2021 Water Mining Research Report

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INTRODUCTION

This report summarizes progress for research projects that were active in 2021 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).

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, Suncor Energy, Syncrude Canada Ltd., Teck Resources Limited.

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The cover photo is Syncrude's Base Mine Lake (2021).

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, Suncor, Syncrude, Teck

Status: Year 4 of 4

PROJECT SUMMARY

Open pit bitumen mining in northern Alberta generates considerable volumes of dust. The dusts are derived not only from the mines, but from wind erosion of dry tailings and gravel roads, construction activities, and quarries, in addition to natural sources such as riverbanks and sand bars. The dusts themselves consist mainly of mineral particles, some of which are chemically reactive (e.g., calcite, a calcium carbonate) whereas others are effectively insoluble (such as quartz, a silicate). There are also ongoing concerns about potentially toxic heavy metals being released to the atmosphere from bitumen mining and upgrading. Most environmental impact studies to date have not clearly distinguished between heavy metals (such as cadmium and lead) from the combustion of fossil fuels needed for bitumen upgrading and heavy metals that are hosted within the crystal lattice of the mineral particles themselves. Heavy metals 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 (e.g., 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, but 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 heavy metals 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 heavy metals may have on the chemical composition of meltwater and peatland surface waters from bogs, fens and swamps that drain into the Athabasca River.

PROGRESS AND ACHIEVEMENTS

1. Snow and dust

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 control site (UTK). These samples were used to develop an analytical method for the determination of trace elements (TEs) in dusty snow by Javed et al, 2022 (see «Presentations and Publications: section 1.1»). To characterize the spatial variation in atmospheric deposition of TEs, snow was also collected along the Athabasca River. In 2016, 25 sites along the river were sampled; in 2017, 14 sites were sampled. In addition, snow was collected from three remote locations: Athabasca Glacier, Maligne Lake and Rock Lake. In total, 234 samples of subsurface snow (3 depths: 5-15, 15-30 and 30 to 45 cm) and bulk snow (entire snow profiles) were processed between July 2021 and January 2022.

1.1. Acid-soluble fraction

To determine the reactivity of TEs in the dusts deposited on the snow, the subsurface samples were leached overnight using 0.5% HNO3 before being filtered with a 0.45 µm PTFE filter for analysis using ICP-MS. Under these extreme conditions of dissolution (pH of approximately 1), the 2017 Athabasca River sites showed increasing concentrations of the conservative lithophile (Al, Y, La, Th) and mobile lithophile elements (Be, Ba, Li, Sr) toward industry: this reflects an increase in dust deposition rates, the chemical reactivity of the dust particles, or both. The difference in this increase between the sampling site furthest from industry and the site closest to the industry was a factor of approximately 100 times. Elements enriched in bitumen such as V, Ni and Mo showed similar trends.

In contrast, the range in concentration of chalcophile TEs such as As, Cd and Sb between the “cleanest” sample along the river (SAR-5) and the “dirtiest” (SAR 17.5), was only a factor 10x. Arsenic, Cd and Sb, therefore are under-represented in the acid-soluble fraction of dust, relative to the lithophile elements. In regard to Tl and Pb, they showed a factor of 100x difference, resembling the behaviour of the lithophile elements. Given that Tl+ and Pb2+ can replace K+ and Ca2+ respectively, in aluminosilicates, the patterns seen in both elements appear to reflect the dissolution of silicate dusts.

For most TEs, the snow from UTK yielded lower acid-soluble concentrations than the snow from far more remote locations (Athabasca Glacier, Maligne Lake, and Rock Lake). To estimate the extent of enrichment of TEs in snow samples collected along the Athabasca River, they were normalized to the concentration of TEs found at UTK. Lithophile elements showed the greatest enrichments at almost all the sampling sites, ranging from 10 to up to 2000x, followed by elements such as V (300x), Pb (150x) and Cd (12x).

The results obtained to date are a conservative estimate of the upper limit of the chemical reactivity of dust emitted from bitumen mining and upgrading operations, and related industrial activities. However, they do not reflect what would occur in nature when the dusts are in contact with far less acidic solutions (e.g. Athabasca River water, pH 8, or even peat bog surface water, pH 4). Silicate mineral dissolution rates increase with decreasing pH and a pH of 1 is extremely low. For this reason, a comparable experiment is needed, using much less acidic solutions to mimic the dissolution of dust in peat bog surface waters which are the most aggressive natural waters in the region. This could be accomplished using e.g. 10^{-4} M solutions of oxalic acid or citric acid, both of which would have a pH of 4.

1.2. Total concentration and size-resolved analysis (in progress)

In the case of the bulk snow which will be used to characterize annual deposition of TEs, 5 fractions were obtained from each sample: i) acid soluble (TEs in the dissolved fraction, <0.45 µm, after allowing melted snow to react with acid); ii) unacidified, “dissolved” (i.e. the filterable fraction consisting of colloidal and truly dissolved TEs: 1 kDa to 0.45 µm and <1KDa respectively.); iii) particulate (TEs in the size fraction: >0.45 µm); iv) total (total concentration of TEs in unfiltered snow, after acid digestion at high pressure and temperature); and v) dust (selected samples of particulate matter for XRD, SEM analysis and sequential extractions).

Up to this point, AF4 (asymmetrical flow field-flow fractionation) ICP-MS analyses of the unacidified, “dissolved” fraction have been completed and the data is being processed. The samples containing the “total” fraction were digested with HNO_3 and the ICP-MS analyses of this and the “dissolved” fraction will be performed in the coming weeks.

1.3. Industrial and natural materials

The industrial materials (e.g. coke and dry tailings) and natural materials (e.g. soil and glacial till) provided by our partners are potential sources of airborne dusts. These samples are being processed (physical, mineralogical, and chemical analyses) by the Bioaccessibility project team. A preliminary experiment to yield «total» concentrations of TEs was conducted using a mixture of HF and HNO_3 to fully digest reference materials and samples with varying contents of mineral and organic matter. Although the results were promising (i.e better recoveries for the rare earth elements and lower blank values for Ag, Sb, Tl and Pb when compared to the use of HBF_4), we had to dismiss this technique due to safety issues in our laboratory. Hence, our focus will be to provide “quasi-total” concentrations using nitric acid alone, at elevated temperatures and pressures. For comparison, these samples will also be sent to a commercial laboratory for complete digestion and analysis using ICP-MS.

2. Peat bog surface water

Surface waters and Sphagnum moss samples were collected in 2019 and 2020 from four bogs within the Athabasca Bituminous Sands Region (ABSR): JPH4 (12 km from the mid-point between Suncor and Syncrude upgraders (reference point)), McK (25 km), McM (49 km), and ANZ (68 km), as well as from a control site (UTK) situated 264 km away from the reference point. Trace elements (TEs) were examined in both surface waters and Sphagnum moss porewaters (top 5-10 cm) as indicators of the dissolution of atmospheric dusts. Overall, an increase in the concentrations of most TEs (excluding potentially toxic TEs) was observed in both surface and Sphagnum moss porewaters with proximity to industry. These preliminary findings suggest that TEs in bog waters (surface and Sphagnum moss porewaters) can be used as indicators of the dissolution of atmospheric dusts. However, additional scrutiny was suggested at JPH4 and McK to ensure that the TEs being measured in surface waters are not influenced by subsurface porewaters or surface runoff.

Surface waters, subsurface peat porewaters, and Sphagnum moss samples were collected again in the summer (June) and autumn (September) of 2021 from all the five bogs aforementioned; 1) to identify ombrotrophic microsites at JPH4 and McK; 2) to examine seasonal variations in the concentrations of TEs in surface and Sphagnum moss porewaters, and 3) to observe inter-annual variations in the concentrations of TEs in the same types of samples. Trace elements were only determined in the dissolved fraction (< 0.45 µm) of water samples.

2.1. Ombrotrophic microsites at JPH4 and McK

JPH4 is a shallow peatland (<100 cm peat depth) and has ombrotrophic and minerotrophic microsites. The surface water chemistry of microsites having pH ≤4 was compared with subsurface porewaters (collected from wells (~60-70 cm deep)). The concentrations of major cations (Ca (>10x), Mg(>5x)) and their ratios with respect to Cl (Ca/Cl (up to 21x), Mg/Cl (up to 9x)) were higher in subsurface porewaters compared to surface waters. The surface waters of some microsites are clearly ombrotrophic and therefore suitable for studying the chemical reactivity of atmospheric dusts.

At McK, surface waters were collected from microsites away from the Canadian Natural highway (~ 300 m) to avoid the possible influence of road salts. Subsurface porewaters were also collected from wells installed at depths of ~100 and ~200 cm. Elevated concentrations of Na and Cl were observed in both surface waters and subsurface porewaters (~100 cm deep) compared to those of all other bogs under study. However, the concentrations of the two elements in the subsurface porewaters near the confined layer (~ 200 cm deep) under the peat deposit were comparable to those of other bogs. This suggests that subsurface porewater (~ 200 cm deep) is not saline and these microsites are receiving saltwater intrusion either from adjacent minerotrophic microsites or horizontal surface flow from the Canadian Natural highway. However, information related to peat stratigraphy and hydrology is required to better understand the input sources to these microsites. Based on the results obtained to date, data obtained from these microsites must be interpreted with caution.

2.2. TEs in Sphagnum moss porewaters as indicators of dust dissolution

In Sphagnum moss porewaters, an increase in the concentrations of TEs including some mobile lithophile elements (Fe, Li, and Be) and conservative lithophile elements (Al, La, Nd, and Th) was observed with proximity to industry. Two potentially toxic TEs (As and Pb) also showed an increase in concentration toward industry. However, elements enriched in bitumen (V, Ni, and Mo) and some other potentially toxic TEs (Cd, Sb, and Tl) showed inconsistent trends toward industry. The concentrations of TEs in the summer samples from the impacted sites were normalized to those of UTK (the control site). Overall, the greatest enrichments were observed for the conservative lithophile elements (up to 56x) followed by Fe (up to 46x) at JPH4 and McK. However, the enrichments of potentially toxic TEs (Pb, Sb, Tl, and Cd) were less than 5x, except for As (up to 23x). Regarding As, selected samples will be measured again, using hydride-generation atomic fluorescence spectroscopy (HG-AFS), to confirm the concentrations obtained using ICP-MS. Overall, the data indicate that TEs in Sphagnum moss porewaters are useful indicators of the chemical reactivity of atmospheric dusts.

2.3. Seasonal variations in TEs abundances in surface and Sphagnum moss porewaters

In surface waters, seasonal variations in the concentrations of TEs were considerable. The concentrations of most mobile lithophile elements (Li, Sr, Be, and Ba), elements enriched in bitumen (V, Ni, and Mo), Co, and Cd were significantly higher in autumn compared to summer. In contrast, the differences in the concentrations of TEs in Sphagnum moss porewaters were insignificant between seasons.

2.4. Inter-annual variations in TEs abundances in surface and Sphagnum moss porewaters

The concentrations of TEs in surface waters were significantly higher in the summer of 2021 compared to 2019. This was attributed to changes in weather conditions between years during the sampling period. However, the differences in the concentrations of TEs in surface waters and Sphagnum moss porewaters were insignificant in the autumn of consecutive years (2020-2021).

3. Sphagnum moss

3.1. Objective

The project aims to estimate the relative abundance of TEs found in the coarse and fine aerosol fractions by comparing TE concentrations in bulk Sphagnum moss and the acid soluble ash (ASA) fraction.

3.2. Sample collection and analysis

Sphagnum mosses had already been collected from 30 ombrotrophic (rain-fed) bogs within the ABS region in the autumn of 2015, prepared for chemical analysis, and frozen. Additional samples were collected in 2019 and 2020, from the five bogs where snow samples had been collected, as well as UTK (the reference site). Total concentrations of TEs in moss were determined using our published procedure, and the ASA fraction was obtained by leaching ash samples in high purity, 2 % nitric acid (pH 0.5) for 15 minutes before filtering through a 0.45 µm PTFE filter. All TE concentrations were obtained using ICP-MS.

3.3. Results

The ash content of Sphagnum moss clearly increased towards industry, consistent with our previously published work on the same topic. In the present study, as expected, total concentrations of conservative, lithophile elements such as Al, Y and Th increased towards industry, along with metals found in bitumen (V, Ni, and Mo) and elements of concern (Pb, Sb, and Tl). With the exception of Mo, the concentrations of these elements in the ASA fraction also showed obvious or slightly increasing trends. Within this acid-soluble fraction, these elements correlated strongly or moderately with acid-soluble Y, suggestion a connection to silicate mineral dissolution. The proportion of TEs that were acid soluble is dichotomous: the soluble proportion was high for Al, Y, V, and Ni, but low for Th, Mo, Pb, Sb, and Tl. This indicates that the former elements might be largely contributed by ultrafine clay minerals such as kaolinite and illite which react in acid because of their very small size, while the latter perhaps occur in larger mineral grains such as feldspars and heavy minerals (e.g., monazite, zircon) which are more stable. Silver and Cd exhibit behaviours more like micronutrients such as Cu and Zn, suggesting that these were impacted by plant uptake in addition to mineral dust deposition.

The above results were supported by the calculated enrichment factors, X-ray diffraction (XRD), particle size distribution, and principal component analysis.

i. The EF values of V, Ni, Pb, and Tl, calculated using Y as the reference element, were generally around or below 2, supporting the hypothesis that most of the dust generated by industry contains TEs in the same proportions as they occur in the Earth's Crust. The EF values of Mo varied among sites, with the largest values at the reference sites which is assumed to reflect plant uptake. The EF values of plant-essential elements (Mn, Cu, and Zn), as well as Ag, Cd, and to some degree Sb showed trends like those of Mo.
ii. XRD was used to compare the mineralogy of the ash obtained from moss collected at JPH4 (peat bog coring site nearest industry) and UTK (control site). The predominant mineral at JPH was quartz JPH4 (36.7%) which contrasts with the abundance of the same mineral at UTK (6.1%). Trace elements are effectively absent from quartz, and the predominance of this mineral in moss close to industry helps to explain the low concentrations of TEs and lack of significant TE enrichment.
iii. The particles found in selected samples of Sphagnum ash tend generally to increase in size with distance toward industry. The greatest differences seen in the cumulative abundance (percent) of particle volume was found for particles ranging in size from approximately 20 µm to 300 µm.
iv. The principal component analysis (PCA) for total concentrations of TEs in the 2015 mosses showed that the conservative lithophile elements (Y, La, Th, Cr, Al), elements enriched in bitumen (V, Ni, Mo), and some potentially toxic elements (Pb, Tl, Sb), were clustered and contributed greatly to PC1 (60 % of variance), while the macro- and micronutrients contributed the most to PC2 (12 %). The PCA for the acid soluble concentrations showed that V and Ni were also closely tied to the conservative lithophile elements (Al, Y, Th, Cr, La), and contributed largely to PC1 (52 % of variance), while Ag and Cd were associated with the plant-essential elements and contributed the most to PC2 (15 %).

LESSONS LEARNED

1. Snow

Taking lithophile elements such as Al as indicators of the extent of dust dissolution in strong acid, it is clear that some potentially toxic TEs (i.e. Pb and Tl) vary in direct proportion to dust dissolution while other TEs of concern (i.e. Cd and Sb) are under-represented in the leachates by an order of magnitude. Given the very low pH of the solutions used (approximately pH 1), much less dissolution of these dusts is expected when they come into contact with natural waters such as the Athabasca River (pH 8).

2. Peat bog surface water

Trace elements in bog surface waters and Sphagnum moss porewaters can be used as indicators of the chemical reactivity of atmospheric dusts. Potentially toxic TEs (Cd, Pb, Sb, and Tl) are enriched (2-5x) in Sphagnum moss porewaters at sites closer to industry compared to the control site. However, concentrations of these TEs showed inconsistent trends toward industry.

3. Sphagnum moss

The study found that the ASA fraction of moss ash, taken to represent the fine aerosol fraction, contained two classes of elements: those exhibiting a large proportion in acid-soluble forms (e.g. Al, Y, V, and Ni), and those with a small proportion in such forms (e.g. Th, Mo, Pb, Sb, and Tl). Thus, the potential bioaccessibility of elements of concern (namely Pb, Sb and Tl) is much lower than that of the elements representing aluminosilicates (i.e. Al and Y) or bitumen (i.e. V and Ni).

Taken together, these studies present a clear illustration of the need to determine not only the concentrations of TEs in surface waters, including peatland waters, but also (and perhaps especially) the chemical reactivity of TEs in aerosols and dusts, to thoroughly evaluate their associated health risks for living organisms.

PRESENTATIONS AND PUBLICATIONS

1. Journal Publications:

1.1. Published

Javed, M.B., Cuss, C.W., Zheng, J., Grant-Weaver, I., Noernberg, T., Shotyk, W., 2022. Size-fractionation of trace elements in dusty snow from open pit bitumen mines and upgraders: collection, handling, preparation and analysis of samples from the Athabasca Bituminous Sands region of Alberta, Canada. Environmental Science: Atmospheres. https://doi.org/10.1039/D1EA00034A

Shotyk, W., Bicalho, B., Cuss, C.W., Donner,M., Grant-Weaver, I., Javed, M.B., Noernberg, T. 2021. Trace elements in the Athabasca Bituminous Sands: a geochemical explanation for the paucity of environmental contamination by chalcophile elements. Chemical Geology 581, 120392. https://doi.org/10.1016/j.chemgeo.2021.120392

1.2. Under review

Shotyk, W. Environmental Significance of Trace Elements in the Athabasca Bituminous Sands: Facts and Misconceptions. Environmental Science: Processes and Impacts. Themed Issue: Biogeochemistry of the Trace Elements. Lenny Winkel and Elsie Sunderland, Guest Editors (invited paper; manuscript submitted February 6, 2022).

1.3. In revision (by the authors)

Shotyk, W., Barraza, F., Cuss, C.W., Grant-Weaver, I., Germani, C., Javed, M.B., , Hillier, S., Noernberg, T. Preferential, natural enrichment of Cd and Tl in the bark of trees from a rural watershed devoid of point sources of metal contamination. To be submitted to Environmental Research.

1.4. In preparation

Chen, N., Barraza, F., Belland, R., Javed, M.B., Grant-Weaver, I., Cuss, C.W., and Shotyk, W. Trace elements in the acid-soluble ash fraction of Sphagnum moss: surrogate for atmospheric deposition of sub-micron aerosols within the Athabasca Bituminous Sands region

2. Conferences, presentations, and workshops:

2.1. Presented:

Barraza, F., Butt, S., Chen, N., Cuss, C.W., Grant-Weaver, I., Javed, M.B., Noernberg, T., Shotyk, W. Characterization of dust particles from bitumen mining in Alberta (Canada) using Sphagnum moss, peat bog waters, and snow. Laboratoire Geosciences Environnement Toulouse (GET), Observatoire Midi-Pyrénées (OMP), Toulouse, France ; December 2, 2021 (in person, invited).

Barraza, F., Shotyk, W., Cuss, C.W., Grant-Weaver, I., Javed, M.B., Germani, C., Noernberg, T. Natural enrichments of Cd and Tl in bark of trees consumed by beaver (Castor canadensis) in a rural watershed devoid of point sources of metal contamination. https://doi.org/10.7185/gold2021.4212

In: Goldschmidt 2021 (Session 11f: "Biota and geochemical cycles: mechanisms of transformation, uptake, and translocation of metal and metalloid species in the critical zone"), July 4-9, 2021 (online, oral presentation).

Barraza, F., Zheng, J., Krachler, M., Cuss, C.W., Oleksandrenko, A., Grant-Weaver, I., Shotyk, W. Geochemical perspectives from the past: understanding the natural enrichment of Cd in pre-industrial and pre-anthropogenic aerosols using polar ice and peat cores from remote locations. https://doi.org/10.5194/egusphere-egu21-1381
In: European Geosciences Union (EGU), General Assembly 2021 (SSS3.5 “Soils as records of past environmental conditions, climate change and anthropogenic impact”), April 19-30, 2021 (online, oral presentation).

Butt, S., Barraza, F., Bujaczek, T., Frost, L., Javed, M.B., Oleksandrenko, A., Shotyk, W. Trace elements (TEs) in peat bog surface waters: indicators of the dissolution of atmospheric dusts from mining activities in the Athabasca Bituminous Sands Region (ABSR). ALES (Agricultural, Life & Environmental Sciences) Virtual Research Symposium. University of Alberta Graduate Students' Association. March 24 and 25, 2022.

Butt, S., Shotyk, W., Barraza, F., Chen, N., Cuss, C., Frost, L., Javed, M. (2021). Trace elements in surface water of ombrotrophic bogs indicate the dissolution of dust particles generated by mining activities in northern Alberta. https://doi.org/10.7185/gold2021.6693
In: Goldschmidt 2021 (Theme 9bO2: Geochemical and statistical techniques for characterizing and/or discriminating between anthropogenic contamination and natural processes: a still current challenge), July 4-9, 2021 (online, oral presentation).

Butt, S., Shotyk, W., Barraza, F., Chen, N., Cuss, C., Frost, L., Grant-Weaver, I., Javed, M., Noernberg, T., Oleksandrenko, A., and Pei, L. Trace elements in peat bog surface waters as indicators of the dissolution of atmospheric dusts from open-pit bitumen mines. https://doi.org/10.5194/egusphere-egu21-1430
In: European Geosciences Union (EGU), General Assembly 2021 (SSS3.5: Soils as records of past environmental conditions, climate change and anthropogenic impact), April 19-30, 2021 (online, oral presentation).

Chen, N., Barraza, F., Belland, R., Javed, M.B., Grant-Weaver, I., Cuss, C.W, Shotyk, W. Trace elements in the acid soluble ash fraction of Sphagnum moss: Surrogate for atmospheric deposition of sub-micron aerosols within the Athabasca Bituminous Sands region. ALES (Agricultural, Life & Environmental Sciences) Virtual Research Symposium. University of Alberta Graduate Students' Association. March 24 and 25, 2022.

