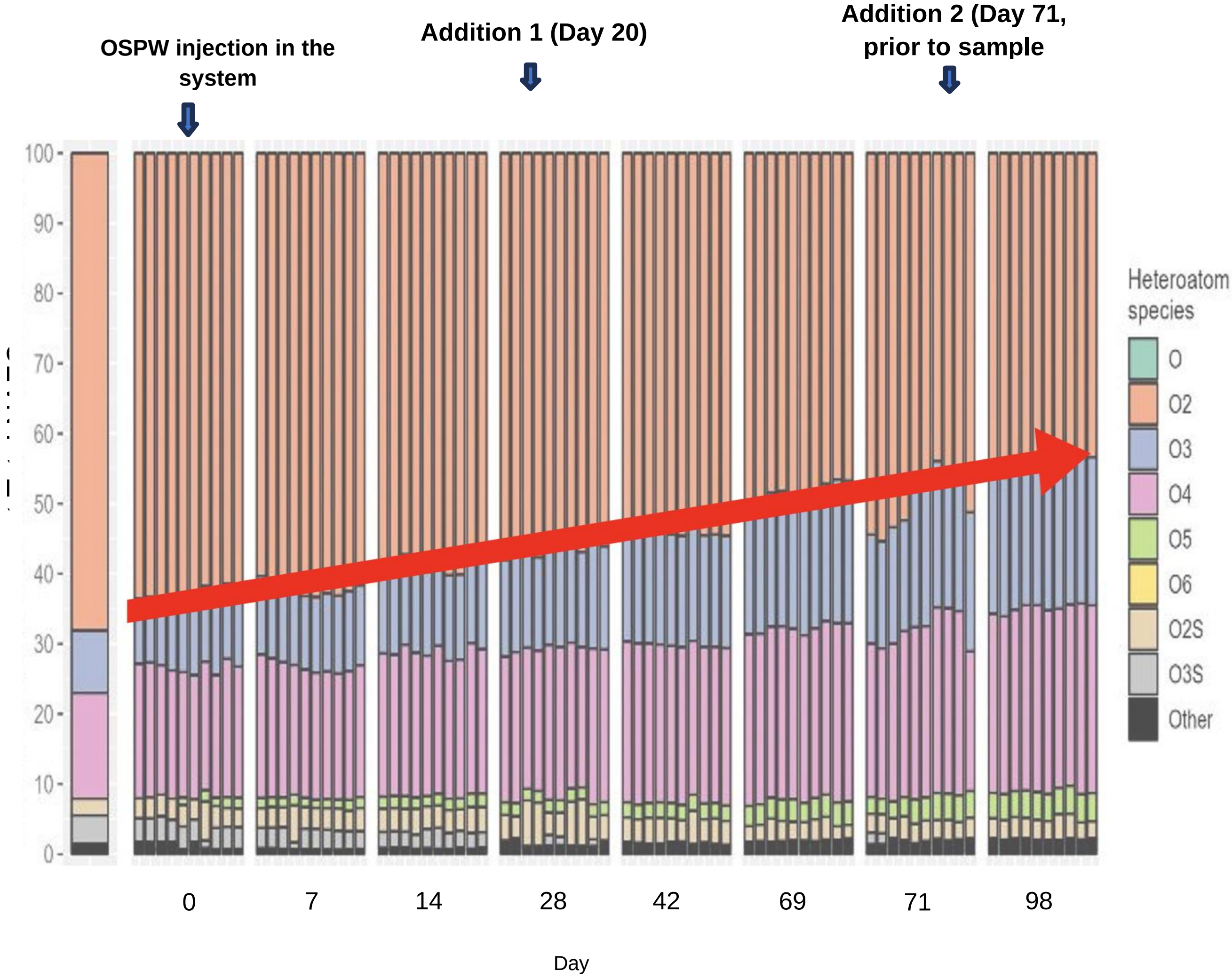

Figure 5. Changes in NAFC heteroatom species over 98 days in the 2022 Kearl wetland. Red arrow demonstrates a consistent decrease in O2 species and increases in O3 and O4 oxy-NAs. Blue arrows indicate initial injection of OSPW in the Kearl wetland on Day 0 followed by additional OSPW transfer events to the system to compensate for water loss through evapotranspiration.