Chen, N., Barraza, F., Belland, R., Javed, M.B., Cuss, C.W., & Shotyk, W. Size distribution of trace elements in Sphagnum mosses within the Athabasca Bituminous Sands Region.
In: Goldschmidt 2021 (Theme 9bO2 - Geochemical and statistical techniques for characterizing and/or discriminating between anthropogenic contamination and natural processes: a still current challenge), July 4-9, 2021 (online, oral presentation).

Chen, N., Barraza, F., Belland, R., Javed, M.B., Cuss, C.W., & Shotyk, W. Distinguishing trace elements in acid soluble ash (ASA) and acid insoluble ash (AIA) of Sphagnum mosses within the Athabasca Bituminous Sands Region. https://doi.org/10.5194/egusphere-egu21-3795
In: European Geosciences Union (EGU) General Assembly 2021 (SSS3.5 “Soils as records of past environmental conditions, climate change and anthropogenic impact), April 19-30, 2021 (online, oral presentation).

Shotyk, W. Environmental Significance of Trace Elements in the Athabasca Bituminous Sands: Facts and Misconceptions. In: COSIA, Mine Water Management Workshop, November 30 and December 1, 2021 (online, invited).

Shotyk, W. Metals versus Minerals: a research update. Presented at the Scientific Advisory Committee meeting of the Athabasca River project and the Metals versus Minerals project. June 15, 2021. Hosted jointly by COSIA and Alberta Innovates (virtual meeting).

Shotyk, W., Bicalho, B., Cuss, C.W., Donner, M.W., Grant-Weaver, I., Javed, M.B., and Noernberg, T. Trace elements in the Athabasca Bituminous Sands: a geochemical explanation for the paucity of environmental contamination by chalcophile elements. In: AER – COSIA Technical Workshop, OSPW Properties, June 8 and 9 2021 (online, oral presentation).

Shotyk, W., Barraza, F., Belland, R., Butt, S., Chen, N., Devito, K., Cuss, C., Dennett, J., Frost, L., Grant-Weaver, I., Javed, M., Nielsen, S., Noernberg, T., and Oleksandrenko, A. Ombrotrophic peatlands: natural, holistic, integrated, long-term monitoring systems for atmospheric deposition of environmental contaminants to terrestrial and aquatic ecosystems. https://doi.org/10.5194/egusphere-egu21-1241
In: European Geosciences Union (EGU), General Assembly 2021 (SSS3.5 "Soils as records of past environmental conditions, climate change and anthropogenic impact"), April 19-30, 2021 (online, invited presentation, keynote).

2.2. Accepted abstracts:

Barraza, F., Shotyk, W. Trace element analyses of soil, water, and plants: challenges and strategies. Post-conference workshop proposal for: 2022 Joint Canadian Society of Soil Science (CSSS) Annual Meeting-Alberta Soil Science Workshop (ASSW), May 23-27, 2022.

2.3. Submitted abstracts:

Barraza, F., Chen, N., Javed, M.B., Noernberg, T., Shotyk, W. Evaluating the chemical reactivity of dusts from mining and upgrading of the Athabasca Bituminous Sands (ABS) in Alberta, Canada using trace elements in moss and snow. Goldschmidt 2022 (Session 13f: "Geochemical processes related to mined, milled, or natural metal deposits in a rapidly changing global environment"). July 10-15, 2022 (Honolulu, Hawaii, and online).

Shotyk, W., Barraza, F., Butt, S., Chen, N., Cuss, C.W., Devito, K., Frost, L., Grant-Weaver, I., Javed, M.B., Noernberg, T. Trace elements in peat bog surface waters and Sphagnum moss porewaters: indicators of dissolution of atmospheric dusts from open pit mining and related industrial activities. Goldschmidt 2022 (Session 13f: "Geochemical processes related to mined, milled, or natural metal deposits in a rapidly changing global environment"). July 10-15, 2022 (Honolulu, Hawaii, and online).

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, Postdoctoral Fellow		
Sundas Butt	University of Alberta	PhD candidate	January 2020	April 2024
Na Chen	University of Alberta	MsC candidate	September 2019	April 2022

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, Suncor, Syncrude, Teck

Status: Year 2 of 3

PROJECT SUMMARY

There is ongoing concern regarding the potential environmental impacts and ecological significance of trace elements (TEs) from open pit bitumen mining and upgrading. Total concentrations of TEs in environmental media have often been interpreted as having biological significance, regardless of the chemical form of the element. This has led to many misunderstandings and concern that may often 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. 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. We hypothesize that bioavailability of TEs is constant, because there is no significant change in pH along this gradient. In contrast, bioaccessibility of TEs increases with distance downstream because of the increasing abundance of small particles. To provide additional perspective and context for the main thrust of the study, 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 also be analyzed.

PROGRESS AND ACHIEVEMENTS

Sample preparation and characterization

Particle size is an important factor influencing the dissolution rate of minerals; in general, the dissolution rate increases with a decrease in particle size. Specifically, the dissolution rate is proportional to the surface area of the mineral. Furthermore, clays tend to concentrate TEs due to their negative surface charge and high surface area. The materials provided by our industry partners, including soils, tailings, etc., are thus separated according to their size by wet sieving into four different size fractions: medium sand (+250 µm), fine sand (+64 µm), silt (+10 µm), and silt/clay (-10 µm) using in-house designed and fabricated, acid-cleaned plastic sieves. Minerals are characterized using scanning electron microscopy (identification of sand- and silt-sized particles) and x-ray diffraction (identification of clay-sized minerals). Currently, mineral characterization has been completed on 28 size fractions of seven samples.

In vitro digestive fluid extraction – bioaccessibility determination

While there is a considerable literature on bioaccessibility of TEs in particulate matter that have employed synthetic gastrointestinal fluids, most studies to date have focused on human bioaccessibility. While the gastrointestinal (GI) tract of humans and other vertebrates, including fishes, share many similarities there are also important differences. Therefore, to ensure that our experimental design is applicable to aquatic life, a comprehensive literature review on fish physiology, fish digestive processes and enzymes, and in vitro digestive fluid extraction of fishes was performed. Gastric secretion of HCl is almost ubiquitous in vertebrates, including fish, amphibians, reptiles, birds, and mammals. Unlike humans and mammals, however, up to 75% of the transit time of the digesta in the GI tract of fishes is residence in the stomach. Thus, our experiments will be carried out using two simple synthetic gastric fluid (SGF) formulations, HCl and HCl + pepsin. These simple formulations will allow the determination of a maximum number of elements, including major elements, which is important to constrain the nature of the dissolution reactions taking place in the GI tract of aquatic organisms. It is important to note that a large number of fish species (~20-25%) are agastric, i.e. they lack a true stomach. Consequently, these fishes do not secrete HCl and any experiments carried out with SGFs do not apply. This is an important consideration for the Athabasca River as two abundant benthic species, the longnose sucker and the white sucker, are agastric. To account for these and other agastric species as well as invertebrates, which also lack a stomach, experiments using simulated intestinal fluids (SIFs) will also be carried out. For the SIFs, two simple formulations were selected: $NaHCO_3$ and $NaHCO_3$ + pancreatin + bile salts. The SGF and SIF formulations without digestive enzymes will be used to assess the bioaccessibility of most TEs, and the formulations containing pepsin and pancreatin + bile salts will be used primarily to assess the bioaccessibility of all elements with reasonably low background values and for comparison with the other methods. In addition, for a subset of samples, experiments will be carried out using a luminal buffer mimicking the composition of the lumen of the fish stomach and intestine (made up of NaCl, KCl, MgSO4, CaCl2, galactose, Na-pyruvate) as well as with animal and vegetal organic matter (coingestion scenarios), which better represent the situations likely to occur in the aquatic environment. The experimental parameters were chosen as follows: The most important parameter influencing the bioaccessibility of TEs is pH; as the pH of gastric fluid in fish typically ranges between 2 and 4, experiments will be carried out at both endpoints. The intestinal pH of fishes is more alkaline than that of humans; experiments will be carried out at a pH of 8. The temperature will be set to 8 °C (to mimic fall and spring) and 20 °C (to mimic summer), with TE bioaccessibility expected to increase with temperature. Material will be reacted with gastrointestinal fluids for 16 hours (at 20 °C) and 36 hours (at 8 °C) to reflect differences in gastric residence time, which is highly dependent on temperature. Two different solid:fluid ratios will be investigated to consider different species, 1:60 for carnivorous fish that generally ingest sediment incidentally and a ratio of 1:10 for benthivorous fish that take up significant amounts of sediment with their food.

Experimental Setup - Hardware

Using an orbital shaker to react gastrointestinal fluids and solids, as is common in in vitro bioaccessibility studies, artificially increases the dissolution of TEs. This is because the collision of particles during shaking leads to abrasion, i.e. fine particles are created, and a decrease in particle size leads to an increase in the dissolution rate. To minimize the contribution due to abrasion we have custom-designed an electrical stirrer. The stirrer utilizes polypropylene reaction cells, which are 3D printed in-house, consisting of a cell body, a propeller with five blades, and a lid, and are connected with the stirrer base via aluminum pins. The electric stirrer rotates the blades of the propeller, gently stirring the solution while minimally disturbing the particles. This decreases the contribution of abrasion to TE dissolution.

LESSONS LEARNED

The project is still in its early stages. However, preliminary experiments have shown that our custom-designed and constructed electrical stirrer, which decreases the contribution of abrasion to TE dissolution, has low background concentrations, and yields uniform dissolution rates. In addition, the determination of background TE concentrations in the reagents used for the SGFs has shown that TE levels vary widely among reagents. In pepsin for example, several elements, including Fe, Zn, Ni, and Cr, are very high, whereas others such as Pb are low. Therefore, it is crucial to consider TE release rates on an individual basis, and the blank values for each reagent solution must be carefully assessed in order to reliably determine TE bioaccessibility.

PRESENTATIONS AND PUBLICATIONS

1. Journal Publications:

1.1. Published

Shotyk, W., Bicalho, B., Cuss, C.W., Donner, M.W., Grant-Weaver, I., Javed, M.B. and Noernberg, T. (2021) Trace elements in the Athabasca Bituminous Sands: a geochemical explanation for the paucity of environmental contamination by chalcophile elements. Chem Geol 581, 120392. Invited paper, Special Issue in honour of Prof. J.D. Kramers. https://doi.org/10.1016/j.chemgeo.2021.120392

1.2. Published

Shotyk, W. Environmental Significance of Trace Elements in the Athabasca Bituminous Sands: Facts and Misconceptions. Environmental Science: Processes and Impacts. Themed Issue: Biogeochemistry of the Trace Elements. Lenny Winkel and Elsie Sunderland, Guest Editors (invited paper; manuscript submitted February 6, 2022).

2. Conferences, presentations and posters:

Shotyk, W. Environmental Significance of Trace Elements in the Athabasca Bituminous Sands: Facts and Misconceptions. COSIA, Mine Water Management Workshop, November 30 and December 1, 2021 (invited). Oral presentation, virtual meeting, attendance ~ 150.

Shotyk, W. Metals versus Minerals: a research update. Presented at the Scientific Advisory Committee meeting of the Athabasca River project and the Metals versus Minerals project. June 15, 2021. Hosted jointly by COSIA and Alberta Innovates. Oral presentation, virtual meeting, attendance ~20.

Shotyk, W., Bicalho, B., Cuss, C.W., Donner, M.W., Grant-Weaver, I., Javed, M.B., and Noernberg, T. Trace elements in the Athabasca Bituminous Sands: a geochemical explanation for the paucity of environmental contamination by chalcophile elements. AER – COSIA Technical Workshop, OSPW Properties, June 8 and 9 2021. Oral presentation, virtual meeting, attendance ~50.

Shotyk, W. Ombrotrophic peatlands: natural, holistic, integrated, long-term monitoring systems for atmospheric deposition of environmental contaminants to terrestrial and aquatic ecosystems. Session SSS3.5 "Soils as records of past environmental conditions, climate change and anthropogenic impact". EGU21: Gather Online. April 27, 2021 (invited presentation, keynote; approximately 50 to 70 participants.

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)
Mandy Krebs	University of Alberta	PhD, Postdoctoral Fellow		
Judy Schultz	University of Alberta	Research Associate		

WE0077 – Athabasca River Project: Creation of Artefacts During Sample Filtration

COSIA Project Number: WE0077

Research Provider: University of Alberta

Industry Champion: Syncrude

Industry Collaborators: Canadian Natural, Shell, Imperial, Suncor, Teck

Status: Year 3 of 4

PROJECT SUMMARY

The development of the Athabasca bituminous sands has received considerable attention due to serious concerns about potential trace element (TE) contributions from industrial activities to surrounding ecosystems. Comprehensive and scientifically sound analyses are therefore required to assess the possibility and extent of such releases. The dissolved fraction (< 0.45 µm) of TEs in natural waters is of special concern because ionic and colloidal forms exhibit greater mobility, bioaccessibility, and potential bioavailability than the corresponding particulate fraction (> 0.45 µm). Within the dissolved fraction, TEs can be roughly divided into three major components based on their composition: 1) free ions and primarily ionic species, 2) species associated with dissolved organic matter (DOM) including metal ions (e.g., Cu^{2+}) or small metallic particles, 3) primarily inorganic species such as oxyhydroxides of Al, Fe, or Mn with trace elements adsorbed to surfaces or encapsulated inside lattice structures. The latter two fractions represent colloidal components. These colloids are critical in geochemical cycling because they govern the fate, transport, and bioavailability of many TEs in natural waters. Filtration through 0.45 µm filters is universally used to obtain the "dissolved" fraction of TEs in natural waters. Following filtration, the concentration and size distribution in the dissolved fraction can be determined in filtrates using asymmetric flow field flow fractionation (AF4) coupled to inductively coupled plasma mass spectrometry (ICP-MS). However, errors can be introduced during sample filtration due to i) sorption of ions onto or desorption of ions from filters, and ii) exclusion of ionic or colloidal TEs in the filtrate due to a progressive reduction in effective pore size of the filter membrane (i.e. filter clogging). These processes are termed filtration artefacts and their significance for the determination of dissolved concentrations of TEs in river waters and peatland waters has received little attention. This project addresses these gaps, while developing new analytical techniques and knowledge, including: 1) Determining the magnitude of the errors introduced to the measurement of dissolved concentrations of TEs that are caused by filtration artefacts and 2) Developing and applying an analytical method for analyzing the colloidal forms of TEs over a size continuum from ca. 1 nm to 5 µm, to avoid the impacts of filtration artefacts.

PROGRESS AND ACHIEVEMENTS

The effects of sample filtration through 0.45-μm syringe filters (Polytetrafluoroethylene [PTFE] filters, 30 mm in diameter) on dissolved TEs in natural waters were critically assessed by experiments undertaken in triplicate. The research objectives, brief descriptions of the experiments, the main results, and provisional interpretation are given below.

- **Objective 1:** To assess the errors introduced by the exclusion of organic colloids caused by filter clogging (pH=8)

  In this work, polystyrene sulfonate sodium salt (PSS) size standards were employed to assess the importance of filtration artefacts for organic colloids. A PSS size standard of 500 nm was used to clog the 0.45-μm syringe filters. A mixture containing 4 PSS size standards (0.89 kDa, 3 kDa, 10 kDa, and 20 kDa) was filtered using clogged or unclogged filters. At pH 8, no significant loss of particles was observed in the small size range (ca. 0.89 – 20 kDa).

- **Objective 2:** To assess the errors caused by the adsorption of TEs onto syringe filters for an Athabasca River sample (pH=8)

  An Athabasca River sample (pH=8) that had been stored in the fridge for two years was employed to assess the adsorption of TEs onto syringe filters. This sample was pre-filtered using 1-μm syringe filters to remove large particles. Size-resolved analyses using AF4-ICP-MS showed that there were no particles larger than 0.45 μm which indicated that the filters could not become clogged during the experiment. Increasing volumes of the pre-filtered sample (10, 20, 30, 40, 50, 60. 70, 80, 90, and 100 ml) were processed through a 0.45-μm syringe filter. The concentrations of 19 TEs (Li, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Y, Mo, Cd, Ba, Pb, Th, and U) were determined in the filtrates using ICP-MS. The size-resolved species of TEs in 10-, 50-, and 100-ml filtrates were determined using AF4-ICP-MS. Compared to the pre-filtered sample, losses during filtration amounted to approximately 4.5 μg/L (83%) of Fe, 0.20 μg/L (62%) of Mn, 0.75 μg/L (42%) of Al, 0.003 μg/L (34%) of Pb, and 0.23 μg/L (30%) of Zn. As the volume of sample processed was increased, more colloidal species of Fe (and Pb) were excluded from the filtrate, indicating an interaction between filter materials and Fe-rich particles that led to particle retention. The point of zero charge (pH_{pzc}) for Al-rich and Fe-rich soil minerals (e.g., gibbsite, goethite, and hematite) are greater than 8, while the pH_{pzc} of PTFE is 2.9. Thus, at the pH of the water samples, the surfaces of these inorganic particles and the PTFE filter membrane were oppositely charged. Therefore, there existed strong forces of attraction between the inorganic particles in the samples and the filter membrane, resulting in particle adsorption during filtration. The loss of Zn might be related to the abundance of negative binding sites on the PTFE filters. Clearly, artefacts caused by adsorption effects can greatly influence TEs associated with inorganic particles.

- **Objective 3:** To assess potential artefacts associated with filter clogging for bog surface waters (pH=4)

  Bog waters differ from Athabasca River waters due to the lower pH of bog water (pH 4 vs. pH 8) and abundance of dissolved organic matter (e.g. 50 mg/L vs. 5 mg/L). The speciation of most TEs in natural water samples may greatly influenced by pH. In addition, pH may also affect the surface properties of filter materials e.g., surface potential, distribution of protons, and availability of metal-binding sites. Thus, the interactions between sample components and filter materials may be significantly different during the filtration of bog waters compared to the Athabasca River waters. Given the importance of peatland drainage waters for the Lower Athabasca River watershed, there is a real need to investigate the potential impacts of filtration procedures on dissolved TEs in bog waters. Increasing volumes of bog water (0.5, 1, 2, 4, 6, 8. 10, 12, 14, and 16 ml) were filtered through a 0.45 μm syringe filter to assess artefacts associated with filter clogging. The maximum volume that could be processed was 16 ml due to filter clogging. The concentration and size distributions of the same 19 TEs were determined using AF4-ICP-MS. The preliminary results showed that larger amounts of TEs were lost as increasing volumes of sample were processed, including Al, V, Cr, Fe, Ni, Cu, Zn, Sr, Cd, and Pb. Filtered volumes of 16 ml led to significant changes in the dissolved concentrations of elements compared to the 0.5 mL filtrate, including: Cu (0.37 µg/L was lost, accounting for 72% of the concentration in the 0.5 mL filtrate), Ni (0.22 µg/L, 27%), Cd (0.024 µg/L, 26%), Cr (0.13 µg/L, 27%), and Zn (4.9 µg/L, 21%): for other elements (Al, V, Cr, Fe, Sr, and Pb), losses were < 5%. Some elements (Al, Sr and Pb) were correlated with Fe concentrations, suggesting an association with Fe-rich particles. Other elements (Cr, Zn and Cd) were correlated with Cu indicating an association with DOM. The losses of V and Ni were correlated with Fe as well as Cu, suggesting the importance of ternary complexes involving both inorganic as well as organic colloids. Clearly, the exclusion of organic and inorganic colloids during filtration causes significant losses of many TEs of environmental relevance.

- **Objective 4:** Developing and applying an analytical method for analyzing the colloidal forms of TEs over a size continuum from ca. 1 nm to 5 µm to avoid filtration artefacts

  The AF4-ICP-MS method has been extended up to 5 µm using size standards. Two methods were needed to characterize the small (ca. 1 nm to 100 nm) and large (ca. 100 nm to 5 µm) colloids/particles and associated TEs. The AF4-ICP-MS method for measuring the truly “dissolved” fraction and metal-bearing colloids <100 nm was already developed by Cuss et al., 2017. A second method was needed for measuring the large particles ≥100 nm. A series of monodisperse size standards of polystyrene (0.1, 0.2, 0.5, 1, 2, and 4 µm) or silicon dioxide (0.27, 0.69, and 0.89 µm) was employed for empirical calibrations. The crossflow program was optimized to achieve high-resolution and fast separation of large particles. The results showed strong linear relationships between the size and retention time over a size range from 0.1 to 5 µm. To date, particle size standards were well separated using AF4, and this method can now be applied to water samples from the Athabasca River and its tributaries.

LESSONS LEARNED

Filtration artefacts for Athabasca River waters (pH 8)

- Organic colloids and associated TEs (e.g. Ni and Cu) in the size range from 0.89 to 20 kDa are not affected by filtration.
- Inorganic colloids (dominated by Fe and Al oxyhydroxides) and associated TEs (e.g. Pb) are affected by filtration.
- Zinc is also affected by filtration, but possibly because of metal adsorption or complexation on the surface of acid-cleaned filters.

Filtration artefacts for bog waters (pH 4)

- Filtration can slightly affect the Fe-rich colloids and their associated elements (e.g., Al, Sr, and Pb).
- Filtration can greatly influence the DOM-associated elements (e.g., Cu, Ni, and Zn).

Filtration artefacts (pH 4 versus pH 8)

- At pH 4, the net surface charge is negative for both the PTFE membrane (pHpzc 2.9) and DOM (pHpzc 3.4). In consequence, repulsive forces between the DOM and filter material may restrict passage of DOM and associated TEs through the pores of the filter.
- The pHpzc of Al-rich and Fe-rich minerals (e.g., gibbsite, hematite, and ferrihydrite) are greater than 8. Therefore, the surfaces of these minerals and their amorphous equivalents are positively charged both at pH of 8 and pH 4. Thus, significant adsorption of inorganic particles to the negatively charged PTFE surface may be expected to result from electrostatic attraction under both alkaline as well as acidic conditions.
- Electrostatic interactions which restrict the passage of organic colloids through filters and promote adsorption of inorganic colloids on their surfaces, may promote the formation of new, larger particles,

via the aggregation of both classes of colloids. The formation of such particles on the surface of the filters would further reduce the successful passage of the TEs associated with these colloids.

PRESENTATIONS AND PUBLICATIONS

1. Presentations:

Wang Yu, Cuss Chad, Butt Sundas, Pei Pei, Luu Andy, Oleksandrenko Andrii, Shotyk William. Filtration artefact 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, December 14, 2021.

Wang Yu, Cuss Chad, Butt Sundas, Pei Lei, Shotyk William. AF4-ICP-MS as a powerful tool to resolve colloidal trace elements in bog waters. Presentation at the Faculty of Agriculture, Life and Environmental Sciences Graduate Student Conference, Edmonton, Alberta, March 24, 2022.

2. Publications:

Wang Yu, Cuss Chad, Butt Sundas, Pei Lei, Shotyk William. AF4-ICP-MS as a powerful tool to resolve colloidal trace elements in bog waters. (In prep.)

Wang Yu, Cuss Chad, Luu Andy, Oleksandrenko Andrii, Butt Sundas, Shotyk William. The impacts of 0.45-μm syringe filters on dissolved trace elements in natural waters: Concentration, and size distribution. (planning)

RESEARCH TEAM AND COLLABORATORS

Institution: SWAMP Lab Facility, Department of Renewable Resources, University of Alberta

Principal Investigator: Dr. 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)
Tommy Noernberg	University of Alberta	Mechanical Engineer/Field Specialist		
Tracy Gartner	University of Alberta	Project Manager		
Chad W Cuss	University of Alberta	Research Associate		
Yu Wang	University of Alberta	MSc (PhD candidate)	2019	2023

OIL SANDS PROCESS-AFFECTED WATER CHEMISTRY AND TOXICITY

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

COSIA Project Number: WJ0116

Research Provider: University of Alberta

Industry Champion: Imperial

Industry Collaborators: None

Status: In progress

PROJECT SUMMARY

Naphthenic acids (NAs) are recognized as contributors to acute toxicity of oil sands process-affected water (OSPW). Due to the seepage potential of NAs from tailings ponds into the surrounding surface water and groundwater, environmental monitoring of NAs in water samples from tailing ponds, surrounding groundwater and surface water, and groundwater wells are a routine part of oil sands mining operations. Commonly used analytical techniques for NA concentrations measurement include Fourier Transform Infrared Spectroscopy, gas chromatography-mass spectrometry, and high-performance liquid chromatography-mass spectroscopy. However, these methods are time-consuming and resource-intensive, and samples need to be sent to an analytical laboratory which can cost up to $1,000 per sample. Hence, developing a fast, low-cost analytical method for on-site quantification of NAs will help address these challenges. Consequently, this project aims to develop a simple microbial electrochemical biosensor to detect oil sands NAs in water samples more rapidly than traditional lab-based analytical methods.

Briefly describing the working principle, microbial electrochemical biosensors use electroactive bacterial biofilms serving as biosensing elements to produce an electrical signal in response to an analyte, which can be a target environmental contaminant. The electrical signal can be linked to the concentration of the target analyte. In recent years, different configurations of microbial electrochemical biosensors have been demonstrated for a wide variety of environmental contaminants. Due to low fabrication costs and quick response time, these biosensors can provide a potential solution for the on-site measurement of NAs in aqueous samples. The specific objectives and timelines of this project include:

- Proof-of-concept tests with microbial electrochemical biosensors for detecting model NAs in water samples (2017-2018)
- Understanding the effects of various environmental parameters (salinity, temperature, petroleum hydrocarbon compounds, etc.) on biosensor's response with model NA compounds (2018-2020)
- Investigating various electrochemical methods for improving calibration precision with cyclohexane carboxylic acid and commercial NAs (2020-2021)
- Studying the feasibility of using an exogenous quorum sensing (QS) autoinducer as a method for improving the sensitivity of biosensors for detecting commercial NAs (2021).
- Investigating microbial electrochemical biosensor as a dual platform for detecting NAs concentrations and their associated toxicity (2021)
- Investigating long-term performance of microbial electrochemical biosensor for detecting NA concentrations in real OSPW samples (in-progress).
- Developing a miniaturized microbial electrochemical biosensor to facilitate portability for field application (to be completed).

PROGRESS AND ACHIEVEMENTS

Optimizing biosensor calibration method with commercial NAs (2020-2021).

A significant portion of our research focused on exploring an effective electrochemical method for calibration precision and biosensor sensitivity for detecting commercial NAs. While earlier research focused on utilizing cyclohexane carboxylic acid for these investigations (*reported in earlier COSIA reports*), our recent experiments validated the results with commercial NAs. Particularly, we investigated three different calibration methods (closed-circuit, cyclic voltammetry, and charging-discharging operation of biosensors. We found that the charging-discharging (CD) based calibration method could provide the best results (Fig. 1) among the three approaches in terms of precision, time-efficiency (<3 hours), sensitivity, and reproducibility for commercial NAs.

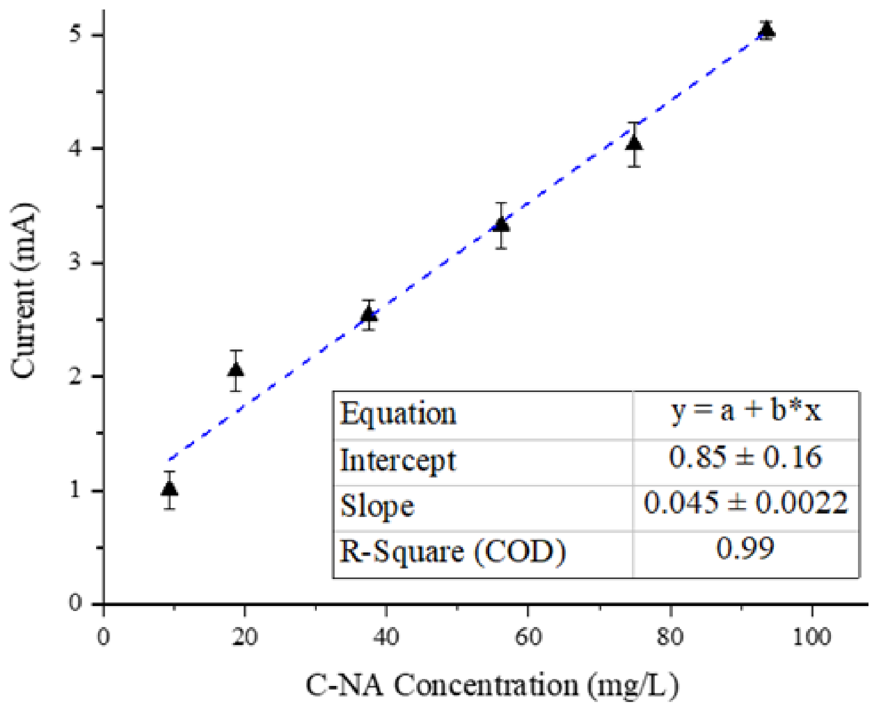

Fig. 1. A calibration curve established based on transient peak currents from CD cycles operated with commercial NAs.

Feasibility of using an exogenous quorum sensing (QS) autoinducer as a method for improving the sensitivity of biosensors for detecting commercial NAs (2021).

We investigated a novel method of enhancing quorum sensing (QS) in biosensing biofilms to further boost the biosensor's sensitivity. In this phase, we investigated acylase enzyme as an exogenous QS autoinducers. On average, the biosensor's performance in terms of electrical signal output was increased by ~1.7 times with the addition of acylase (Fig. 2). Thus, the results suggested that using acylase can potentially assist in achieving low detection limits for NAs.

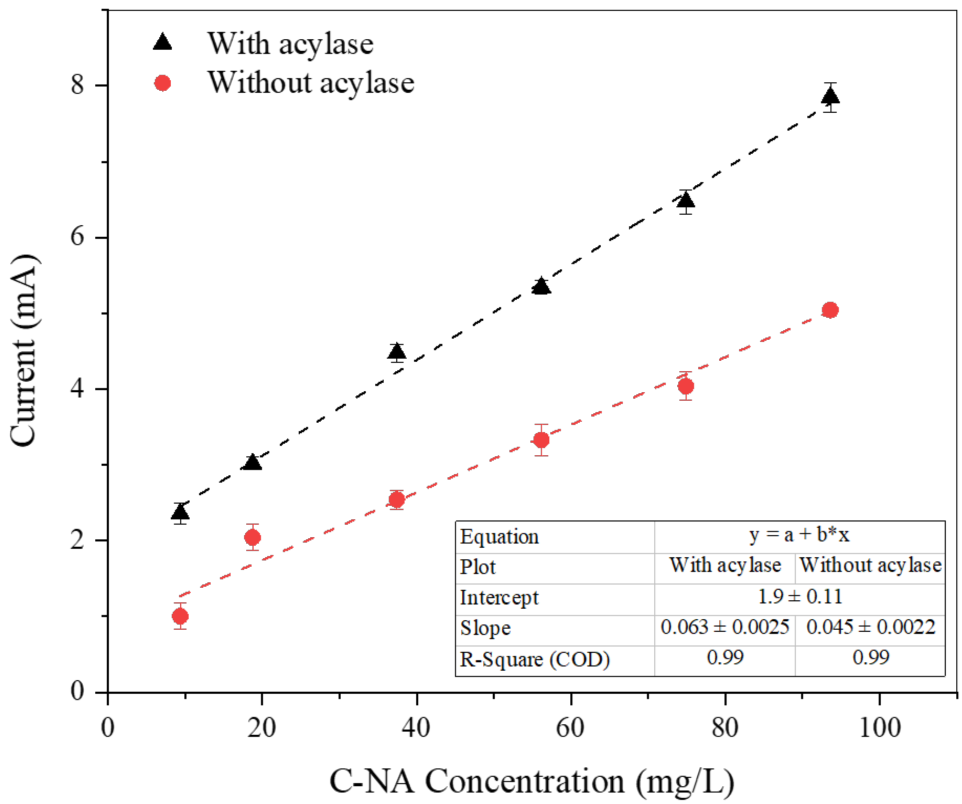

Fig. 2. Calibration curves established from CD cycles with and without (control) the addition of acylase enzyme.

Microbial electrochemical biosensor as a dual platform for detecting NAs concentrations and their associated toxicity (2021).

We investigated the feasibility of the biosensor for measuring NAs-associated toxicity. Currently, the Microtox® bioassay test is more routinely utilized for assessing the toxicity of OSPW. We found that once the biosensor is calibrated, the current outputs can be correlated to toxicity levels of water samples measured with Microtox® bioassay test. Thus, the microbial electrochemical biosensor can provide a quick monitoring tool for assessing the toxicity levels of OSPW. However, further investigations using real OSPW are warranted.

LESSONS LEARNED

The results with model NAs (including commercial NAs mixture) have been promising and suggested that microbial electrochemical biosensors can be potentially applied as a simple bioanalytical tool for monitoring NA concentrations and assessing NA toxicity in water samples. However, more work is needed before the biosensor is ready for use in the field. Particularly, experiments related to the feasibility of microbial electrochemical biosensors for detecting NAs concentrations in real OSPW are ongoing.

PRESENTATIONS AND PUBLICATIONS

1. Publications:

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.

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., 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. Under preparation.

2. Presentations:

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.

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.

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)
Dr. Mohamed Meshref	University of Alberta	Postdoc	2020	2021
Tae Chung	University of Alberta	Ph.D. Student	2021	2024
Tae Chung	University of Alberta	M.Sc. Student	2018	2020
Basem Zakaria	University of Alberta	Ph.D. Student	2017	2021
Sajib Barua	University of Alberta	M.Sc. Student	2017	2018

Research Collaborators: Dr. Karen Budwill, InnoTech Alberta Inc.

WJ0168 – Protecting the Athabasca River Basin: Bacterial Biosensors for Detection and Bioremediation of Oil Sands Process-Affected Water (OSPW)

COSIA Project Number: WJ0168

Research Provider: Athabasca University / Dr. Shawn Lewenza

Industry Champion: Canadian Natural

Industry Collaborators:

Status: Year 4 of 5

PROJECT SUMMARY

The project has advanced a novel detection and quantification system for naphthenic acids (NAs). There is infrastructure in place around tailings ponds to collect seepage water and to prevent leakage of oil sands process water (OSPW) from the mine site. No untreated OSPW is released from the mine sites. To release OSPW from the mine sites in the future, upon regulatory approval, it will be necessary to ensure that all water quality criteria are met, including potential guidelines pertaining to NAs. Current analytical chemistry methods exist to determine the concentration of NAs in OSPW. However, these methods require complex sample extraction methods and either an FTIR analyzer or a sophisticated and expensive mass spectrometer to detect and characterize the compounds present in acid extracts. These methods are slow and not ideal for high throughput sample measurement. Current methods are costly, and the method proposed is expected to be far more cost effective. The previous *E. coli* biosensors can detect NA that are mostly commercially available acyclic compounds. Accordingly, there is a need for biosensors that detect a wide range of compounds, and ideally those that are common in OSPW.

Biosensors are engineered bacteria that can be used as an alternative assay to indicate the presence of NA in water. A biosensor technology has been developed that has applications in environmental monitoring and for rapid identification of novel bacterial strains that can degrade naphthenic acids. The researchers have established a process using bacterial genomics to identify how bacteria sense and respond to naphthenic acids, as well as a synthetic biology approach to rapidly construct naphthenic acid biosensor strains. The availability of these biosensors will enable rapid, cost-effective testing and monitoring of OSPW storage ponds and surrounding environments.

The biosensors permit the rapid identification of novel bacterial isolates that that can degrade naphthenic acids. Novel strains and genes have been identified that are able to degrade simple mixes of acyclic and single ringed NA compounds. The high throughput screening will be soon carried out to identify bacterial genes that are required to degrade NA extracted from OSPW. This novel strain and genetic information will increase our understanding of how bacteria degrade NA, which can be used to optimize bioremediation strategies.

PROGRESS AND ACHIEVEMENTS

The researchers cultivated *Pseudomonas* isolates directly from oilsands process-affected water (OSPW). These are relevant environmental species to construct whole cell biosensors because they are abundant in tailings ponds and OPSW, and many Pseudomonas species are known to degrade naphthenic acids. The genomes of OSPW isolates were sequenced and a complete genome of Pseudomonas OST1909 has been assembled and published. This isolate is likely a novel species according to their digital DNA-DNA hybridization analysis.

Bacterial genes were identified that are highly induced by the presence of naphthenic acids and the genes/promoters were prioritized for biosensor construction if their predicted function was involved in bioremediation, efflux, transport, or transcription regulation. Genetic biosensor circuit were designed, and these were then used in gene expression assays to measure the bioluminescence response to known amounts of naphthenic acids. There is a linear increase in gene expression by the biosensor in response to increasing concentrations of different naphthenic acid mixtures. The dose-dependent gene expression responses allow these biosensors to provide a semi-quantitative indication of the concentration of NA in a sample. All sensors can detect NA at concentrations known to exist in tailings ponds (10-120 mg/L).

In summary, the researchers constructed and validated a panel of biosensors, where one biosensor detects acyclic NA, another detects simple ringed structures, and a third biosensor detects OSPW specific NA, including compounds with N containing rings. Additional specificity experiments are ongoing, but preliminary data suggests that other hydrocarbons like BTEX, alkanes or polyaromatic hydrocarbons are not detected by their panel of NA biosensors.

The lab has recently received additional funding with a multi-institution Genome Canada LSARP grant involving many industry and academic researchers. They will expand the studies of NA bioremediation genes and biosensor development, including a focus on biosensors that detect the “toxic” fraction of OSPW. In addition, the researchers will be able to test the biosensors to detect the presence of naphthenic acids in OSPW water that has passed through laboratory scale mesocosms or a constructed wetland, as a rapid analytical tool to determine if the treatment was successful to remove naphthenic acids.

LESSONS LEARNED

The Biosensor Program is in year four of its five year duration. Thus far, 62 gene sequences have been identified and incorporated into biosensor constructs and evaluated. Testing these requires significant effort and to date only a few have been evaluated as genetic biosensors. There is a linear increase in gene expression by the biosensor in response to increasing concentrations of different naphthenic acid mixtures. The dose-dependent gene expression responses allow these biosensors to provide a quantitative indication of the concentration of NA in a sample. All sensors can detect NA at concentrations known to exist in tailings ponds (10-120 mg/L). While the lab has limited access to actual OPSW samples, they have tested a panel of 24 OSPW extracts and shown detection using biosensors of almost all samples where NA was previously quantitated using mass spectrometry. Preliminary data with OSPW itself is also promising, as there is no water processing needed and samples can be tested directly without extraction. The high throughput screening for bacteria that degrade NA was successful, and they are currently investigating the genetics and molecular biology of the novel NA degradation genes identified.

PRESENTATIONS AND PUBLICATIONS

Published manuscript:

Shideler S, Headley J, Gauthier J, Kukavica-Ibrulj I, Levesque RC and S Lewenza. 2021. Complete genome sequence of a *Pseudomonas* isolate species isolated from tailings pond water in Alberta, Canada. Microbiol Resour Announc. 2021 Mar 4;10(9):e01174-20. doi: 10.1128/MRA.01174-20.

Manuscripts in Preparation:

Bacterial biosensors as an alternative environmental monitoring technology to detect naphthenic acids in oil sands process-affected water. Tyson Bookout, Steve Shideler, John Headley, Stephanie Wallace, Jaron Dominquez, Shawn Lewenza

Biosensor screening of oil sands metagenomic libraries for the identification of naphthenic acid bioremediation genes. Kira Goff, Tyson Bookout, Steve Shideler, Lauren Bowman, Shawn Lewenza.

Provisional Patent. Bacterial biosensors for monitoring and detection of naphthenic acids in the environment. Sept 2021

Poster presentation. T Bookout, S Shideler, J Headley and **S Lewenza**. Transcription Factor-based biosensors for Naphthenic Acids detection in oil sands tailings ponds. Canadian Society for Microbiology, June 2021, Virtual Conference

Invited Presentations:

- McGill University Microbiology and Immunology Student's Association, Feb 8, 2022, *Virtual*
- Science Outreach Athabasca University, Nov 9, 2021 Athabasca, BC *Virtual*
- Canadian National Resources Limited, June 8 2021, Calgary, BC *Virtual*
- FredSense (company), May 7 2021, Calgary, BC *Virtual*
- Canadian Society of Microbiology Conference, June 10-13, 2019, Sherbrooke, QC
- Oil sands Innovation Summit, June 3-4, 2019, Calgary, AB

RESEARCH TEAM AND COLLABORATORS

Institution: Athabasca University

Principal Investigator: Dr. Shawn Lewenza

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. S. Lewenza	Athabasca University	Associate Professor		
Steve Shideler	University of Calgary	MSc	Sept 2017	Sept 2019
Tyson Bookout	University of Calgary	MSc	July 2019	July 2022
Kira Goff	Athabasca University	PDF	Nov 2021	Nov 2024

PIT LAKES

WE0083 – Literature Review and Proposed Study Design in Support of the Proposed 2022/23 Demonstration Pit Lake Mesocosm Study

COSIA Project Number: WE0083

Research Provider: Kilgour & Associates/Bruce Kilgour

Industry Champion: Canadian Natural

Industry Collaborators: Imperial, Suncor, Syncrude, Teck

Status: Complete

PROJECT SUMMARY

The project comprises a literature review of research assessing the potential effects of salinity and naphthenic acids (NAs), separately and in conjunction with each other. It advances the oil sands industry knowledge and understanding of water capped pit lake design and supports eventual water release. Understanding the separate and synergistic effects of these constituents on aquatic biota will help oil sands mining companies develop effective pit lake plans to enhance in-pit performance and to treat and manage the release of site waters, which are known to have high concentrations of these constituents. The work builds upon the existing Pit Lake Mesocosm program by utilizing the research to date and addressing gaps identified by the member companies as high priority. Furthermore, the Pit Lake Mesocosm program is uniquely able to facilitate this evaluation because it allows for longer-term exposures of aquatic organisms to waters with specific attributes.

The Report identifies the various approaches to measuring salinity and a formula to convert measured salinity to a chloride (Cl) concentration, as a means to evaluate the results against a known water quality guideline (i.e. CCME in this case). It includes work examining the biological effects of salinity and NAs, provides background on the guideline development, and identifies and reviews numerous studies that been designed to understand the effects of salinity on aquatic organisms most recently. The Report summarizes research on total dissolved solids, major ion mixtures, and the interactions between salinity and other constituents, with a specific focus on NAs. Finally, the Report utilizes the existing research to make recommendations for the study design of an upcoming mesocosm project trials, led by Canadian Natural.

PROGRESS AND ACHIEVEMENTS

The Report outlines how the upcoming mesocosm study design can capitalize on several findings from the literature review in terms of designing the concentration gradients of both Cl and NAs in the mesocosms, identifying aquatic biota that may sensitive to the COCs and identifying response variables that may not be as valuable to measure. Ultimately, the Report lays out various study design options and provides the substantiation for each of the options presented.

LESSONS LEARNED

The Pit Lake Mesocosm Program has been in effect for five years, since 2017. Thus far, it has focused on evaluating the effects of combinations of tailings materials and oil sands process water (OSPW) on aquatic biota. Analysis of data collected from 2017-2020 suggests that a number of constituents associated with OSPW contribute to effects on the aquatic biota under investigation, including salinity and organic acids such as NAs. However, it has been difficult to separate the effects of salinity from those of NAs in oil sands studies to date. The Report outlines recommendations to separate the effects of these two stressors and evaluate synergistic effects. The results of the Pit Lake Mesocosm research will enable operators to enhance pit lake design with regards to ecological functioning and determine targeted water treatment options to address regulatory and stakeholder concerns regarding water capped pit lakes and eventual release of treated OSPW.