Characterization of microbial communities of the Kearl CWTS 2022 samples have also been completed in the past year. A 16S rRNA gene and ITS2 metabarcoding approach was used to characterize microbial communities in water, sediment, and plant samples collected in the CWTS. The various sample types showed distinct communities and temporal trends. Water prokaryotic communities consistently shifted throughout the season (Fig. 5), following the same trend as physicochemical properties, while in soil, roots, and rhizosphere, a shift was mostly observed following the addition of OSPW in the CWTS, indicating these communities were more stable. Vegetation was identified as an important driver of microbial communities, with distinct communities found when comparing highly vegetated shallow areas to deeper areas, as well as the rhizosphere and roots of the two dominant plant species in the system, *Carex aquatilis* and *Typha latifolia*. Overall, our findings indicate microbial communities are a key component of constructed wetlands and a great target for the optimization of these systems for NAFC degradation.

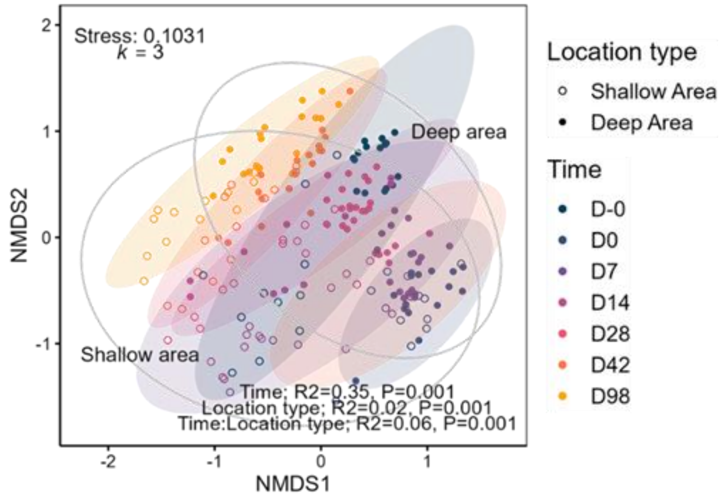

Figure 6. NMDS based on Bray-Curtis dissimilarity matrix calculated from square root transformed and Wisconsin double standardization bacterial community matrix showing water prokaryotic communities over time with 95 per cent confidence interval ellipse around groups based on 16S rRNA gene amplicon sequencing. Results from PERMANOVA are indicated at the bottom left of the figures

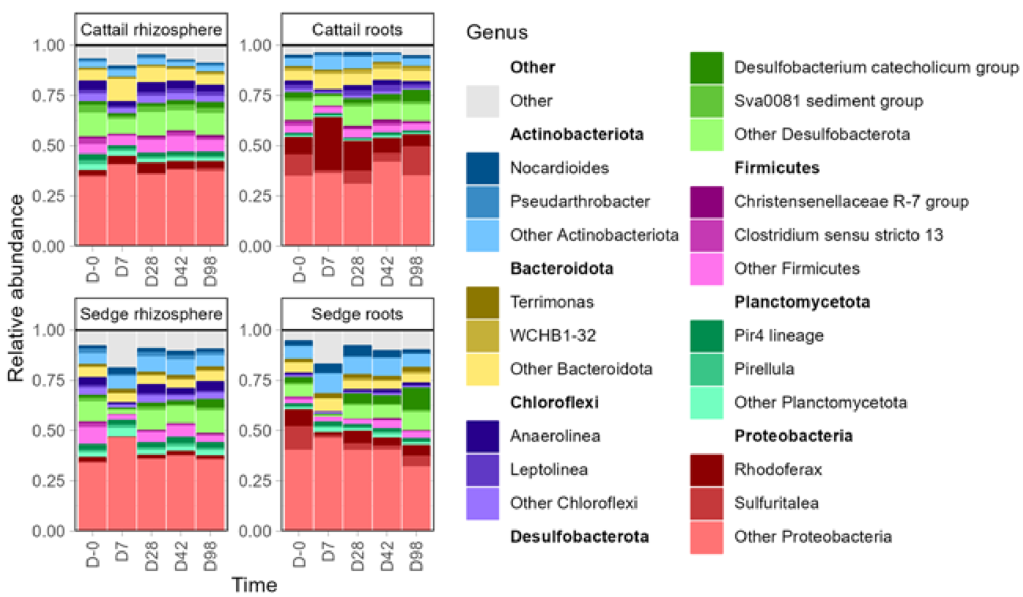

Figure 7. Relative abundance of the most abundant bacterial taxa by location type and timepoint in plant rhizosphere and roots based on 16S rRNA gene amplicon sequencing.