PRESENTATIONS AND PUBLICATIONS

N/A

RESEARCH TEAM AND COLLABORATORS

Institution: Kilgour & Associates Ltd.

Principal Investigator: Bruce Kilgour

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Bruce Kilgour	Kilgour & Associates	PhD, President		

WJ0013 - Mesocosm Research in Support of Pit Lakes

COSIA Project Number: WJ0013

Research Provider: InnoTech Alberta

Industry Champion: Imperial

Industry Collaborators: Canadian Natural, Suncor, Teck

Status: Active

PROJECT SUMMARY

From the spring of 2017 to the fall of 2018, a study funded by COSIA Demonstration Pit Lake (DPL) participants was undertaken to investigate the chemical, biological and physical effects of oil sands process water (OSPW) and untreated fluid fine tailings (FFT) on aquatic ecosystems to support the development of PL (pit lake) technology. From the spring of 2019 to the fall of 2021, a second iteration of the study was undertaken on a new set of experimental groups (Table 1) using treated and untreated tailings to investigate similar factors (with increased focus on biological attributes).

This study utilized thirty 15,000 L mesocosms, simplified and replicated aquatic ecosystems, which had been designed and constructed by InnoTech Alberta at their Vegreville facility in 2016. Mesocosms are simplified aquatic ecosystems and as research tools, they afford more realism than bench-scale experimentation, while providing more control and replication than field studies.

Table 1: 2019/20/21 experimental groups

Experimental Group	OSPW content	Sediment	Extraction Process	Replicates
CTL (control)	0%	Filter Sand	NA	5
TRT 1	0%	Coarse Sand Tailings (CST)	Paraffinic	4
TRT 2	0%	Thickened Fluid Fine Tailings (TT)	Paraffinic	4
TRT 3	0%	Froth Treatment Tailings (FTT)	Paraffinic	4
TRT 4	0%	Fluid Fine Tailings (FFT)	Paraffinic	4
TRT 5	100%	Fluid Fine Tailings (FFT)	Paraffinic	4
TRT 6	50%	Thickened Froth Treated Tailings (TFTT)	Naphthenic	5

The purpose of the study was to determine how different tailings streams affect the water column in terms of physical, chemical, biological and toxicological properties. A broad range of chemical, physical and ecological attributes were measured to answer two main questions: (1) what effect do tailings have on these attributes over time, and (2) what effect does OSPW have on these attributes in the presence of treated and untreated tailings over time. The effects on ecological attributes were also examined over time.

In the second iteration of the study, the mesocosms were filled with Athabasca River water in late April 2019, followed by a period of establishment and homogenization before exposure to treatment materials in June of 2019, followed by four months of data and sample collection. The study ended October 2021.

A multivariate analysis of the 2017-20 data was undertaken to summarize and better understand the data and interactions between measured variables to date.

PROGRESS AND ACHIEVEMENTS

In 2019, field measurements showed that the introduction of OSPW and tailings was associated with higher turbidity levels. The highest recorded turbidity was for TRT 4 and TRT 5 (where FFT was present) from the bottom (125 cm) depth at 92+/-17.1 FNU (90 times that of the control). Turbidity decreased significantly with time to levels below 5 FNU, regardless of depth with TRT 1, 2, and 3 (CST, TT, FTT) not differing significantly from CTL except at the beginning of 2019 and TRT 4-6 (FFT, TFTT) only varying from the CTL in 2020 periodically. Dissolved oxygen levels initially decreased with the introduction of tailings and OSPW to values < 1 mg/L, particularly for TRT 6. However, this effect did not persist, and dissolved oxygen levels were not significantly different from CTL by fall 2019 where all treatments exhibited levels between 8 and 11 mg/L. Mean pH varied within an alkaline range of 7.5 and 9.5, with treatments with tailings and OSPW (TRT 5 and TRT 6) mainly exhibiting slightly lower pH.

Laboratory (and field) measurements showed that combined OSPW and tailings (TRT 5 and TRT 6) treatments were associated with significantly higher concentrations of most constituents but only arsenic, boron, chloride, molybdenum, and selenium were exceeded as per CCME surface water quality guidelines for the protection of aquatic life (Table 1). For the most part, the chemical effects of OSPW decreased over time. Notably, TRT 4, 5 and 6 showed significantly higher naphthenic acid levels compared to CTL, though the concentrations decreased with time. Hydrocarbons (BTEX, PAHs) associated with OSPW and tailings treatments were near or below detection limits in 2020. The effects of tailings alone (TRT 1, 2, 3, and 4) were similar to those attributed to OSPW and tailings (TRT 5 and TRT 6) but often of lesser magnitude. Some of these effects were mediated by the slow efflux of solutes from the tailings layer (CST, TT, FTT, FFT) into the overlying water. In 2020, a gradient of multiple parameters (depth-wise variation) formed in concert with the spring thaw, and the persistence was proportionate to the conductivity (and TDS) levels prior to freezing.

Tailings and OSPW (TRT 5 and TRT 6) decreased viability of some floating and submergent vegetation. *C. demersum,* a sensitive species, did not remain viable in mesocosms containing 50% or 100% OSPW and tailings treatments (TRT 5 and TRT 6) in 2020. Conversely, the presence of 50% OSPW and TFFT (TRT 6) had a significant stimulatory effect on the growth of emergent vegetation *(C. aquatilis, T. latifolia, A. americanus, C. atherodes).* By the end of 2020, adventitious vegetation species abundantly colonized installed submerged soil in CTL and TRT 1, 2, 3 (CST, TT, FTT) mesocosms, but to a much lesser extent in TRT 4-6 mesocosms, indicating that inhibition is limited to some, but not all submerged macrophyte species.

The toxicity of mesocosm water was assessed using rainbow trout 96-hour LC_{50} and fathead minnow 7-day assay LC_{50} and IC_{25}. Only TRT 5 (FFT + 100% OSPW) was found to have a rainbow trout LC_{50} less than 100% (~55%) in June 2019 sampling. Rainbow trout LC_{50} increased to more than 100% by the end of 2020 sampling period, with the exception of one mesocosm. Fathead minnow LC_{50} was >100% (non-lethal) for all experimental groups in both years, with some TRT 4, 5, and 6 mesocosms showing IC_{25} below 100% (80%+) in 2019.

All mesocosms were found to support populations of zooplankton and macroinvertebrates in 2019 and 2020. The presence of OSPW and tailings affected zooplankton communities occasionally in terms of richness, abundance, diversity, and biomass. For example, during 2019 sampling season, treatment materials (except CST) reduced the zooplankton abundance at least once compared to CTL, while elevating the diversity (Shannon-Wiener) of the zooplankton community at the beginning of 2019.

Phytoplankton (metaphyton) coverage was rarely observed in 2019, however from mid to end of 2020 sampling season, metaphyton coverage in control mesocosms was significantly higher than that observed in TRTs mesocosms. In 2020, algal mats were observed in TRT 6 (TFTT and 50% OSPW) mesocosms in the spring of 2020. This observation, along with that of macrophytes, indicates that the photosynthetic community in the water column is affected and further study may be warranted.

The mesocosms were not decommissioned in the fall of 2020, but instead were overwintered for a second time to continue the study in 2021. All materials were removed from the mesocosms in the fall of 2021.

Table 2. Comparison of some constituents to CCME guideline values* for the 2019/20 Aquatic Mesocosm Study

Constituent (total)	CCME limit		Time	CTL	TRT 1	TRT 2	TRT 3	TRT 4	TRT 5	TRT 6
	Acute	Chronic								
Hardness (mg/L)			Start	123.6	127.3	119.8	124.8	115.8	135	92.2
			End	84.2	104.5	88.3	97.3	117.2	127	82.8
pH		6.5-9.0	Start	8.24	7.96	8.23	8.02	8.45	8.69	7.97
			End	9.37	8.84	9.02	9	8.91	8.76	8.77
DOC (mg/L)			Start	11.4	11.1	11.8	11.8	13.7	43.8	45
			End	11.1	11.3	12.6	10.9	14.6	39.6	43.6
Naphthenic acids (mg/L)			Start	0.021	0.111	0.943	0.258	2.49	33.2	22
			End	0.019	0.151	0.51	0.384	1.27	14.5	9.62
Arsenic (ug/L)	NA	5	Start	1.1	1.07	1.2	1.09	1.13	2.73	5.8
			End	1.25	1.23	1.29	0.67	1.06	1.86	4.9
Boron (mg/L)	29	1.5	Start	0.034	0.048	0.05	0.058	0.135	1.04	1.84
			End	0.032	0.072	0.101	0.11	0.219	1.04	2.16
Chloride (mg/L)	640	120	Start	15.2	15.5	15	14.6	15	36.5	359.4
			End	14.3	13.6	14.4	13.7	14.1	32.8	356.6
Copper (ug/L)	Equation	7	Start	2.97	2.84	2.51	2.02	1.79	2.11	1.64
			End	1.81	1.65	1.66	1.23	1.48	1.24	1.26
Molybdenum (ug/L)		73	Start	0.99	0.98	1.65	1.97	4.84	57.8	173
			End	1.47	1.01	2.8	2.53	6.37	51.9	115
Nickel (ug/L)	NA	Equation	Start	1.2	4.7	2.1	2.5	3	7	5.6
			End	1.5	3.5	3	2.2	3.9	6.6	4.7
Selenium (ug/L)		1	Start	0.18	0.22	0.15	0.15	0.2	0.68	3.74
			End	0.4	0.3	0.3	0.28	0.32	1	4.26
Vanadium (ug/L)	NA	NA	Start	0.24	0.49	0.91	3.17	5.63	14.82	7.65
			End	0.52	0.48	0.77	0.45	1.34	3.2	5.78

* Exceedances of CCME Guideline values highlighted in gold

LESSONS LEARNED

Some learnings from the mesocosms include:

- DO decreased significantly with the introduction of tailings and OSPW, and turbidity increased. However, this effect did not persist, returning to levels not significantly different from the CTL by Fall 2020;
- Higher levels of naphthenic acids were associated with the presence of OSPW, and concentration decreased significantly with time;
- All mesocosms were found to have diverse populations of zooplankton and macroinvertebrates.

Multivariate analysis found that:

- Overall, the data suggests that there are multiple potential stressors that could have contributed to variations in biological responses;
- Elevated concentrations of total dissolved solids and naphthenic acids are negatively associated with zooplankton and macroinvertebrate community indices; however,
- Total dissolved solids and naphthenic acids tend to covary, so future studies should aim to isolate the constituents in order to determine effect of each.

PRESENTATIONS AND PUBLICATIONS

Conference Presentations/Posters:

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**.

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.**

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

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**.

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**

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

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.**

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**.

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**.

RESEARCH TEAM AND COLLABORATORS

Institution: InnoTech Alberta

Principal Investigators: Ryan Melnichuk and Zhongzhi Chen

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 Melnichuk	InnoTech Alberta	PhD- Research Scientist		
Zhongzhi Chen	InnoTech Alberta	PhD- Research Scientist		
Craig Aumann	InnoTech Alberta	PhD, MSc-Senior Researcher		
Jim Davies	InnoTech Alberta	MSc, DVM-Researcher		
Brian Eaton	InnoTech Alberta	PhD-Manager/Research Scientist		
Bruce Kilgour	Kilgour and Associates	PhD-Principal		

WJ0091 – Suncor Lake Miwasin – Demonstration Pit Lake

COSIA Project Number: WJ0091

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

Industry Champion: Suncor Energy

Industry Collaborators: Canadian Natural, Syncrude, Alberta Innovates

Status: Year 4 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)), which uses the Permanent Aquatic Storage Structure (PASS) process, an inline tailings treatment process of coagulant addition followed by flocculant addition. The PASS process enables:

- more rapid reclamation of the treated fluid tailings (FT) into a freshwater lake environment;
- integration of the lake into the surrounding watershed; and
- mitigation of potential adverse environmental effects.

The goal of the Lake Miwasin pilot study is to monitor and evaluate if the PASS process, when combined with the closure landform design, will accelerate the reclamation of a DDA 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.

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

- Phase 1: Dewatering and treatment of 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 ~2022)
- Phase 4: Water release under natural flow (~2023)

The Lake Miwasin project completed Phases 1 and 2 operations by the end of 2018 and is currently in Phase 3. Research and monitoring activities are planned to take place over a 15-year period (2018-2033) in order to meet the goal and objectives.

<u>Lake Miwasin Research and Monitoring Program</u>

The Lake Miwasin Research and Monitoring (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 that they are 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 modelling; 4) landform design; and 5) performance trajectories.

The first 5-year Lake Miwasin Research and Monitoring program was developed and implemented in 2019 following the overarching R&M Plan. Currently, the core monitoring program 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 multiple universities, focusing on watershed hydrology, long-term fate and transport of COPCs (e.g. trace elements and organic compounds), and ecotoxicity.

1. Water fluxes and system evolution of Lake Miwasin (Athabasca University and University of Waterloo; PIs: Dr. Scott Ketcheson and Dr. Richard Petrone)
2. Investigation of trace element sources, transport and impacts at Lake Miwasin (SWAMP Lab, University of Alberta; leading PI: Dr. William Shotyk)
3. Experimental column, bioindicator and microbiology study (University of Alberta; PIs: Dr. Mohamed Gamel El-Din, Dr. James Stafford, and Dr. Patrick Hanington)
4. Advanced approaches to aqueous exposure and hazard characterization (University of Saskatchewan; PI: Dr. Karsten Liber)

Refer to the 2020 Water Mining Research Report (COSIA 2021) for a detailed description of each research program. A 5-year Lake Miwasin modelling program was started end of 2019. The Year 2 modelling work is ongoing.

PROGRESS AND ACHIEVEMENTS

The first 5-year phase of the Lake Miwasin research and monitoring program started in 2019, with the first field sampling campaign in March 2019. Hatfield Consultants is retained to collect a full suite of physical, chemical and biological monitoring data from Lake Miwasin and its watershed, including the following monitoring components:

- detailed data on the physical structure Lake Miwasin;
- continuous monitoring data on climate, evaporation/evapotranspiration, and water flows;
- groundwater levels and chemistry;
- surveys of vegetation and aquatic life; and
- extensive characterization of water quality, including metals, hydrocarbons, and toxicity.

Analyses of the results of the 2021 program are underway, but key themes from the monitoring program are the following:

- Treated tailings deposit continues to consolidate and has settled by ~ 3.5 m. Consolidation performance is slightly ahead of predictions from the 2018 model.
- No groundwater seepage to the underlying Wood Channel Sand Aquifer has been observed.
- Tailings and water quality conditions generally meet performance expectations, with variation in sediment quality between the placed treated tailings and constructed littoral and upland areas.
- Our understanding of the water budget and physical dynamics of the Lake Miwasin continues to develop. The lake experiences typical patterns of stratification and mixing. The climatic variation between 2020 (an unusually wet year) and 2021 (a drier year, but with significant precipitation events) is providing further insight into the hydrological network and water budget of the Lake Miwasin watershed.
- Vegetation continues to grow and expand across the upland, riparian, and littoral areas. A mix of volunteer, including some exotics, and planted species are successful. Trees, such as aspen and white spruce, are mixed with rough cinquefoil, raspberries, willows, and foxtail barley.

- Lake Miwasin has been colonized with native boreal aquatic organisms, including insects, plankton, and amphibians. Natural processes such as primary production, nutrient and carbon cycling, and community succession are established in the lake, and are supporting the establishment of the aquatic ecosystem.

AECOM is conducting all aspects of the air quality monitoring and sampling program, including 1) SUMMA canisters to speciate Volatile Organic Compounds (VOCs) including (C2-C9) non-methane hydrocarbons, methane, and H_2S around the Lake; 2) Hi-Vol samplers to quantify 24-hr average concentrations of particulates upwind and downwind of the lake; and 3) Passive Air Samplers with Polyurethane Foam Disk (PUF-PAS) to identify the Poly Aromatic Hydrocarbon (PAH) species in the air surrounding the Lake. In addition, in 2021 measurements began using an Open Path Fourier Transform InfraRed (OP-FTIR) spectrometer for 6 weeks to measure concentrations of the target VOCs and their fluctuations over time. The first analyses of all data sets are currently underway and will be reported in the 2022 report. After completing sampling in all seasons and from an initial program of OP-FTIR measurements, initial observations were:

- The PUF-PAS sampling is a useful method of measuring PAHs present in the air. A balance needs to be sought that minimizes the detection limit while providing a useful time series of data for seasonal interpretation, as seasonal variability in emissions is expected.
- Treatment of background concentrations is critical when using measured concentrations to estimate emissions, as the Lake emissions are expected to be low compared to other site sources.

The research programs continued laboratory and field studies in 2021. Program progress and early observations and findings from each research program include:

- Early field observations indicate the strong prevalence of near-surface hydrological processes, with observations of a shallow “perched” groundwater systems, likely key for understanding hydrological functioning of upland. Heterogeneity of materials and their hydrological properties persists across the upland; continued monitoring of their evolution will increase understanding of these shallow groundwater processes. Snowmelt runoff appears to be the most significant contributor of water to the lake and as such will be critical to continue studying to understand the impact of annual variations. The wet conditions present in 2020 and dry conditions present in 2021 provided an opportunity to contrast the ability of the uplands to supply water to the lake and how that may relate to internal lake processes under different climate conditions; results are pending. Evapotranspiration rates follow typical seasonal trend, with an approximate average rate of ~1.5 mm/d. The role of the opportunistic wetlands in the upland water budget is being evaluated to assess if the wetlands represent evapotranspiration sinks or groundwater recharge windows.
- Early findings from the trace elements research and monitoring program suggest that the trace element constituents of tailings are largely stabilized following the PASS treatment process and the concentrations of most trace elements have declined since the placement of aquatic cover. Fluctuating redox conditions and turnover may mobilize some soluble constituents from the tailings, and constituents that are expressed in porewaters during consolidation. Rhenium concentrations may be an effective indicator of these settling and consolidation processes. The Lake also serves as a sink for some trace elements contributed from the upland. The waters and sediments that are present following the PASS process do not have lethal effects for D. magna in acute toxicity experiments; however, some limited chronic toxicity was apparent. Further

research is required to assess the constituents of these matrices and toxicological pathways which are responsible for these impacts.

- Experimental columns (twelve columns; height: 2.4 m, diameter: 200 mm) have been established at the University of Alberta under both oxic and anoxic conditions to investigate the long-term impacts of treated tailings characteristics on the development of the lake ecosystem. Preliminary results from the experimental columns have shown that naphthenic acid (NA) concentration increased slightly in capping water over time, while the mobility of several metals/ions has been reduced or stayed unchanged. Monitoring data from four columns over eight months suggested that differential chemical processes are occurring in the columns, in the absence of external environmental influences. Data collection from the experimental columns is ongoing and a comprehensive data analysis will be performed.
- Examining water bioactivity using immune cells shows that each water sample tested has its own unique signatures. Specifically, using the murine macrophage RAW 264.7 cell line, the bioactivity (i.e., macrophage activating status) of two Lake Miwasin water samples (collected before and after water capping) and their fractions were established. Significant inflammatory bioactivity was associated with the after-water capping sample and its organic fraction, whereas the before-water capping sample had reduced bioactivity that was primarily associated with its inorganic fraction. At this point, we are encouraged that immune cell bioassays are sensitive, reproducible, and reliable for examining different water samples. Furthermore, bioactive-guided profiling of OSPW represents a promising in vitro tool for the continued monitoring of various water samples undergoing both passive and active remediation treatment protocols.
- 16S (bacterial) profiling of water and sediment samples and optimization for DNA extraction for sediment samples have been completed. Finalization of the sequencing pipeline for 18S (eukaryotic heterotrophs) and 23S (autotrophs) has begun. Water and sediment (from both the experimental columns and Lake Miwasin) yield unique microbial signatures. The distinction between the bacterial profiles of sediment and water warrants continued investigation of both matrices. The sediment in particular contains evidence of bacterial genus' that may be participating in important processes related to the breakdown of OSPW constituents. A consistent sample processing pipeline that yields high quality DNA from such complex starting samples is in place, which is an essential first step for generating reliable and comparable datasets related to the bacterial, heterotroph and autotroph communities.
- The autonomous sensor network performed well to date, collecting high-frequency water quality data at multiple sites and water depths. These data show that concentrations of dissolved salts have been progressively decreasing in the surface water of Lake Miwasin with time. Results to date suggest that treated tailings are a source of salts and trace metals to overlying water, either from pore water expression or geochemical redox processes. Thermal stratification of the water column occurs during summer and this has implications for bottom water quality and exposure to aquatic organisms. Nevertheless, bottom water collected from Lake Miwasin was not toxic to standard laboratory test zooplankton (Cladocera). Both treated tailings and shallow slope sediments in Lake Miwasin are acutely toxic to midge larvae. Additional data will be collected to confirm the observations made to date using the autonomous sensors. The water and sediment toxicity testing are ongoing and will be completed next year.

LESSONS LEARNED

Lake Miwasin is still in an early stage for pit lake development. Preliminary results from the research and monitoring program indicate that Lake Miwasin has been performing as expected since the commencement of the project. More insights and lessons learned will be gained with the progress of lake development and the completion of the first 5-year R&M program. Lessons learned across all components of the Lake Miwasin program will be discussed in detail at the end of the 5-year monitoring program.

PRESENTATIONS AND PUBLICATIONS

Conference Presentations/Posters:

- Choi S, Cuss CW, Nagel AN, 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., and 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).

RESEARCH TEAM AND COLLABORATORS

Institution: Multiple consultants and research institutions

Principal Investigator: Multiple principal investigators

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WJ0121 – Base Mine Lake Monitoring and Research Program

COSIA Project Number: WJ0121

Research Provider: Multiple researchers and institutions

Industry Champion: Syncrude

Industry Collaborators: Imperial, Suncor, Canadian Natural

Status: Multi-year project, ongoing

PROJECT SUMMARY

BML is the first, and currently the only full-scale commercial demonstration of the end pit lake technology in the oil sands industry. An oil sands end pit lake (EPL) is an area where overburden and oil sand has been removed and is then filled with fluids prior to closure. An EPL contains water (from the process of oil sands extraction or freshwater or both) and may or may not contain treated or untreated fluid tailings (FT), or other solids (for example, coarse tailings sand, or overburden).