This project also aims to enhance and develop simple and efficient ways of testing for OSPW toxicity and NA remediation efficiency. These tools have the potential to reduce costs and effort, use small water volumes, and eliminate the use of animals for toxicity testing. Biomimetic Extraction - Solid Phase Micro Extraction (BE-SPME) has been shown to be an effective "passive sampler" of the bioavailable NAFCs in treated OSPW. This project aimed at further calibrating the BE-SPME assay approach using rainbow trout and walleye embryo development. The analysis of data from 30-day toxicity tests with these two species was completed and concentration-response relationships for survival and reproduction using BE-SPME was generated.

Sensitive and specific biosensors relying on the diverse environmental and metabolite sensing mechanisms of bacteria are also being developed and tested in this project as a simple, rapid, inexpensive and high throughput technology to detect and quantify NAs. Testing of OSPW samples from mesocosm experiments and Kearl CWTS using these biosensors showed minimal responses, indicating low NA concentrations. A rapid extraction method using dichloromethane (DCM) and small volumes of OSPW (1-5 mL) has been developed to improve the sensitivity.

Activity 4 – Integration and synthesis of CWTS and genomics data using bioinformatics and mass balance modeling

The development of mass balance and genomic-based models are used in this project to (i) explore the role of genomic data in relation to other physical, chemical and ecological characteristics/data affecting wetland treatment; (ii) relate observations at the lab, mesocosm and field scales; (iii) extrapolate results from this study to alternative conditions in the wetland or other wetlands in Canada; and (iv) document and formalize the findings of this study for future studies. Contaminant fate modeling allowed integration of findings on plant uptake and metabolism, microbial degradation, wetland characteristics (e.g., dimensions, hydraulic retention), environmental conditions and toxicity. An updated contaminant-fate model was developed for application to the mesocosm experimental units. The model now consists of four compartments (water, sediment, plant root, plant leaf), which corresponds with the expected concentration measurements available from the experiments. NAFC concentrations will be modeled in each compartment using a mass-balance approach. Model parameterization to the mesocosm units is currently underway. In-silco methods are being explored to determine the physical-chemical properties (e.g. octanol-water distribution coefficient, Henry's Law constant, pKa, etc.) of NAFCs, which are needed for model application. Data for model development, evaluation and testing continues to be generated in other activities and will be integrated in the model as they become available. Genomic-based modeling has also been progressing in the past year. The models generated yielded convincing results allowing to identify differentially abundant phyla, genus and KEGGS linked to higher NA removal and could potentially be used to optimize CWTS.

Activity 5 – Using advanced social science methods to provide technical recommendations and social perspectives related to the use of genomics for improving water treatment with CWTS

This activity examines social, cultural, economic, legal and artistic dimensions associated with genomic-informed bioremediation and aims at better understanding public perceptions and preferences on the topic. The components of this activity are integrated throughout the project (Activities 1 through 4) and will combine multiple advanced social science methods, including engaged research in the form of initial and progressively deepening experimental decision laboratories (EDL), focus groups, Q-sorting, a national survey, and arts-based research-creation. This research is progressing well, however, details are not provided here as this research is outside of the scope of this report.

LESSONS LEARNED

This project is advancing knowledge and understanding of the mechanisms underlying NAFC degradation and OSPW toxicity reduction in CWTS by applying state-of-the-art genomic tools to the study of 1) meso-scale replicated experimental systems, allowing the measurement of the effect of multiple treatments under controlled conditions and 2) a pilot-scale experimental system reflecting *in situ* conditions. This work has shown plant-associated microbial communities are dynamic in response to OSPW exposure and vegetation type can influence what microorganisms are colonizing CWTS, with potential impacts on NAFC remediation. Further work is needed to clearly identify microorganisms, genes and pathways that drive NAFC biodegradation and develop strategies to enhance this process. The detection of several NA degradation genes in our samples, the isolation of multiple NA-tolerant bacterial and algal strains, and the identification of plant genetic variants that demonstrate growth tolerance on high levels of NAs are all important first steps towards achieving project goals.

PRESENTATIONS AND PUBLICATIONS

Journal Publications:

Published

Reis PCJ, Correa-Garcia S, Tremblay J, Beaulieu-Laliberté A, Muench DG, Ahad JME, Yergeau E, Comte J, Martineau C (2023) Microbial degradation of naphthenic acids using constructed wetland treatment systems: metabolic and genomic insights for improved bioremediation of process-affected water. FEMS Microbiol Ecol 99(12):fiad153. https://doi.org/10.1093/femsec/fiad153

Trepanier KE, Vander Meulen IJ, Ahad JME, Headley JV, Degenhardt D (2023) Evaluating the attenuation of naphthenic acids in constructed wetland mesocosms planted with Carex aquatilis. Environ Monit Assess 195(10):1228. https://doi.org/10.1007/s10661-023-11776-8

Hindle R, Headley J, Muench DG (2023) Pros and cons of separation, fractionation and cleanup for enhancement of the quantitative analysis of bitumen-derived organics in process-affected waters – A Review. Separations. 10:583. DOI: https://doi.org/10.3390/separations10120583

Conferences, presentations, and workshops:

Talagbé Gabin Akpo, Sara Correa-Garcia, Étienne Yergeau and Amadou Barry. An ecologically sustainable solution to mitigate the environmental impact of tar sands oil. Comité Intersectoriel en Santé Durable (CISD) student seminar, University to Québec at Chicoutimi (UQAC). December 06 2023.

Alexander M. Cancelli. Development and testing of a mechanistic model for wetland treatment of neutral and polar organic contaminants in oil sands process-affected water. SETAC 2023. Louisville, KY. November 12 – 16, 2023.

Talagbé Gabin Akpo, Sara Correa-Garcia, Étienne Yergeau and Amadou Barry. Modeling metagenomic data for oil sands impact reduction, 13ème Congrès Armand-Frappier, Manoir Saint Sauveur, QC. Octobre 30 – Novembre 1, 2023.

Alvarez, A., Bradford, L., (2023). Traditional and Scientific Knowledge in Environmental Solutions. Case Study: Constructed Wetlands for Oil Sands Processed Water Remediation. Poster Presentation. The 10th International Conference on Energy and Environment Research (ICEER 2023) Madrid, Spain, October 7-9, 2023.

Paula Reis, Xiangbo Yin, Julien Tremblay, Marie-Josée Bergeron, Jason Ahad, Carolina Berdugo-Clavijo, Jérôme Comte, Christine Martineau. Metagenomics and stable isotope probing insights into naphthenic acids degradation in constructed wetland treatment systems. RE3 conference in Quebec city. June, 2023.

Aurélie Beaulieu-Laliberté, Paula Reis, Marie-Josée Bergeron, Carolina Berdugo-Clavijo, Christine Martineau and Jérôme Comte. Characterization of microbial communities in a constructed wetland treatment system for the remediation of oil sand processed-affected waters. RE3 conference in Quebec City. June 2023.

Christine Martineau, Xiangbo Yin, Aurélie Beaulieu-Laliberté, Jérôme Comte, Douglas Muench. Application of Genomics to Enhance Wetland Treatment Systems for Remediation of Process Water in Northern Environments. 72nd Annual Conference of the Canadian Society for Microbiologists, Halifax. June 2023.

Renata Mont'Alverne. A social unveiling of natural genomic researchers. International Association for Society and Natural Resources (IASNR) conference, Portland, ME/US. June 2023.

Brook Forbes et al.. Locating social perspectives relevant to genomically-enhanced bioremediation strategies. Global Water Futures Finale conference, Saskatoon. May 2023.

Renata Mont'Alverne. A social unveiling of natural genomic researchers. Global Water Futures Finale conference, Saskatoon. May 2023.

Michelle Tilford-Shaw. Gaining Perspective – What do affected persons think about oil sands process-affected water remediation using constructed wetlands enhanced by genomics? Global Water Futures Finale conference, Saskatoon. May 2023.