BML 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 fine tailings (FFT). Fluid fine tailings are comprised of silt, clay, process-affected water and residual bitumen. The FFT 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 in to 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. This flow through process dilutes the BML water cap over time and will be in place until a more substantial upstream surface watershed is reclaimed and connected to BML, and outflow is established into the 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.

A key purpose of the BML Monitoring and Research Program (MRP) is to support an adaptive management framework. The BML MRP is designed to assess lake performance against key performance indicators and evaluate the need for management interventions. The initial focus of the research program is to support the demonstration of water-capped tailings technology, and to provide a body of scientific evidence that demonstrates that BML 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 and measure these trends against some key performance metrics as outlined above. 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
		Sediment Toxicity
Physical Limnology Assessment	Groundwater Assessment	
	Chemical Mass Balance	
Meteorological Monitoring		
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 methane production, transport, oxygen	*To understand methane production and release, the sources of naphthenic acids and petroleum hydrocarbons to the BML water cap, and the role of ebullition in*	*McMaster University*	*Greg Slater*

consumption, and NA persistence	*transporting FFT constituents into the water cap*		
Base Mine Lake Process Dynamics	*To understand bitumen liberation to water surface, and develop monitoring and mitigation tools for bitumen.*	*Syncrude*	*Barry Bara*

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 FFT is 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 (2021) report can be found here: Syncrude 2021 Pit Lake Monitoring and Research Report

PRESENTATIONS AND PUBLICATIONS

Albakistani E. 2018. Methane Cycling and Methanotrophic Bacteria in Base Mine Lake, a Model End-Pit Lake in the Alberta Oilsands. PhD Thesis. Calgary, AB: University of Calgary. https://prism.ucalgary.ca/handle/1880/107699

Aguilar M, Richardson E, Tan B, Walker G, Dunfield PF, Bass D, Nesbø C, Foght JM, Dacks JB. 2016. Next-generation sequencing assessment of eukaryotic diversity in oil sands tailings ponds sediments and surface water. *J. Eukaryotic Microbiol.* 63:732-743. DOI: 10.1111/jeu.12320

Arriaga D. 2018. The Interplay of Physical and Biogeochemical Processes in Determining Water Cap Oxygen Concentrations within Base Mine Lake, the First Oil Sands Pit Lake. PhD Thesis. Hamilton, ON: McMaster University.

Arriaga, D, Colenbrander Nelson T, Risacher FR, Morris PK, Goad C, Slater GF and Warren LA. 2019. The co-importance of physical mixing and biogeochemical consumption in controlling water cap oxygen levels in Base Mine Lake. *Applied Geochemistry. 111:104442*

Bowman DT. 2017. Chemical Fingerprinting of Naphthenic Acids by Comprehensive Two Dimensional Gas Chromatography Mass Spectrometry at Reclamation Sites in the Alberta Oil Sands. PhD Thesis. Hamilton, ON: McMaster University. http://hdl.handle.net/11375/21963

Bowman DT, Jobst KJ, Ortiz X, Reiner EJ, Warren LA, McCarry BE, Slater GF. 2018. Improved coverage of naphthenic acid fraction compounds by comprehensive two-dimensional gas chromatography coupled with high resolution mass spectrometry. *J. Chromatography A.* 1536:88-95. DOI: 10.1016/j.chroma.2017.07.017

Bowman DT, McCarry BE, Warren LA, Slater GF. 2017a. Profiling of individual naphthenic acids at a composite tailings reclamation fen by comprehensive two-dimensional gas chromatography mass spectrometry. *Environmental Science & Technology* 649: 1522-1531 DOI: 10.1016/j.scitotenv.2018.08.317

Bowman DT, Jobst KJ, Ortiz X, Reiner EJ, Warren LA, McCarry BE, Slater GF. 2017b. Improved coverage of naphthenic acid fraction compounds by comprehensive two-dimensional gas chromatography coupled to a high resolution mass spectrometer. *Journal of Chromatography A* 1536: 88-95. DOI: 10.1016/j.chroma.2017.07.017

Brandon JT. Turbidity Mitigation in an Oil Sands End Pit Lake through pH Reduction and Fresh Water Addition. MSc Thesis. Edmonton, AB: University of Alberta. DOI: 10.7939/R3ST7F72D

Chen, L-X., R. Meheust, A. Crits-Christoph, K.D. McMahon, T.C. Nelson, G.F. Slater, L.A. Warren and J.F. Banfield. 2020. Large freshwater phages with the potential to augment aerobic methane oxidation. Nature Microbiology https://doi.org/10.1038/s41564-020-0779-9

Clark MG, Drewitt GB, Carey SK. 2021. Energy and carbon flux from an oil sands pit lake. *Science of the Total Environment*. 752:1141966. DOI: 10/1016/j.scitotenv.2020.141966

Dereviakin, M. 2020. Monitoring Spatial Distribution of Solvent Extractable Petroleum Hydrocarbons in Pit Lake Fluid Fine Tailings SGES McMaster University

Dompierre KA. 2016. Controls on mass and thermal loading to an oil sands end pit lake from underlying fluid fine tailings. PhD Thesis. Saskatoon, SK: University of Saskatchewan. 157 pp. https://harvest.usask.ca/handle/10388/7772

Dompierre KA, Barbour SL. 2016. Characterization of physical mass transport through oil sands fluid fine tailings in and end pit lake: a multi-tracer study. *Journal of Contaminant Hydrology* 189:12-26. DOI: 10.1016/j.jconhyd.2016.03.006

Dompierre KA, Lindsay MBJ, Cruz-Hernández P, Halferdahl GM. 2016. Initial geochemical characteristics of fluid fine tailings in an oil sands end pit lake. *Science of the Total Environment* 556:196-206. DOI: 10.1016/j.scitotenv.2016.03.002

Dompierre KA, Barbour SL. 2017. Thermal properties of oil sands fluid fine tailings: Laboratory and in-situ testing methods. *Canadian Geotechnical Journal* 54(3): 428-440. DOI: 10.1139/cgj-2016-0235

Dompierre KA, Barbour SL, North RL, Carey SK, Lindsay MBJ. 2017. Chemical mass transport between fluid fine tailings and the overlying water cover of an oil sands end pit lake. *Water Resources Research* 53: 4725-4740. DOI: 10.1002/2016WR020112

Goad C. 2017. Methane biogeochemical cycling over seasonal and annual scales in an oil sands tailings end pit lake. MSc Thesis. Hamilton, ON: McMaster University. http://hdl.handle.net/11375/21956

Haupt E. 2016. Methanotrophic Bacteria and Biogeochemical Cycling in an Oil Sands End Pit Lake. MSc Thesis. Calgary, AB: University of Calgary. http://dx.doi.org/10.11575/PRISM/26893

Hurley DL. 2017. Wind waves and Internal Waves in Base Mine Lake. MSc Thesis. Vancouver, BC: University of British Columbia. 91 pp. DOI: 10.14288/1.0351993

Lawrence GA, Tedford EW, Pieters R. 2016. Suspended solids in an end pit lake: potential mixing mechanisms. *Can. J. Civ. Eng.* 43:211-217 DOI: 10.1139/cjce-2015-0381

Mori, JF, Chen L, Jessen GL, Slater GF, Rudderham S, McBeth J, Lindsay MBJ, Banfield JF and Warren LA. 2019. Putative mixotrophic nitrifying-denitrifying gammaproteobacterial implicated in nitrogen cycling within the ammonia/oxygen transition zone of an oil sands pit lake. *Frontiers in Microbiology* https://doi.org/10.3389/fmicb.2019.02435

Morris PK. 2018. Depth Dependent Roles of Methane, Ammonia and Hydrogen Sulfide in the Oxygen Consumption of Base Mine Lake, the pilot Athabasca Oil Sands Pit Lake. MSc Thesis. Hamilton, ON: McMaster University. 97 pp. http://hdl.handle.net/11375/23040

Poon HY. 2019. An Examination on the Effect of Diluent on Microbial Dynamics in Oil Sands Tailings and the Mechanistic Insight on Carbon Dioxide-mediated Turbidity Reduction in Oil Sands Surface Water. PhD Thesis. Edmonton, AB: University of Alberta. 207 pp. DOI: 10.7939/r3-fek4-7t49

Poon HY, Brandon JT, Yu X, Ulrich A. 2018. Turbidity mitigation in an oil sands pit lake through pH reduction and fresh water addition. *Journal of Environmental Engineering* 144. DOI: 10.1061/(ASCE)EE.1943-7870.0001472

Rawluck S. 2017. The effect of chemical treatment on oil sand end-pit-lake microbial communities: an Investigation for a proxy of reclamation status. MSc in Sustainable Energy Development Capstone Project. https://haskayne.ucalgary.ca/files/haskayne/2017-Capstone-Abstracts.pdf

Richardson, E. 2020. The cell biology and ecology of heterotrophic eukaryotes in a tailings reclamation site in Northern Alberta. University of Alberta. https://era.library.ualberta.ca/items/8904ed02-2119-4ee4-adf0-330149c5af8a

Risacher FF. 2017. Biogeochemical development of the first oil sands pilot end pit lake. MSc Thesis. Hamilton, ON: McMaster University. http://hdl.handle.net/11375/22274

Risacher FF, Morris PK, Arriaga D, Goad C, Colenbrander Nelson T, Slater GF, Warren LA. 2018. The interplay of methane and ammonia as key oxygen consuming constituents in early stage development of Base Mine Lake, the first demonstration Oil Sands pit lake. *Applied Geochemistry* 93: 49-59. DOI: 10.1016/j.apgeochem.2018.03.013

Rochman FF. 2016 Aerobic hydrocarbon-degrading microbial communities in oilsands tailings ponds. PhD Thesis. Calgary, AB: University of Calgary. DOI: 10.11575/PRISM/24733

Rochman FF, Sheremet A, Tamas I, Saidi-Mehrabad A, Kim JJ, Dong X, Sensen CW, Gieg LM, Dunfield PF. 2017. Benzene and naphthalene degrading bacterial communities in an oil sands tailings pond. *Frontiers in Microbiology* 8: article 1845. DOI: 10.3389/fmicb.2017.01845.

Rochman FF, Kim JJ, Rijpstra WIC, Sinninghe Damsté JS, Schumann P, Verbeke TJ, Dunfield PF. 2018. *Oleiharenicola alkalitolerans* gen. nov., sp. nov., a new member of the phylum Verrucomicrobia isolated from an oilsands tailings pond. International *Journal of Systematic and Evolutionary Microbiology* 68:1078-1084. DOI: 10.1099/ijsem.0.002624

Rudderham SB. 2019. Geomicrobiology and geochemistry of fluid fine tailings in an oil sands end pit lake. MSc Thesis. Saskatoon, SK: University of Saskatchewan. 98 pp. https://harvest.usask.ca/handle/10388/11975

Saidi-Mehrabad A, Kits DK, Kim JJ, Tamas I, Schumann P, Khadka R, Rijpstra WIC, Sinninghe Damsté JS, Dunfield PF. 2020. *Methylicorpusculum oleiharenae* sp. nov., an aerobic methanotroph isolated from an oil sands tailings pond in Canada. *International Journal of Systematic and Evolutionary Microbiology* 7:908-921 DOI: 10.1038/ismej.2012.163

Samadi N. 2019. Partitioning of contaminants between fluid fine tailings and cap water under end-pit lake scenario: Biological, chemical and mineralogical processes. MSc Thesis. Edmonton, AB: University of Alberta. 152pp. DOI: 10.7939/r3-8730-4k32

Tedford EW, Halferdahl GM, Pieters R, Lawrence GA. 2018. Temporal variations in turbidity in an oil sands pit lake. *Environmental Fluid Mechanics*. 19:457-473. DOI: 10.1007/s10652-018-9632-6

Yu X. 2019. Improving Cap Water Quality in An Oil Sands End Pit Lake with Microbial Applications. PhD Thesis. Edmonton, AB: University of Alberta. DOI: 10.7939/r3-g0s1-by42

Yu X, Lee K, Ma B, Asiedu E, Ulrich A. 2018. Indigenous microorganisms residing in oil sands tailings biodegrade residual bitumen. *Chemosphere*. 209: 551-559. DOI: 10.1016/j.chemosphere.2018.06.126

Yu X, Lee K, Ulrich A. 2018. Model naphthenic acids removal by microalgae and Base Mine Lake cap water microbial inoculum. *Chemosphere* 234: 796-805. DOI: 10.1016/j.chemosphere.2019.06.110

Xhao K, Tedford EW, Zare M, and Lawrence GA. 2021. Impact of atmospheric pressure variations on methane ebullition and lake turbidity during ice-cover. *Limnology and Oceanography Letters.*

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Jared Robertson	University of Saskatchewan	Post Doc Fellow	2017	2018
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Katherine Norris	University of Toronto	Undergraduate research assistant	2019	2020
Karen Chu	University of Toronto	Undergraduate research assistant	2019	2020
Julia Reman	McMaster University	Undergraduate research assistant	2018	2018
Mike Dereviankin	McMaster University	MSc	2019	2021
Peter Dunfield	University of Calgary	PI		
Lisa Gieg	University of Calgary	Co-PI		
Joel Dacks	University of Alberta	Collaborator		
Evan Haupt	University of Calgary	MSc	2014	2016
Emad Albakistani	University of Calgary	MSc	2015	2018
Sam Rawluck	University of Calgary	MSc	2016	2017
Angela Smirnova	University of Calgary	Research Associate		
Elizabeth Richardson	University of Alberta	PhD	2014	2020
Lucas Paoli	University of Alberta	BSc	2012	2016
Felix Nwosu	University of Calgary	PhD	2015	2020
Chunzi Wang	University of Calgary	BSc	2012	2016
Azriel Abraham López Jáuregui	University of Calgary	BSc	2013	2018
Fauziah Rochman	University of Calgary	PhD	2011	2016
Gul Zeb	University of Calgary	MSc	2015	2018
Tobin Verbeke	University of Calgary	Postdoctoral Fellow		
Triet Tran	University of Calgary	MSc		
Chantel Biegler	University of Calgary	MSc		
Dr. Greg Lawrence	University of British Columbia	Professor		
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	Masters student	2015	2017
Tomy Doda	EPFL	Masters student	2016	2017

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
Industry Collaborators: Canadian Natural, Imperial, Suncor, Teck
Status: Year 5 of 6

PROJECT SUMMARY

Rationale

As one of COSIA's identified priority areas, water management is vital not only in the continuous development of the oil sands industry but also in managing current and future water allocations and preserving healthy ecosystems and human well-being. Currently, the majority of water used for surface mining operations is recycled from settling basins, while the remainder of the required water is withdrawn from the Athabasca River.

Oil sands process water (OSPW) is generated during the extraction process. OSPW will need to be treated and released into the environment. Therefore, water treatment/reclamation approaches are required to ensure OSPW quality is safe for its release.

Project Scope and Objectives

The NSERC IRC Program - Second Term (2017-2023) focuses on developing and assessing innovative water treatment/reclamation technologies and strategies through a combination of passive (low-energy) and semi-passive treatment approaches that will help promote and protect both the environment and public health.

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

- 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 four large field pilots on active mine sites.
- Develop a "toolbox" with the best available technologies for different water stream scenarios.

The long-term objectives, including those beyond the 6-year 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 OSPW by facilitating the transfer of knowledge and new discoveries.
- Integrate the knowledge gained into actual water management options by the oil sands industry.

Methodology

To achieve the objectives of the NSERC IRC Program – Second Term, 30 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: NSERC IRC Program – Second Term Projects

Project ID #	Research Area	Title	Status
1	Water and Tailings Quality	Long-Term Assessment of Oil Sands Process Water Quality Due to Self-Attenuation	Ongoing
2a	Advanced Oxidation Processes	Solar Photocatalytic Treatment of OSPW Using Bismuth Tungstate Based Photocatalysts	Ongoing
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	Ongoing
2g	Advanced Oxidation Processes	Treatment of NAs in OSPW by Solar-Driven Membrane-Photoelectrocatalysis using Blue/PVDF Catalytic Membrane and Calcium Peroxide	Ongoing
3	Advanced Oxidation Processes	In-Situ Generation of Reactive Oxygen Species Using Sewage Sludge Biochar as a Catalyst	Ongoing
4	Biological Treatments	Understanding of Engineered Passive Processes for OSPW Treatment Using Mesocosms	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	Ongoing
5c	Electro-Oxidation Processes	Treatment of OSPW by Packed Bed Electrode Reactor	Completed
5d	Electro-Oxidation Processes	Removal of Organic Pollutants in OSPW by Electrochemically Activated Persulfate with MOF-derived (MoS_2, Fe_3O_4)/ Catalyst	ongoing
5e	Electro-Oxidation Processes	Electro-Oxidation of NAs in OSPW by Polyaniline Modified Biochar/Graphene Electrode	Ongoing
6	Biological Treatments	Remediation of OSPW Using Deep Biofilters – From Bench to Scale-up Tests	Ongoing
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	Ongoing
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	Ongoing
9	Piloting Tests	Coke-Treatment Piloting	Postponed
10	Piloting Tests	Wetland Piloting	Ongoing
11	Piloting Tests	Vegreville Mesocosm Piloting	Ongoing
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	Ongoing
15	Water and Tailings Quality	Assessing the Effects of Polymers and Polymer Degradation on Water Chemistry and the Quality of the Tailings	Ongoing
16	Water and Tailings Quality	Development of Mass Spectrometry Based Analytical Methods for the Detection of Multiple NAs and Identification of Byproducts	Ongoing

Significance of the Research to the Industry

The NSERC IRC Program - Second Term aligns with ongoing efforts for the sustainable economic development of Alberta oil sands resources. Assessment of the various types of low energy OSPW treatment processes (i.e., semi-passive and engineered passive approaches) will contribute to a better understanding of how treated/reclaimed OSPW could be safely discharged into the environment. The comprehensive characterization of OSPW before and after treatment, the dose-response analysis of toxic effects induced by different OSPW fractions, and the use of different treatment processes for OSPW will allow for the development of reclamation strategies for the safe release of OSPW into the environment and, ultimately, protection of public health.

PROGRESS AND ACHIEVEMENTS

The NSERC IRC Program - Second Term is achieving many short and long term objectives, including: training of highly qualified personnel with multidisciplinary expertise; researching technical issues of strategic importance to Canada; and promoting cooperation and knowledge exchange between academia, industry and government.

In terms of water and tailings quality, we are assessing the OSPW quality due to self-attenuation (Project #1) and studying the stability and degradation of anionic polyacrylamides (PAM) in oil sands tailings (Project #15). We have also developed a method using atmospheric pressure gas chromatography time-of-flight mass spectrometry (APGC-TOF-MS) combined with solid-phase microextraction (SPME) for the simultaneous analysis of hydrocarbons and naphthenic acids (NAs) species. We have conducted solid phase micro-extraction (SPME) and analyzed polydimethylsiloxane (PDMS)-coated fibers using gas chromatography with flame ionization detector (GC-FID) to quantify bioavailable organics (Project #14). The BE-SPME technique developed in this project could serve as a benchmark technology and as a quick assessment method to monitor the transformation of bioavailable organics in different treatment processes (e.g., wetland biodegradation) and in the natural environment. We have also developed analytical methods for the analysis of multiple NAs in a single run and methods for the identification of treatment by-products (Project #16). This has allowed a more accurate study of the degradation of NAs in real systems and to understand the removal mechanisms involved in different treatment processes.

Studies conducted under the NSERC IRC Program have shown that advanced oxidation processes (Projects #2c, #2d, #2f) will play a critical role in enhancing the remediation of OSPW in pit lakes or wetlands when applied as a pretreatment step to accelerate the degradation of NAs and other organics in OSPW. Our findings also suggest that the photodegradation efficiency of OSPW treatment strategies can be enhanced in the presence of the inorganic photosensitizer in OSPW (Project #2b). Our results have shown that nitrate could be utilized as a natural photosensitizer to induce photo-oxidation of organic compounds in OSPW and could potentially be utilized in a low-cost passive solar system for the remediation of OSPW with extended exposure time. Simulating the formation process of reactive oxygen species based on iron complexes in nature to degrade organic compounds would also be an environmentally friendly remediation process for OSPW (Project #2e). We have also demonstrated that NAs in OSPW could be efficiently degraded by solar photocatalytic treatment using bismuth tungstate (Project #2a). Our findings also suggest that zinc oxide (ZnO)-based photocatalytic degradation of naphthenic acids (NAs) and polyaromatic hydrocarbons in OSPW could be a significant treatment process aimed at detoxifying OSPW. We have demonstrated that the immunotoxicity of the OSPW was considerably reduced by the ZnO-based photocatalytic treatment (Project #2f).

Considering the nature and structure of NAs and the characteristics of OSPW, with its high electrical conductivity, electro-oxidation seems to be an effective and cost-efficient option for OSPW treatment (Projects #5a, #5b, and #5c). Applying anodic oxidation by using inexpensive electrodes materials, such as graphite, and under low voltage conditions can preferentially degrade NAs of higher cyclicity and carbon number and decrease the number of rings and molecular weight without resulting in complete mineralization. Therefore, the application of electro-oxidation could enhance OSPW biodegradability and reduce the toxicity. The lower voltages required for the treatment will result in a sustainable and environmentally friendly process that can be operated by solar energy, and the exclusion of the need for chemicals addition will prevent the production of any additional hazardous sludge. Electro-oxidation using BDD was also found to be an efficient treatment technique for the remediation of dissolved organic in OSPW as complete degradation of NAs and PAHs was obtained within 2 h of electrolysis at 5 mA cm^{-2} or above and complete dissolved organic carbon removal attained in 6 h at similar current densities (Project #5b). We are in the process to develop new electrode materials (Project #5e).