RESEARCH TEAM AND COLLABORATORS

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Principal Investigators: Christine Martineau and Doug Muench

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Jason Ahad, PhD	Geological Survey of Canada, NRCan	Research Scientist		
Lori Bradford, PhD	Engineering Design, University of Saskatchewan	Assistant Professor		
Jérôme Comte, PhD	Centre Eau Terre Environnement, INRS	Associate Professor		
Dani Degenhardt, PhD	Northern Forestry Service, NRCan	Research Scientist		
Diane Dupont, PhD	Economics, Brock University	Professor		
Lisa Gieg, PhD	Biological Sciences, University of Calgary	Associate Professor		

Frank Gobas, PhD	Resource & Environmental Management, SFU	Professor		
John Headley, PhD	Environment and Climate Change Canada	Research Scientist		
Shawn Lewenza, PhD	Environmental Health, Athabasca University	Professor		
Jason MacLean, BCL/LLB	Faculty of Law, UNB	Assistant Professor		
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Mitchell Alberts, PhD	Department of Biological Sciences, University of Calgary	Post-doctoral Fellow		
Dilini Atugala, PhD	Department of Biological Sciences, University of Calgary	Post-doctoral Fellow		
Alex Cancelli, PhD	Resource & Environmental Management, SFU	Post-doctoral Fellow		
Sara Correa García, PhD	Centre Armand-Frappier Santé Biotechnologie, INRS	Post-doctoral Fellow		
Xiangbo Yin, PhD	Centre Eau Terre Environnement, INRS	Post-doctoral Fellow		
Paula Reis, PhD	Centre Eau Terre Environnement, INRS	Post-doctoral Fellow	2021	2023
Kira Goff, PhD	University of Calgary	Post-doctoral Fellow		
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WJ0197 - Demonstration of SolarPass Combined with Constructed Wetlands for Treatment of Diverse Contaminants of Potential Concern in Oil Sands Process-Affected Water (OSPW)

COSIA Project Number: WJ0197

Research Provider: H2nanO Inc.

Industry Champion: Canadian Natural

Industry Collaborators: Imperial Oil Resources Ltd.

Status: Complete

PROJECT SUMMARY

Background:

Oil sands process-affected water (OSPW) may require treatment of dissolved organic compounds, such as naphthenic acid fraction components (NAFCs). To this end, H2nanO has developed the SolarPass™ solar photocatalytic passive water treatment solution. The SolarPass technology uses buoyant photocatalyst (BPC) beads deployed to open pools, which naturally float at the water surface and absorb sunlight to passively generate powerful oxidants from water, capable of degrading even the most persistent contaminants. SolarPass demonstrated promise in prior COSIA joint industry projects (JIPs) for treating OSPWs from different members and mine sites.

Scope: This project aimed to evaluate SolarPass for OSPW treatment in a hybrid system with constructed treatment wetlands, to better understand potential to integrate the technology into existing oil sands reclamation and closure plans.

Objectives:

1. Assess capabilities of SolarPass, both alone and in combination with biological treatment (constructed wetlands), to treat contaminants of potential concern (COPCs) in OSPW to below CCME guidelines for the protection of aquatic life.
2. Evaluate synergistic advantages of hybrid passive SolarPass-wetlands OSPW treatment.
3. Provide necessary engineering parameters and hybrid system designs to prepare for potential future field pilot of SolarPass, alone or in combination with constructed treatment wetlands.

Methods:

The project was conducted in three main phases:

1. Bench-scale sequential batch treatment coupling photocatalysis and aerobic microbial biodegradation.

Figure 1. Solarpass + constructed wetland mesocosms hybrid outdoor water treatment system for OSPW.

2. Bucket-scale treatment coupling photocatalysis with indoor wetland microcosms.
3. Outdoor continuous flow treatment coupling photocatalysis with wetland mesocosms.

Each phase involved treating OSPW samples from Imperial Oil Resources Ltd. (IOL) and Canadian Natural Resources Ltd. using H2nanO's SolarPass treatment system and photocatalytic materials, and assessing treatment performance toward diverse organic and inorganic COPCs, as well as whole effluent toxicity (WET) with fish bioassays.

Within the context of frameworks for safe management of oil sands mine water and tailings pond reclamation, and consideration of the best available technology economically achievable (BATEA), it is crucial to evaluate SolarPass's capabilities to address a broader scope of OSPW COPCs and understand how to integrate the technology into reclamation strategies.