In terms of material development, studies conducted under the NSERC IRC Program have reported, for the first time, the mechanism of adsorption of NAs onto carbon xerogels (Project #8a). Our results have demonstrated that mesoporous carbonaceous materials such as carbon xerogels can successfully be used to adsorb persistent and toxic organic contaminants from OSPW, resulting in a treated water that may be less acutely and chronically toxic to aquatic and mammalian life. We have also developed non-toxic and biodegradable cellulose nanofibers (CNFs) for adsorption treatment (Project #8b). The vast sources of raw material, only one step in aqueous modification, together with the semi-commercialized production allow the tailored CNF material to be applied in large scale in industrial process water treatment. We have also developed sludge-based biochar (Project #8c) and biochar-chitosan composite (Project 8d). Our results have shown that sludge-based biochar exhibits excellent adsorption performance due to its highly mesoporous character, so it could be used as a passive treatment method in tailing ponds for the removal of organic matter.

In terms of biological treatment, biofiltration and mild ozonation show complementary advantages for the degradation of NAs (Project #6). The biofiltration-ozonation-biofiltration process shows higher NA removal than the biofiltration of raw OSPW. The biofiltration pretreatment can benefit the ozonation of NAs while the post-biofiltration process shows its contribution to the improved removal of the oxidized NAs from OSPW. We have also found that bioaugmentation could be a useful strategy to improve the existing remediation potential of petroleum coke-based biofilters.

LESSONS LEARNED

The following are the key outcomes achieved so far:

- The characterization and treatment of OSPW pose many challenges, including the presence of dissolved organic compounds such as NAs, other organic acids, total suspended solids, bitumen, salinity, trace metals, and other dissolved organic and inorganic compounds. The water characterization and toxicity assessment of the OSPW in both untreated and treated OSPW will help to achieve a much better understanding of the potential impacts of treated OSPW on the environment.
- The BE-SPME method presented in the NSERC IRC program could serve as a rapid and convenient analytical screening tool for estimating the toxicity of raw and treated OSPWs due to dissolved organics. The BE-SPME technique could serve as a benchmark technology to monitor the transformation of bioavailable NAs in treatment processes (e.g., wetland biodegradation), as well as to monitor the natural transfer and transformation of bioavailable NAs in the natural environment.
- Atmospheric pressure gas chromatography time-of-flight mass spectrometry (APGC-TOF-MS) combined with solid-phase microextraction (SPME) will allow the simultaneous analysis of hydrocarbons and naphthenic acids (NAs) species.
- Using sewage sludge as a precursor for the production of sewage sludge-based material (sludge-based biochar) has many advantages. It can be used to adsorb organic compounds from OSPW. The sludge-based biochar can also be used as catalysts for advanced oxidation processes.
- Low-current electro-oxidation is a promising pre-treatment option for OSPW while being routed to pit lakes and/or wetlands as it can lead to improved biodegradability and reduced toxicity of OSPW organics. The lower voltages required and low-cost graphite electrodes will result in a sustainable and environmentally-friendly process that can be operated by solar energy or can be used for in-pipe treatment.
- In situ catalytic oxidation may play a critical role in enhancing the remediation of OSPW when applied as a pre-treatment step to accelerate the degradation of NAs, among other organics, in OSPW.

- Biofiltration possesses remarkable advantages, such as low energy costs and low capital demand. The fixed-bed biofilm reactor shows high potential to be applied and scaled-up for the in situ treatment of OSPW.

Providing innovative multi-barrier treatment approaches and water reuse/release scenarios will help promote and protect environmental and public health, enhance water quality, and support the ongoing efforts that assist the economical and sustainable development of Alberta oil sands resources.

PRESENTATIONS AND PUBLICATIONS

To date there have been 65 publications in peer reviewed journals and 101 presentations.

Journal Publications:

Ten recent publications are listed below.

Abdalrhman, A.S., C. Wang, Z.T. How, and M. Gamal El-Din. 2021. *Degradation of cyclohexanecarboxylic acid as a model naphthenic acid by the UV/chlorine process: Kinetics and by-products identification*. J. Hazard. Mater., 402, 123476.

Arslan, M., J.A. Müller, and M. Gamal El-Din. 2022. *Aerobic naphthenic acid-degrading bacteria in petroleum-coke improve oil sands process water remediation in biofilters: DNA-stable isotope probing reveals methylotrophy in Schmutzdecke*. Sci. Total Environ., 815, 151961.

Ganiyu, S.O., M. Arslan, M. Gamal El-Din. 2022. *Combined solar activated sulfate radical-based advanced oxidation processes (SR-AOPs) and biofiltration for the remediation of dissolved organics in oil sands produced water*. Chem. Eng. J., 433, Part 1, 134579.

Huang, R., L. Yang, Z.T. How, Z. Fang, A. Bekele, D.J. Letinski, A.D. Redman, and M. Gamal El-Din. 2021. *Characterization of raw and ozonated oil sand process water utilizing atmospheric pressure gas chromatography time-of-flight mass spectrometry combined with solid phase microextraction*. Chemosphere, 266, 129017.

Luo, Z., L. Meng, Z.T. How, P. Chelme-Ayala, L. Yang, C. Benally, M. Gamal El-Din. 2022. *Treatment of oil sands process water by the ferric citrate under visible light irradiation*. Chem. Eng. J., 429, 132419.

Meng, L., Z.T. How, S.O. Ganiyu, and M. Gamal El-Din. 2021. *Solar photocatalytic treatment of model and real oil sands process water naphthenic acids by bismuth tungstate: Effect of catalyst morphology and cations on the degradation kinetics and pathways*. J. Hazard. Mater., 413, 125396.

Messele, S.A., P. Chelme-Ayala, and M. Gamal El-Din. 2021. *Catalytic ozonation of naphthenic acids in the presence of carbon-based metal-free catalysts: Performance and kinetic study*. Catalysis Today, 361, 102-108.

Song, J., Z.T. How, Z. Huang, and M. Gamal El-Din. 2022. *Biochar/iron oxide composite as an efficient peroxymonosulfate catalyst for the degradation of model naphthenic acids compounds*. Chem. Eng. J., 429, 132220.

Suara, M.A., S.O. Ganiyu, S. Paul, J.L. Stafford, and M. Gamal El-Din. 2022. *Solar-activated zinc oxide photocatalytic treatment of real oil sands process water: Effect of treatment parameters on naphthenic acids, polyaromatic hydrocarbons and acute toxicity removal*. Sci. Total Environ., 819, 153029.

Zhang, L., Y. Zhang, Y. Zhang, and M. Gamal El-Din. 2021. *Application of an indigenous microorganisms-based fixed-bed GAC-biofilm reactor for passive and sustainable treatment of oil sands process water through combined adsorption and biodegradation processes*. Chemosphere, 280, 130635.

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		
Grant Hauer	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)
Soliu Ganiyu	University of Alberta	Postdoctoral Fellow		
Zou Tong How	University of Alberta	Postdoctoral Fellow		2022 (completed)
Muhammad Arslan	University of Alberta	Postdoctoral Fellow		
Ming Zheng	University of Alberta	Postdoctoral Fellow		
Muhammad Usman	University of Alberta	Postdoctoral Fellow		
Zhijun Luo	University of Alberta	Visiting Professor		2019 (completed)
Abdallatif Abdalrhman	University of Alberta	Ph.D. Student	2014	2019 (completed)
Rui Qin	University of Alberta	Ph.D. Student	2014	2019 (completed)
Lei Zhang	University of Alberta	Ph.D. Student	2014	2018 (completed)
Lingjun Meng	University of Alberta	Ph.D. Student	2017	2022
Chelsea Benally	University of Alberta	Ph.D. Student	2012	2018 (completed)
Jia Li	University of Alberta	Ph.D. Student	2019	2023
Monsuru Suara	University of Alberta	Ph.D. Student	2019	2023
Zhexuan An	University of Alberta	Ph.D. Student	2019	2023
Akeen Bello	University of Alberta	Ph.D. Student	2019	2023
Foroogh Mehravaran	University of Alberta	Ph.D. Student	2019	2023
Deborah Medeiros	University of Alberta	Ph.D. Student	2019	2023
Jerico Fiestas Flores	University of Alberta	Ph.D. Student	2020	2024
Ziang Chang	University of Alberta	Ph.D. Student	2020	2024
Zhi Fang	University of Alberta	Visiting Ph.D. Student	2017	2017 (completed)
Hande Demir	University of Alberta	Visiting Ph.D. Student	2019	2019 (completed)
Junying Song	University of Alberta	Visiting Ph.D. Student	2019	2019 (completed)
Yue Ju	University of Alberta	Visiting Ph.D. Student	2019	2021 (completed)
Qi Feng	University of Alberta	Visiting Ph.D. Student	2021	2022
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	
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, Associate 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, T.A. Graham Professor of Strategy and Organization and the Director of the Canadian Center for Corporate Social Responsibility (CCCSR), Alberta School of Business.
- Dr. M. Anne Naeth, Professor of Land Reclamation and Restoration Ecology, Department of Renewable Resources, Associate Dean Research and Graduate Studies in the Faculty of Agricultural, Life and Environmental Sciences, Director of the Land Reclamation International Graduate School (LRIGS) and Director of the Future Energy Systems (FES), 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.
- Dr. Sandra Contreras Iglesias, Professor, Department of Chemical Engineering, Universitat Rovira, Spain.
- Dr. Peng Liang, Professor, State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, China.
- Dr. Bin Xu, Associate Professor, College of Environmental Science and Engineering, Tongji University, China.
- Dr. Chunmao Chen, Associate Professor, State Key Laboratory of Heavy Oil Processing, State Key Laboratory of Petroleum Pollution Control, China University of Petroleum-Beijing, China.
- Dr. Zhijun Luo and Dr. Zhiren Wu, Professor, School of the Environment and Safety Engineering, Jiangsu University, China.

Non-COSIA Collaborators:

- EPCOR Water Services
- Alberta Innovates
- Alberta Environment and Parks

WJ0042.05 – In-Pit Treatment of Selenium and Nitrate

COSIA Project Number: WJ0042.05

Research Provider: Teck

Industry Champion: Teck

Industry Collaborators: None

Status: Complete

PROJECT SUMMARY

In pit treatment was identified as a potential source control approach to reduce constituents of interest, such as selenium and nitrate. In-pit treatment is a type of passive water treatment that involves adding amendments directly to a pit lake and allowing treatment to take place within the mined out- pit structure prior to discharge. This study of in-pit treatment was conducted to determine whether an amendment can be added to active or inactive mined-out pits, in the most “passive” manner practicable, and result in the reduction of at least one constituent of interest (CI), therefore reducing the burden to downstream active water treatment. There are three phases of this project: literature review, bench-top mesocosm testing, and bench-top column testing.

PROGRESS AND ACHIEVEMENTS

A literature review was completed to evaluate in-pit treatment as a technology option and identify organic and inorganic amendments for treatment. The treatment methods considered in the review were separated into two types: physicochemical treatment and biological treatment. Physicochemical treatment reagents utilize mechanisms such as adsorption, reduction, and chemical precipitation to immobilize CI. Biological treatment utilizes microorganisms to facilitate the development of reducing conditions, in this case to reduce nitrate (NO_3) and Se(VI), typically under sub-oxic to anoxic conditions.

Based on the results from the preliminary screening and literature review, laboratory mesocosm tests were conducted. The tests evaluated the effectiveness of methanol, as a simple organic carbon source, solid organic carbon (SOC) of mulch and hay as a complex organic carbon source, and zero-valent iron (ZVI). Water for the mesocosm test contained high Se, moderate nitrate and sulphate concentrations, and near neutral pH. The results from the mesocosm study indicate that the SOC system was highly effective at reducing CI. ZVI was also effective for CI reduction, but high concentrations of ammonia were generated and could not be mitigated with zeolite, due to passivation of sites on the zeolite particles. The MeOH systems were less effective overall but have the potential to be combined with SOC systems which could improve the flexibility of use in the field. The addition of tailings contributed to pH control in the SOC mesocosms and incrementally increased Se reduction. Based on these results, the SOC, SOC/tailings, methanol (MeOH), and MeOH/tailings systems were carried forward to laboratory column testing.

The laboratory column experiments were intended to build on the previous mesocosm experiments. The amendments initially added to each of the columns include variations of: tailings, MeOH, mulch, and hay. The results from the column study indicate the potential for mine tailings, SOC in the form of mulch and hay, and methanol, to reduce CI in water.

LESSONS LEARNED

The study demonstrated that SOC achieved faster, more effective Se and NO_3 reduction, compared to MeOH alone; however, high doses of SOC alone could result in the generation of undesirable by-products. The results suggest that the microbial community is an important factor. Furthermore, small amounts of SOC, in combination with mine tailings and MeOH, may produce conditions favourable for Se and nitrate reduction in pit lakes.

PRESENTATIONS AND PUBLICATIONS

No public reports or presentations.

RESEARCH TEAM AND COLLABORATORS

Institution: Technical Services, Trail

Principal Investigator: Louiza Bell

WJ0042.06 – Tank Based Treatment of Nickel and Cobalt

COSIA Project Number: WJ0042.06

Research Provider: Teck

Industry Champion: Teck

Industry Collaborators: None

Status: Year 1 of 2

PROJECT SUMMARY

This project aims to identify and evaluate water treatment technologies to manage nickel and cobalt in mine-impacted water (MIW) by using tank-based water treatment methods. Typical concentrations of nickel in MIW range from 0.2-0.3 mg/L, with target concentrations post treatment of 5 ug/L nickel. The following technologies were selected for pilot testing:

1. Ion Exchange (IX)
2. High Density Lime (HDS)

PROGRESS AND ACHIEVEMENTS

The progress for each project is described below:

IX: Studies in 2020 using IX technology showed promise in removing nickel to below guideline concentrations, being protective of the receiving environment, and producing a relatively low quantity of residuals in a bench-scale program. A larger pilot facility to test IX was designed using commercially available resins, and constructed at Technical Services, Richmond (TSR). The pilot was constructed to evaluate a worst-case scenario for nickel and was designed to run at the upper range of the IX to allow design parameter to be determined under freshet conditions. Water was sourced from Location 1 Operations, and logistics developed to transport water from the mine site to the testing location in Vancouver. The pilot was commissioned in January 2022 and is currently in operation.

HDS: Studies in 2020 using lime precipitation, HDS technology, showed promise in removing nickel to below guideline concentrations while being protective of the receiving environment. A larger pilot facility to test HDS was designed and constructed at Technical Services, Richmond (TSR). The pilot was constructed in 2021 to evaluate nickel removal from Location 1 Operations, including modifications to allow for longer solids settling time. The pilot will be commissioned in March 2022.

LESSONS LEARNED

The early results from the IX system indicates that a pre-treatment step to remove ultra-fine solids is required, to prevent solids hold-up in the resin bed. Early results also indicate that the water is strongly scaling and that approaches are required to minimize precipitation of solids and bed cementation.

The HDS pilot is not in operation yet and will be commissioned in March 2022.

PRESENTATIONS AND PUBLICATIONS

No public reports or presentations.

RESEARCH TEAM AND COLLABORATORS

Institution: Technical Services, Richmond

Principal Investigator: Arash Iranshahi

WJ0042.07 - Weep Berm Technology Review

COSIA Project Number: WJ0042.07

Research Provider: Teck

Industry Champion: Teck

Industry Collaborators: None

Status: Complete

PROJECT SUMMARY

Technical Services, Trail (TST) completed a literature review of weep berm technologies for the purpose of improving water quality at mine sites. Weep berms (also known as check dams or flexible reactive berms) at the base of Mined Rock Stockpiles (MRS), were identified as having the potential to create suboxic zones (SOZ) where reduction of constituents of interest (CI), such as selenium and nitrate, could occur (Figure 1). The objective of this review is to summarize the available information in the literature and to assess the applicability of the technology. Following the technology review, a site selection study was completed to identify locations for a small-scale field trial in the field.

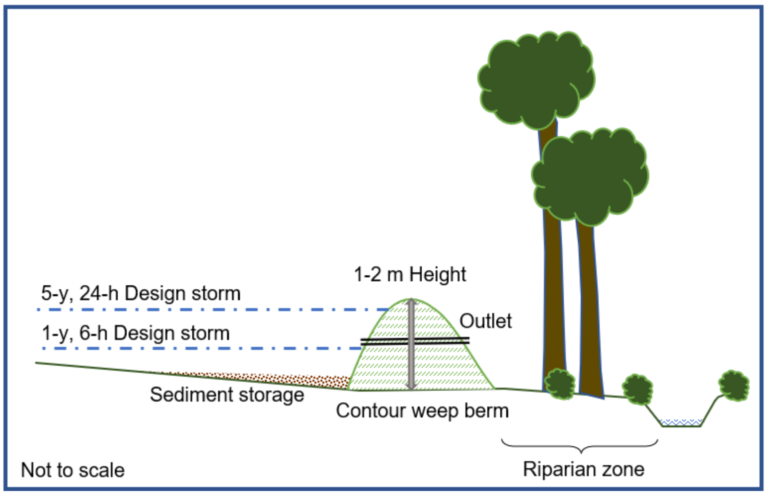

Figure 1. Side view of weep berm structure. Figure developed by KCB Consultants Ltd.

PROGRESS AND ACHIEVEMENTS

The concept of weep berms at the base of a MRS is being evaluated as part of the overall SOZ project. The technology review and site selection study were completed, and some key learnings are presented below.

LESSONS LEARNED

The literature identified some key challenges of this technology:

- Geochemical effectiveness is dependent on the hydrogeological setting and the ambient temperature – reaction rates slow down as temperature decreases – this is expected to impart a strong seasonal bias on efficacy.
- Easily damaged during spoil advancement and extreme flow events.
- Consumption of labile carbon and/or the potential for diminishing permeability over time (e.g., clogging, compaction) is expected to require ongoing maintenance. Maintenance activities may involve dredging or re-construction and would require easy access to the structures. Dredged material must be disposed with consideration of the geochemical stability of trapped CI.

The benefits of properly constructed weep berms include:

- Effective at peak flow reduction – return to natural hydrological setting;
- Traps sediment (TSS) and CI typically sorbed onto sediment, such as Ni and Cd;
- Inexpensive;
- Easily constructed and designed;
- Used at closure or during active care phase; and
- Effective at reduction of specific conductivity in spoil runoff by settling TSS
- Potential for selenium and nitrate to be immobilized through microbial reactions

The site selection study identified some limitations to the application of the weep berm. One challenge was the predominance of concentrated seep flow rather than diffuse surface runoff from MRS. Weep berms are not typically intended to attenuate concentrated seep flow, therefore the design of the berm may need to be modified. However, concentrated seep flow has the added potential benefit of supporting development of a permanent SOZ behind the berm. Locations from the site selection study are currently being reviewed and the next phase of the study will include a field trial.

PRESENTATIONS AND PUBLICATIONS

No public reports or presentations.

RESEARCH TEAM AND COLLABORATORS

Institution: Technical Services, Trail

Principal Investigator: Louiza Bell

WJ0042.08 – Alternative Mine Rock Stockpile Construction Methods

COSIA Project Number: WJ0042.08

Research Provider: Teck

Industry Champion: Teck

Industry Collaborators: None

Status: Complete

PROJECT SUMMARY

Currently, most Mine Rock Stockpiles (MRS) at Location 1 are constructed using end-tipping from the MRS crest, which results in grain-size segregation along the slope, with coarser material creating a rubble zone at the base of the structure. This is believed to encourage advective gas transport through the MRS, which provides atmospheric oxygen for continued sulphide oxidation and release of selenium, sulphate, and other constituents of interest (CI) which are leached from the MRS as water travels through the structure. This project was conducted to identify alternative construction methods that might reduce advective gas transport, manage contact water flow paths, or create suboxic zone (SOZs) within MRS, under the conditions present at Location 1. There are three parts to this project: 1) a literature review to understand the industry's current state of knowledge and potential issues around the practice; 2) a geotechnical assessment to identify potential issues with the alternative methods to be modelled; and 3) modeling of three alternative methods to understand how fundamental construction variables affect outcomes.

PROGRESS AND ACHIEVEMENTS

The literature review identified three alternative construction method options for modelling:

- The use of toe berms and fine-grained "aprons" within the end-dumped mine rock piles
- A combination of bottom-up and end-dumped construction
- Bottom-up construction with engineered layers

Numerical modeling was completed for the three construction methods as well as some variations to investigate parameter sensitivity. Steady state analysis showed that material permeability and oxygen consumption rates were the two variables with the highest influence on the final extent of a simulated SOZ within the mine rock pile. Transient analysis indicated that early action/intervention may reduce the degree of advective oxygen ingress into a mine rock pile and thus improve the development of a SOZ. The geochemical conceptual model indicates that mechanisms for selenium and sulphate release and immobilization are complex and depend on site-specific geochemical conditions. One of the key findings of this work was that alternative construction methods alone are unlikely to achieve desired outcomes if they cannot achieve low air permeability within the MRS.

LESSONS LEARNED

The analysis identified some construction techniques that could be implemented in current mine plans, even
though a fulsome analysis has not been completed. These include the following:

- Implementation of a top cap/layer wherever possible to limit air and water transport through the MRS.
- Addition of toe wraps to reduce air entry into the larger diameter mine rock (rubble zone).
- Slope MRS surfaces to shed as much water as possible and limit water infiltration.
- Identify and limit features that encourage oxygen exchange to minimize oxygen ingress and mineral oxidation within an MRS.
- Design MRS facilities to interface with low permeability, natural features wherever possible, to limit air entry through side slopes.

PRESENTATIONS AND PUBLICATIONS

No public reports or presentations.

RESEARCH TEAM AND COLLABORATORS

Institution: Technical Services, Trail

Principal Investigator: Louiza Bell

WJ0042.09 – Nickel Cobalt Non-tank Based Treatment

COSIA Project Number: WJ0042.09

Research Provider: Teck

Industry Champion: Teck

Industry Collaborators: None

Status: Complete

PROJECT SUMMARY

This project aims to identify and evaluate water treatment technologies to manage nickel and cobalt in mine-impacted water (MIW). Typical concentrations of nickel in MIW range from 0.2-0.3 mg/L, with target concentrations post treatment of 5 ug/L nickel. The following technologies were selected for bench-scale and/or field pilot testing:

1. Saturated Rock Fill (SRF)
2. In-pit treatment using hydrated lime
3. Chelating agents to reduce nickel bioavailability in water

PROGRESS AND ACHIEVEMENTS

The progress for each project is described below:

SRF: Studies initiated in 2020 investigated the suitability of saturated rock fills (SRFs) to treat dissolved nickel in water. The addition of carbon leads to biological reduction of sulphate to sulphide resulting in the precipitation and immobilization of nickel as a nickel sulphide. Bench-scale batch and column tests were also conducted to better understand the attenuation mechanisms and process controls. In 2021, a containerized pilot was designed, constructed, and commissioned to assess the technology for removal of nickel from mine contact water. The pilot is currently still ongoing.

In-pit Treatment: The evaluation of in-pit treatment of nickel and cobalt via physical and chemical technologies for pit lakes was conducted, and included technology reviews, laboratory studies and a mini-pilot. In 2021, a larger field pilot was conducted to further evaluate the effectiveness of lime amendment on dissolved nickel and cobalt concentrations in pit lakes. The key results from the field pilot are listed below:

- Removal of dissolved nickel to <5.3 µg/L and dissolved cobalt to <4.0 µg/L was observed at a pH of 10.5-11.5 and 10-10.5, respectively
- Characterization of solids indicated the presence of nickel and cobalt sequestered in calcium magnesium precipitates. Limited leaching tests suggested low potential for remobilization of the sequestered nickel and cobalt.

Chelating Agents: Initial bench-top laboratory testing evaluated the efficacy of four chelators including nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), citric acid, and oxalic acid. The degree of toxicity reduction was determined through laboratory testing (i.e., chronic whole effluent toxicity testing) with Ceriodaphnia dubia (C. dubia). The 2020 program identified that chelators have the potential to reduce nickel bioavailability in water and identified NTA as the most consistent chelator for improvement of aquatic toxicity. The 2021 program focused on evaluating the efficacy of NTA to reduce nickel toxicity in mine water through bench-top testing. The results indicate that C. dubia survival with NTA was high (90-100%) in all three test rounds and mean reproduction varied between (79% to 111%) of the mean laboratory control reproduction.

LESSONS LEARNED

The early results from the SRF treatment study indicate evidence for iron and sulphate reducing microbial growth in one of the three columns by sporadic increases in ferrous iron and sulphide concentrations as well as nickel removal. Selenium and nitrate removal was also observed with the addition of 5 mg/L of dissolved organic carbon.

The results from the in-pit treatment study indicates the potential for removal of nickel and cobalt from pit lakes using hydrated lime. A larger scale demonstration is required to better understand the site-specific characteristics of the site including the effect of lake turnover.

The results from the chelator project indicate that chelators can be effective tools to reduce residual nickel toxicity and that effectiveness can be achieved within a range of discharge water chemistries. Key questions to consider for this technology include those related to scale-up of the study and NTA as a full-scale water treatment.

PRESENTATIONS AND PUBLICATIONS

No public reports or presentations.

RESEARCH TEAM AND COLLABORATORS

Institution: Technical Services, Trail

Principal Investigator: Anna Ho

WJ0042.10 – Co-mingling of Mine Rock and Tailings

COSIA Project Number: WJ0042.10

Research Provider: Teck

Industry Champion: Teck

Industry Collaborators: None

Status: Complete

PROJECT SUMMARY

Amendments have been identified as facilitating the alteration of conditions within a Mined Rock Stockpiles (MRS) and could either minimize oxidation and mobilization of a constituents of interest (CI) or act as a reactive medium to sequester CI. This project is focused on the use of tailings and waste rock as potential material to create favourable conditions within a MRS to limit oxidation, create a suboxic zones (SOZ), or capture CI that have already been mobilized. Previous investigations with tailings storage facilities have shown that nitrate and selenium can be attenuated as water passes through the structures. Biological reduction has been shown to be the key mechanism, although it is believed that the tailings also play a role. The basis of this work package is to investigate the feasibility and potential options around the use of tailings within MRS to utilize similar mechanisms occurring in tailings storage facilities (TSFs) for source control. This study was conducted in two parts: 1) a literature review to understand industry experience with co-mingling tailings and mine rock and to examine potential issues around the practice; and 2) a trade-off study to identify options and conduct fundamental evaluations to eliminate any with obvious flaws.

PROGRESS AND ACHIEVEMENTS

The results from the literature review indicate that most co-storage methods are feasible; however, some may be uneconomical or impractical. Strategies that rely on a narrow range of optimally blended material would either be constructed separately from other MRS or in a limited area within a larger MRS. Strategies that do not rely on high degrees of mixing are expected to be easier to implement; however, they may not provide the expected geochemical and geotechnical benefits. Successful implementation will require adaptation of configurations to the by-product characteristics and the life of mine (LOM) plan.

LESSONS LEARNED

The study indicated that there was no clear front-runner for the co-storage options. The potential options available will be site-specific; dependant on the stage of MRS construction (not started, in progress, completed), topography, whether adequate materials are available and in what form (slurry or dewatered tailings, CCFR), and MRS construction methodology (top-down, bottom up).

PRESENTATIONS AND PUBLICATIONS

No public reports or presentations.

RESEARCH TEAM AND COLLABORATORS

Institution: Technical Services, Trail

Principal Investigator: Louiza Bell

WJ0046 – Wetland Treatment of Oil Sands Process-Affected Water

COSIA Project Number: WJ0046

Research Provider: Simon Fraser University

Industry Champion: Imperial

Industry Collaborators: None

Status: On-going

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 fresh water requirements during bitumen extraction; but, to date industry has adhered to a zero-release practice. 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 several technologies with the potential to improve water quality of OSPW. Treatment wetlands have emerged as viable solutions to various wastewater challenges including municipal and domestic wastewater, mine water, agricultural runoff, leachate, and industrial wastewaters. To investigate the application of treatment wetlands in the oil sands mining sector, a 1-ha surface-flow wetland was constructed on Imperial's Kearl Oil Sands site in 2013.

The overall goal of the study 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 (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. Wetland treatment to remove toxicity was also evaluated using biomimetic extraction of hydrocarbons with solid-phase microextraction (SPME) fibres and through bulk OSPW toxicity testing. The specific objectives of this project are to:

(i) investigate the ability of the Kearl Treatment Wetland to treat OSPW from Kearl Oil Sands site (Imperial Oil Resources Ltd.) in northern Alberta,
(ii) apply, test, and calibrate a contaminant-fate model of the Kearl treatment wetland, and
(iii) evaluate changes to OSPW toxicity as a result of wetland treatment

PROGRESS AND ACHIEVEMENTS

OSPW from the West External Tailings Area (WETA) was introduced into the wetland on May 30, 2021, and continuously recycled. This was the first year to introduced fresh effluent tailings water into the wetland. In 2018 and 2019, OSPW was sourced from a drainage pond (DP1A) adjacent to WETA. No OSPW was introduced in 2020 due to logistical constraints occurring from the COVID-19 pandemic. Aqueous grab samples of OSPW in the wetland were collected during the 30-day study to measure concentrations of PAHs and NAs in OSPW over time.

Polycyclic aromatic hydrocarbons

The total concentration of PAHs in OSPW entering the wetland on day 0 (2021) is 67.5 (SE 1.86) ng/L and individual PAHs ranged from 0.17 (SE 0.04) ng/L for 1,7-dimethylphenanthrene to 9.67 (SE 0.38) ng/L for chrysene. The concentration of total PAHs in OSPW decreased through the wetland at a rate of 0.05 day^{-1}, and the greatest concentration-reduction efficiencies were observed for 5/6-methylchrysene and 5,9-dimethylchrysene at 96 and 97%, respectively. Fig 1. Demonstrates the reduction in total PAH concentration in OSPW over time in the wetland for concentration measurements taken in 2018, 2019, and 2021. The reduction in total PAH concentration in OSPW was statistically significant in all years ($p < 0.05$; $R^2_{(2018)} = 0.34$; $R^2_{(2019)} = 0.67$; $R^2_{(2021)} = 0.68$).

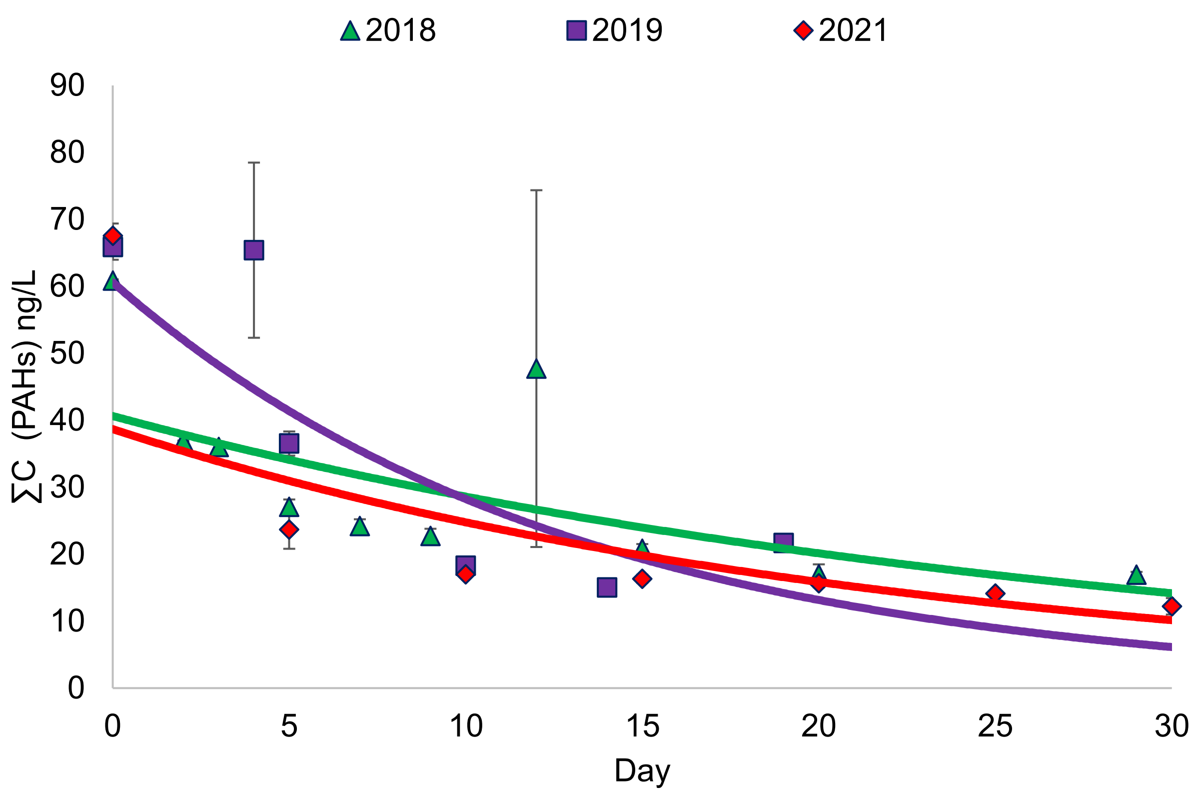

Fig. 1: The concentration of total PAHs in OSPW in the Kearl Treatment Wetland over time.

O_2-Naphthenic acids

The total concentration of O_2-NAs in OSPW entering the wetland on day 0 (2021) is 47.6 (SE 3.6) mg/L. The concentration of individual O_2-NAs in OSPW entering the wetland ranged from 0.015 (SE 0.001) mg/L for $C_{20}H_{34}O_2$ to 5.87 (SE 0.38) mg/L for $C_{15}H_{24}O_2$. The relative abundance of NA congeners in the OSPW entering the wetland was greatest for C14 to C15 O_2-NAs with double bond equivalents (DBE) of 3 or 4 (z = -4 or -6) which corresponds with previous years despite using a different source of OSPW. Fig. 2 demonstrates the reduction in total O_2-NA concentration in OSPW in the wetland over time in 2018, 2019, and 2021. The reduction in total O_2-NA concentration in OSPW was statistically significant in 2019 and 2021 ($p < 0.05$; $R^2_{(2019)} = 0.51$; $R^2_{(2021)} = 0.66$). The rate of reduction for the concentration of total O_2-NAs in OSPW was 0.03 and 0.02 day^{-1} in 2019 and 2021, respectively. The half-life of individual O_2-NAs in the wetland ranges from 6.9 to 60 days, where shorter half-life was measured for O_2-NAs with higher carbon numbers. These half-life estimates reveal a substantial reduction in half-life times compared with the half-life of O_2-NAs reported for tailings ponds or laboratory studies.

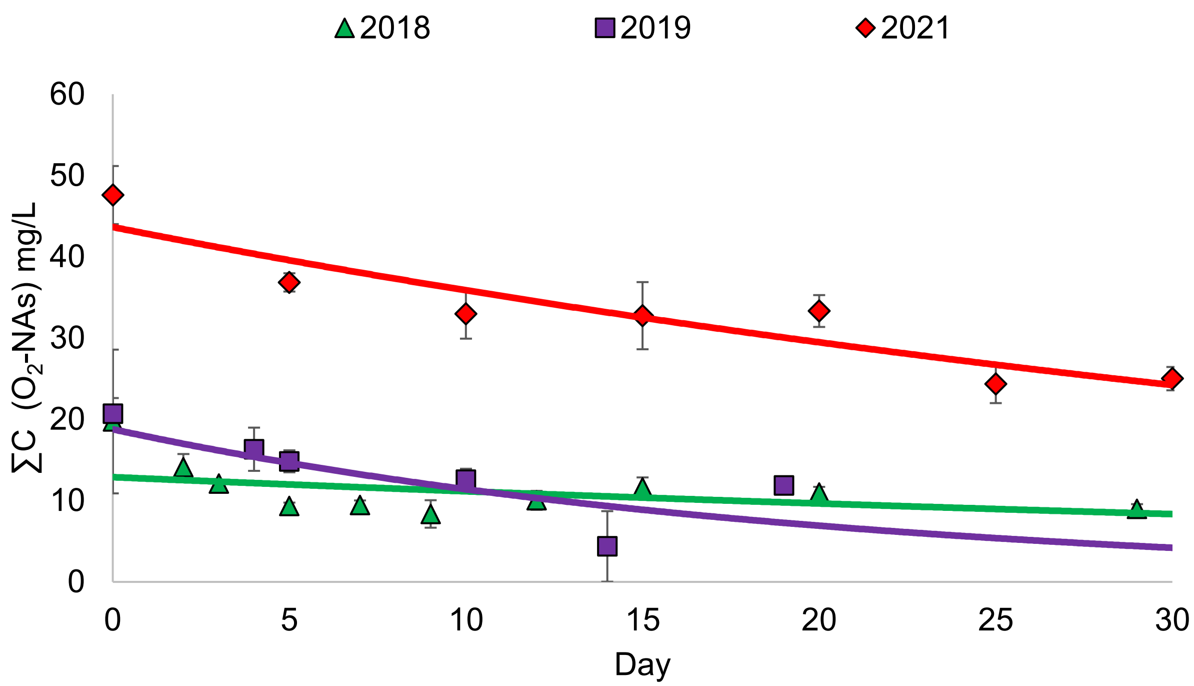

Fig. 2: The concentration of total O_2-NAs in OSPW in the Kearl Treatment Wetland over time.

The average concentration-reduction efficiency for all O_2-NAs entering the wetland was 33% in 2021. The average E_c is not as high as in our 2019A study period (E_c = 62%) but was higher than 2018 (E_c = 13%) and 2019B (E_c = 3.2%). The highest concentration-reduction efficiency (E_c) was 66% for $C_{19}H_{34}O_2$. E_c was found to increase with increasing carbon number and decreasing double bond equivalents (DBE) in the O_2-NA molecule.

BE-SPME

Concentrations of freely available hydrocarbons in OSPW collected from the wetland in 2021 were analyzed at the ExxonMobil Biomedical Sciences Laboratory (New Jersey, USA) using a biomimetic extraction (BE) technique with solid phase microextraction fibres (SPME). Fig. 3 presents the data and shows a decrease in BE-SPME concentration over time. This reduction implies that wetland treatment reduces overall toxicity of the OSPW.

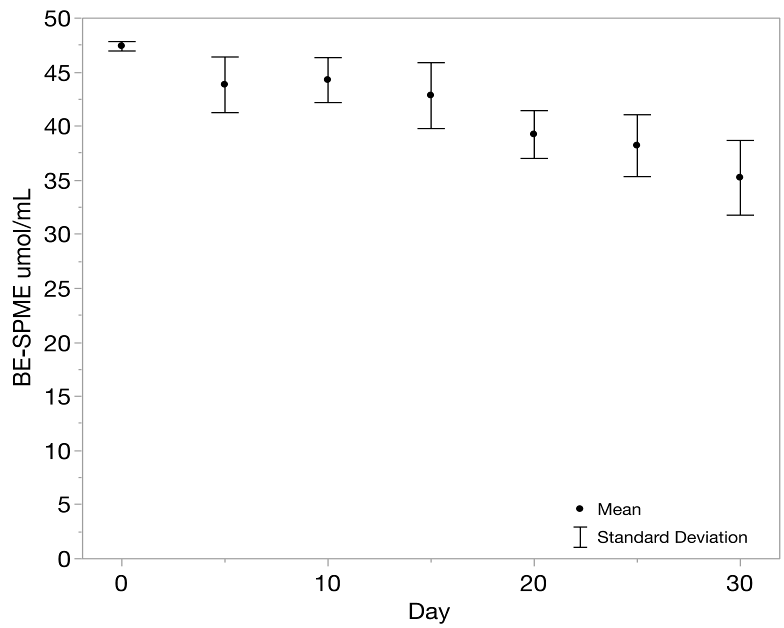

Fig 3: BE-SPME (µmol as 2,3-dimethylnaphthalene / mL PDMS) concentrations of OSPW over time in the Kearl Treatment Wetland in 2021.

The BE-SPME measurements indicate that after 30 days of wetland treatment, a reduction in (4d) deformity of *D. rerio* from 53 to 43% was observed based on dose-response data reported in Redman et al[1]. However, all BE-SPME measurements including measurements at day 0 exhibited less than 1% toxic response for less sensitive toxicity endpoints including *D. rerio* fish embryos (4d) survival, *C. dubia* (4d) survival, and *C. dubia* (7d) reproduction and therefore could not reveal significant reductions in toxicity.

LESSONS LEARNED

The total concentration of PAHs in WETA OSPW that was pumped into the wetland in 2021 is relatively low (i.e., ng/L) and similar to the total concentration of PAHs in OSPW from a WETA drainage pond used to source OSPW in previous years. The total concentration of O_2-NAs from WETA OSPW (2021) is roughly two-fold greater than the total concentration of O_2-NAs from the WETA drainage pond (2018, 2019). Treatment efficiencies are consistent with previous years indicating that higher O_2-NAs concentrations did not significantly affect wetland biogeochemistry.

The concentration-reduction efficiency of O_2-NAs increased with increasing carbon number and decreasing double bond equivalents (DBE). The toxicity of O_2-NAs has also been found to correlate with carbon number such that higher molecular weight O_2-NAs elicit a greater toxic response compared to lower molecular weight O_2-NAs[2]. Therefore, this suggests treatment wetlands show a strong potential to remediate OSPW, reduce risk to wildlife, and offer a feasible treatment option.

The estimated half-life times for O_2-NAs the Kearl TW are substantially lower than those measured in tailings ponds (i.e., 12.9 to 13.6 years[3]) and laboratory studies (i.e., 44 – 315 days[4]). These results suggest that wetland treatment offers an effective treatment alternative to tailings ponds and that biodegradation alone does not explain the total removal of O_2-NAs from OSPW in wetlands.

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[1] Redman et al., 2018. ES&T, 52(14), 8039–8049. https://doi.org/10.1021/acs.est.8b00614
[2] Frank et al., 2010. *Journal of Toxicology and Environmental Health - Part A: Current Issues*, *73*(4), 319–329. https://doi.org/10.1080/15287390903421235; Hughes et al., 2017. *ET&C*, *36*(11), 3148–3157. https://doi.org/10.1002/etc.3892
[3] Han, X., Mackinnon, M. D., & Martin, J. W. 2009. *Chemosphere*, 76(1), 63-70. https://doi.org/10.1016/j.chemosphere.2009.02.026
[4] Han et al., 2008. *ES&T*, *42*(4), 1290–1295. https://doi.org/10.1021/es702220c; Mahdavi et al., 2015. *Bioresource Technology*, *187*, 97–105. https://doi.org/10.1016/j.biortech.2015.03.091

PRESENTATIONS AND PUBLICATIONS

Cancelli, A. M., & Gobas, F. A. P. C. (2021). Treatment of naphthenic acids in oil sands process-affected waters with a surface flow treatment wetland: mass removal, half-life, and toxicity-reduction. Manuscript submitted for publication.

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		
Julia Brueggeman	Simon Fraser University	Ph.D. Student	2019	2023

WJ0132 – Clean Water Return Demonstration Pilot – Phase 1

COSIA Project Number: WJ0132

Research Provider: Syncrude Canada Ltd.

Industry Champion: Syncrude Canada Ltd.

Industry Collaborators: Canadian Natural, Imperial, Suncor, Teck, University of Alberta, Alberta Innovates.