PROGRESS AND ACHIEVEMENTS

SolarPass treatment successfully detoxified the OSPW samples within ≤one week, with significant removal of OSPW COPCs, including NAFCs, polycyclic aromatic hydrocarbons (PAHs), F2-F3 hydrocarbons, and trace elements (Al, Fe, Mn, V, Zn), demonstrating the technology's simultaneous multi-target treatment capabilities. Key achievements include:

1. **Rapid OSPW detoxification**: SolarPass achieved 100 per cent removal of acute toxicity for rainbow trout within one to two days of treatment.
2. **Effective organics remediation**: SolarPass hybrid treatment removed 95-98 per cent of NAs, 79-94 per cent of F1-F4 hydrocarbons, and 91-97.5 per cent of bioavailable organics as measured by BE-SPME, within a solar UV dose of 60-100 kJ/L.
3. **Trace element removal**: SolarPass effectively removed dissolved iron and manganese in OSPW via oxidative precipitation, coupled with the co-precipitation of additional trace elements including Al, As, Ni, Pb, V, and Zn.
4. **Improved biological treatment**: SolarPass pre-treatment improved subsequent aerobic biotreatment kinetics for AEOs and COD by 5.9× and 2.6×, respectively.
5. **Enhanced wetland health**: SolarPass pre-treatment of OSPW resulted in healthier wetland plants, as determined by reduced cattail root rot prevalence and increased cattail rhizome propagation.
6. **Comprehensive hybrid treatment**: The integration of SolarPass pre-treatment and wetland systems displayed more comprehensive treatment of COPCs in OSPW, with the wetland stage providing effective polishing of remaining organic COPCs and additional trace elements not sufficiently removed by SolarPass (e.g., B, Cu, Mo, and Se).

LESSONS LEARNED

1. **SolarPass enables comprehensive COPC treatment**: The project demonstrated that SolarPass can simultaneously treat multiple organic and inorganic COPCs in OSPW, including NAFCs, PAHs, hydrocarbons, and trace elements. This multi-target treatment capability positions SolarPass as a promising technology for meeting potential future regulatory guidelines for OSPW treatment.
2. **Hybrid SolarPass-wetland systems offer synergistic benefits**: The combination of SolarPass pre-treatment with constructed wetlands provided more comprehensive OSPW treatment than

either technology alone. SolarPass pre-treatment improved wetland health and treatment efficiency, while wetlands offered additional polishing of remaining COPCs.

3. **SolarPass improves wetland sustainability**: Pre-treatment of OSPW with SolarPass resulted in healthier wetland ecosystems, as evidenced by reduced cattail root rot and increased rhizome propagation. This suggests that SolarPass can enhance the long-term viability and treatment efficacy of constructed wetlands in oil sands reclamation strategies.
4. **Optimized treatment sequence**: The project identified that a treatment sequence of bio → PC → bio → PC may be optimal for hybrid systems, as biological pre-treatment was shown to improve the photocatalytic COD degradation rate by 3×.
5. **Scalability considerations**: The successful demonstration of SolarPass in outdoor, continuous flow conditions provides valuable insights for scaling up the technology and integrating it into mine water management frameworks.

These lessons learned provide a strong foundation for further development and potential field-scale implementation of the SolarPass technology in combination with constructed wetlands for OSPW treatment in oil sands reclamation strategies.

PRESENTATIONS AND PUBLICATIONS

Conferences, presentations, and workshops:

Sunlight and plants: working with nature for sustainable mine water detoxification and healthy ecosystems. COSIA 2023 Mine Water Management Science Workshop, Edmonton, AB, Oct. 12-13 2023.

Solar photocatalytic treatment of oil sands process-affected water: a compendium of five years of demonstration projects. SETAC North America 44th Annual Meeting, Louisville, KY, Nov. 13, 2023.

Sustainable Sunlight Treatment for Accelerated Oil Sands Process-Affected Water Remediation. Alberta Innovates 2024 Water Innovation Forum, Calgary, AB, May 27-28 2024.

RESEARCH TEAM AND COLLABORATORS

Institution: H2nanO Inc.

Principal Investigator: Frank Gu

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
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