Status: In-Progress

PROJECT SUMMARY

Since 1967, operators have subscribed to a “zero-release” practice for oil sands process water (OSPW). Water and fluid materials have been and continue to be stored in “out-of-pit” and “in-pit” tailings facilities. To reduce long-term containment requirements, minimize landscape disturbances, expedite terrestrial and aquatic reclamation activities, mitigate OSPW salinization, and achieve mine closure outcomes, appropriately treated OSPW will have to be returned to the environment.

Consequently, the oil sands industry has been conducting Research and Development activities to assess water treatment technologies and practices to treat OSPW for safe return to the environment. A key objective is to reduce concentrations of certain constituents present in OSPW to ensure the treated water can be released to the Athabasca River at a rate that is protective of human and ecological health. Previous studies have shown that contact between OSPW and petroleum coke, a by-product of Syncrude’s Fluid Coking process, will reduce concentrations of dissolved organic compounds based on an adsorption process (Zubot et al 2012). Syncrude’s Fluid Coking operation requires coke to be constantly withdrawn from the fluid coker. It is mixed with OSPW to form a slurry that is hydraulically transported by pipeline to a designated storage area. Presently, this is the Mildred Lake Settling Basin (MLSB). Following deposition of the slurry, the water runs off the beach and reports to the operational inventory of OSPW. However, a unique water treatment opportunity is possible if the slurry transport water is suitably isolated and collected. Operationally, this may be achievable by discharging the slurry into a dedicated containment structure with engineered underdrainage to allow collection of the porewater.

This is the basis of Syncrude’s Water Return Demonstration Project (WRDP), which was commissioned in 2019. A simplified process flow diagram is provided in Figure 1 and shows the three treatment components (i.e., reactors) that comprise the process. Firstly, the petroleum coke (i.e., activated carbon) which is produced from the fluid cokers is mixed with OSPW (i.e., untreated water) that has been sourced from tailings ponds. The water/coke is then transported in a pipeline (Part 1) as a slurry and deposited into a large containment cell that is equipped with engineered under-drainage (Part 2). The hydraulically placed coke deposit contained within the earthen cell is subsequently under-drained to perform as a filter bed. The purpose of Parts 1 and 2 is to reduce concentrations of total suspended solids (e.g., clay particles), free phase hydrocarbons (e.g. bitumen) and dissolved organic constituents (e.g. naphthenic acids). Part 3 is the final stage of treatment. It is an aerated pond with an eight-day residence time to permit biological degradation of ammonia and to serve as a holding facility to allow for final water quality testing.

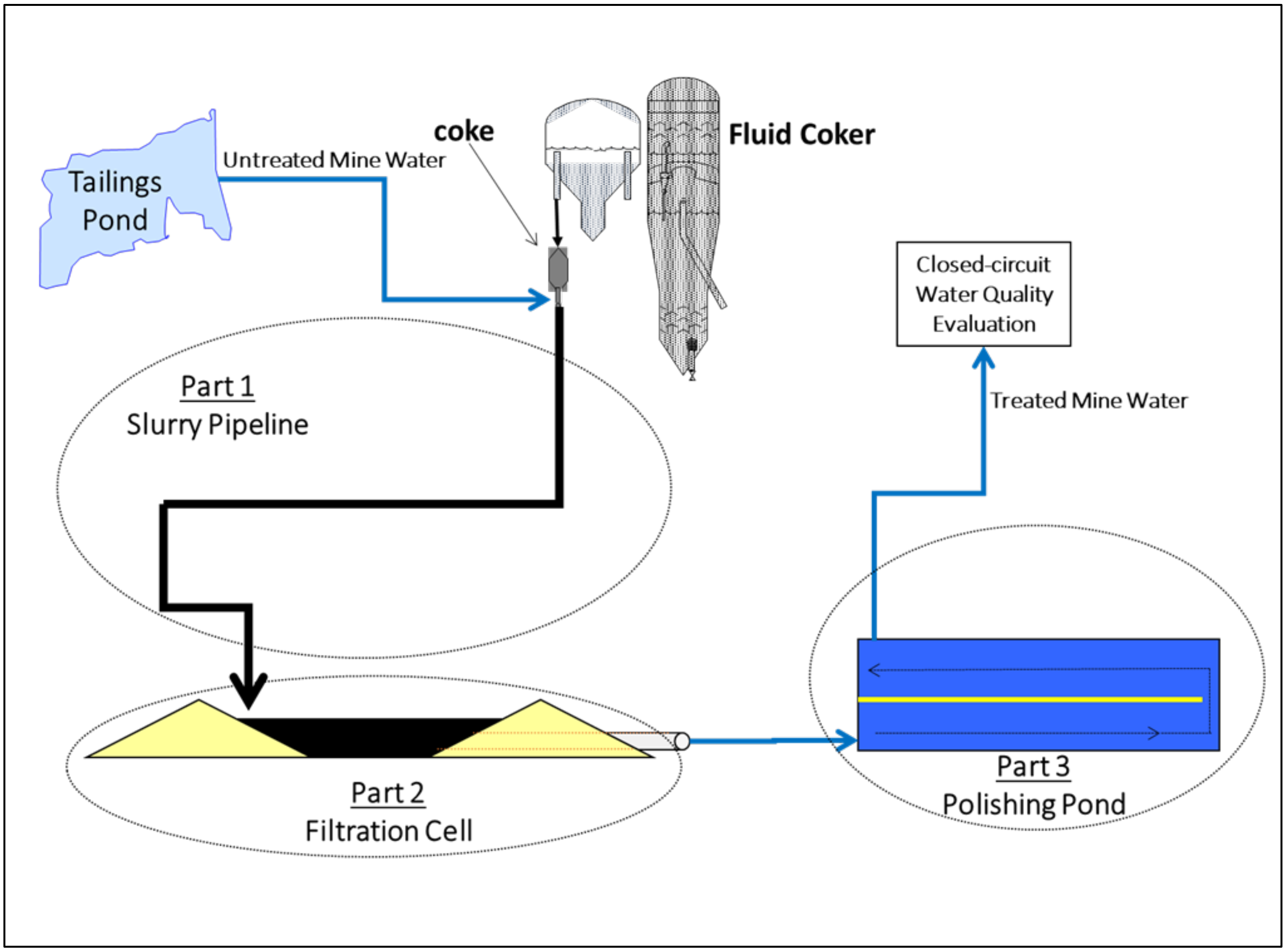

Figure 1: Three Reactor OSPW Treatment Process (WRDP)

The 2019 WRDP has been informed by a smaller pilot program that was completed at the Syncrude site in 2012. Details on the 2012 pilot along with key findings are covered in the 2020 Water Mining Research Summary.

In 2017, Syncrude received approval from the Alberta Energy Regulator (AER) to operate the WRDP as a closed circuit process (Phase 2) which was initially commissioned in 2019. A photograph of the un-commissioned treatment facility is provided in Figure 3. The size of the filtration cell (Reactor 2) is approximately 500 m long x 150 m wide by 5 m deep and has an ultimate capacity to produce about one million cubic meters of treated OSPW, making this pilot about 100 times larger than the 2012 pilot. It is located on the south-east corner on the dyke of the MLSB tailings structure.

A key program purpose of the WRDP pilot program is to execute a comprehensive chemical, biological, and toxicological evaluation program of the treated water exiting the polishing pond to produce a body of relevant scientifically defendable data to enable evaluation for potential future release to the Athabasca River.

Figure 3: Treatment facility for the 2019 Water Return Demonstration Project.

The assessment of treated OSPW using the technology comprising the WRDP is being evaluated using a "triad approach" to ensure the treated water presents negligible risk if released to the Athabasca River. Specifically, the study incorporates the following components:

- Chemical characterization of untreated and treated OSPW;
- Toxicological testing of treated OSPW; and
- Mesocosm assessment of aquatic invertebrate community responses to treated OSPW.

A detailed aquatic toxicity study has been designed to test the effectiveness of the treatment process over an approximately six-week period using a large-scale field trial, and a broad suite of toxicity tests. This phase incorporates both laboratory and on-site testing of the treated OSPW. The on-site component includes on-lease chronic toxicity testing using a mobile testing facility and the use of mesocosms (i.e., artificial streams) inoculated with periphyton and benthic macroinvertebrate assemblages from the Athabasca River watershed. This approach combines precise evaluation of toxicity using standard test organisms and recognized protocols, with the evaluation of community responses of river biota to chronic exposure to treated OSPW.

Mesocosms are regularly used to test hypotheses of change among benthic assemblages exposed to contaminants or other substances and allow separation and replication of treatments with physical and chemical diagnostics. Tight control of potential confounding variables that are typical in field studies (e.g., flow, depth, habitat and substrate characteristics, water temperature and chemistry, etc.) is a key rationale for undertaking mesocosm studies.

Supporting the WRDP pilot are off-lease standard and non-standard acute and sub-lethal toxicity testing at external laboratories. Water quality analyses conducted at each step of the treatment process and during the on-lease testing ensure causal inference conclusions. Results from all three tests components will contribute technical information to support decisions regarding potential release of treated OSPW directly to the Athabasca River.

Operational challenges in the Syncrude upgrader prevented the testing program from operating in 2019 and the COVID-19 pandemic prevented the pilot from running in 2020. This pilot operated for a two-month period in August and September 2021. However, testing and data analysis is ongoing, so the results of the pilot will be reported in the 2022 Water Mining Research Summary. A primary objective of the 2021 program was to demonstrate that treated OSPW will be protective of ecological and human health. Figure 4 provides a summary of the specific elements of the 2021 study and the related decision points. The work was conducted in two phases: (1) preliminary screening of treated OSPW; and (2) a detailed aquatic toxicity study incorporating chronic assessments of treated OSPW at environmentally relevant concentrations.

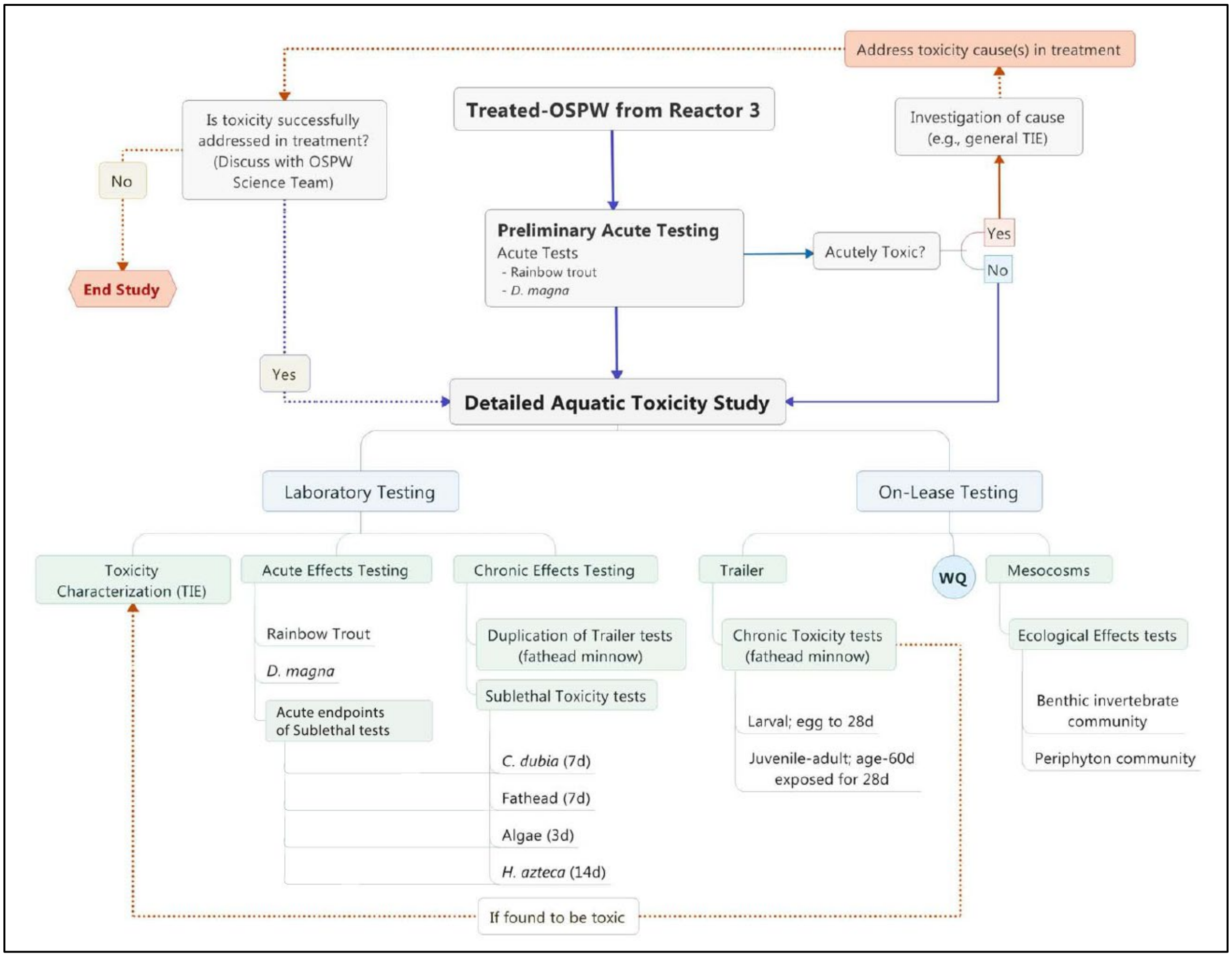

Figure 4: Summary the 2021 aquatic toxicity study

PROGRESS AND ACHIEVEMENTS

The pilot was successfully operated for two months in 2021. The testing and analysis as shown in Figure 4 is on-going and will be reported in the 2022 Water Mining Research Summary.

PRESENTATIONS AND PUBLICATIONS

Zubot, W., MacKinnon, M.D., Chelme-Ayala, P., Smith, D.W., Gamal El-Din, M., 2012. Petroleum coke adsorption as a water management option for oil sands process-affected water. Sci. Total Environ. 427-428, 364-372.

RESEARCH TEAM AND COLLABORATORS

A project team of highly experienced individuals have been assembled to advance the closed-circuit phase of the WRDP and collect a defendable body of scientific information to support potential release of treated water to the Athabasca River. Because Reactor 1 of the WRDP is an operating coke sluicing line that is an integral component of Syncrude's crude oil production process, the entire treatment facility will be operated and maintained by Syncrude staff. To support the toxicological and biological evaluation of the treated water, Syncrude has retained the expertise of Hatfield Consultants Inc. Hatfield is a leading provider of aquatic environmental monitoring in western Canada with clients in various sectors including pulp and paper, mining, oil and gas, and government.

In addition, Hatfield has retained the professional services of Limnotek Research and Development, Nautilus Environmental, and Environment Canada and Climate Change (ECCC) to provide additional scientific expertise to support the closed-circuit evaluation. Limnotek has been providing research and consulting services since 1984 and has extensive experience in the design, field implementation and interpretation of mesocosm studies. They have worked on numerous jointly implemented studies with ECCC and have a history of innovative custom equipment design for field-based studies. Nautilus Environmental operates toxicity testing laboratories in Calgary and Vancouver that are accredited by the Canadian Association of Laboratory Analyses (CALA). They have extensive experience operating mobile testing laboratories and conducting long-term tests with species such as fathead minnows and other organisms. Modern approaches to the use of mesocosms to evaluate water quality were pioneered by ECCC in the 1980s. ECCC scientists have been supporting the mesocosm experiments with respect to design and construction. They will continue to provide a key role by informing data analyses and interpretation.

WJ0139 – Carbonix Activated Carbon Project

COSIA Project Number: WJ0139

Research Provider: Carbonix Inc, Trent University/SGS Lakefield Research

Industry Champion: Suncor

Industry Collaborators: Suncor

Status: Year 2 of 2

PROJECT SUMMARY

Since 2011 Carbonix has been refining the protocols and unit operations required to manufacture tailored activated carbons (AC), using petroleum coke, to be used for remediation applications in the resource extraction industries. Through measured manipulation of process conditions, Carbonix has learned to control product attributes which have been integrated at pilot scale and iteratively tested using various analytical methods to examine product efficacy.

For oil sands mining operations nearing end of mine life, the thrust of innovation required today is to support the restoration efforts needed to execute mine closure activities, re-establish the boreal forest, and have this done in a sustainable and economical manner.

The oil sands industry has strict requirements for mining operations and closure compliance. Provincial regulators will shortly outline target thresholds required as part of oil sands remediation and mine closure activities. In efforts to support industry compliance, Carbonix has developed a series of products that will enable operators to execute and achieve their reclamation targets. Carbonix uses the nano porous framework available in their products as a kind of scaffold that can be functionalized to create different categories of products. For oil sands fluid tailings applications, Carbonix products have been engineered to perform as flocculants, adsorb organics and metals, and reduce inorganics such as chlorides through ion exchange processes. These products will enable oil sands operators to achieve greater water recovery at lower costs, enabling efficient and economic release back to the natural environment, while reducing GHG emissions that would otherwise be released to the environment as a result of methanogenic or other biologic activity within the fluid tailings.

The organics present in the Oil Sands Process-Affected Water (OSPW), Fluid Fine Tailings (FFT) and Mature Fine Tailings (MFT) are the source of GHG emissions from fluid inventories in tailings ponds. Organics include oils and greases, diluent, naphthenic acids and other lighter or heavier hydrocarbon fractions. The decomposition of these organic species through microbial or fugitive activity account for the annual GHG emissions released from fluid tailings. By way of example, naphthenic acid reductions from OSPW on a computed mols basis, 1 M^3 of OSPW releases 0.016 kg CH4 annually. Thus, with a known adsorption efficacy of ~80 mg/g of naphthenic acids this has a direct impact on reducing methane emissions.

As an Indigenous Clean Technology company, Carbonix understands the responsibility of being part of the underrepresented groups in clean technology. Carbonix is committed to supporting the Government of Canada's commitment to increase the participation of underrepresented groups in clean technology through education, inclusiveness and promotion of the opportunities related to our own objectives and that of the clean tech industry in general. As part of our ongoing and integrated Environmental, Sustainability and Governance (ESG) efforts, relationships and connections with Indigenous communities have been established and enhanced through inviting participation and sharing strategies that can be used to remediate affected sites situated within their traditional territories, while creating new employment opportunities for Indigenous persons.

PROGRESS AND ACHIEVEMENTS

Carbonix products are tailorable for different applications including complex water reuse and aquatic ecosystem remediation needs. These products can be designed to be ballasted to reach specific depths and The products are multi-modal and can have a tailored ionic charge density, used to disassociate, or flocculate a colloid through particle charge neutralization and by way of their engineered porosity and functionalization adsorb the target adsorbates. In other applications, Carbonix products are designed to meet specific kinetics requirements for deployment within existing fluid tailings transport piping infrastructure. Figure 1 below demonstrates the significance of how product attributes such as pore-size-distribution impacts adsorbate kinetics.

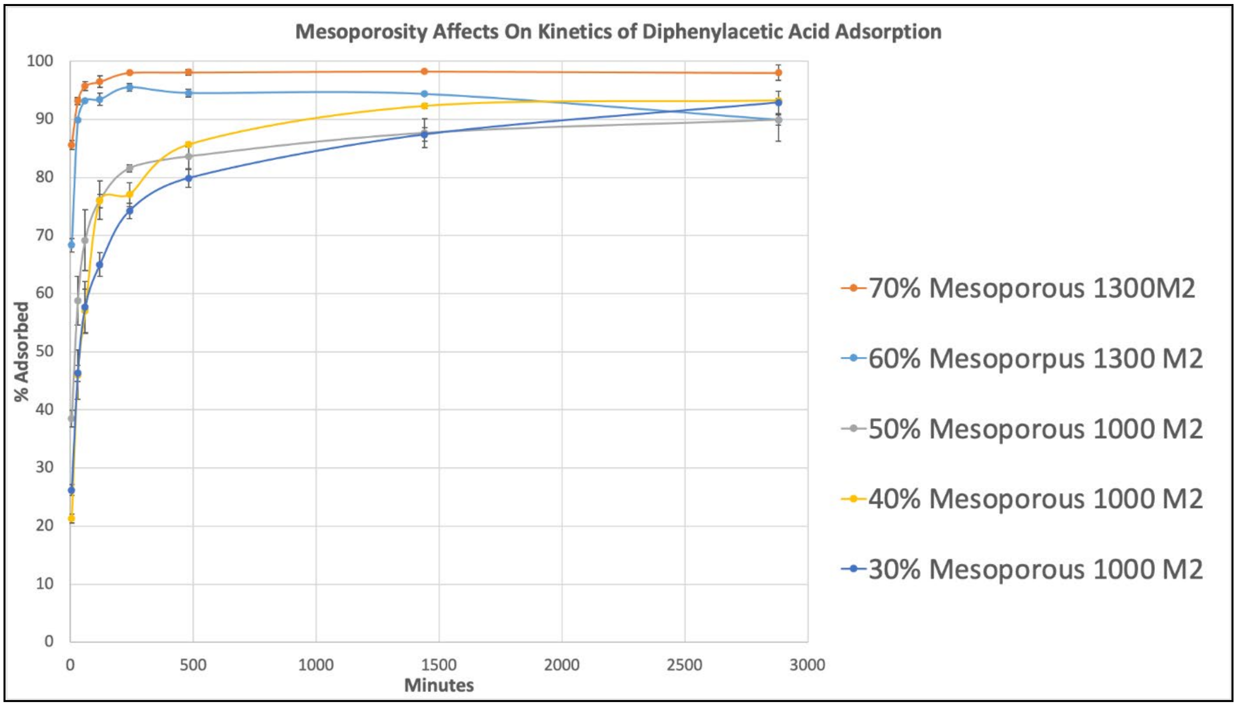

Figure1: Mesoporosity Effects on Kinetics of Diphenyl Acetic Acid Adsorption

Carbonix products and application methods are designed for both recovery and remediation of oil sands process water from Mature Fine Tailings (MFT). The flocculation products are designed to perform much like incumbent flocculants however they possess the added benefit of adsorption capacity. The following figures (2 and 3) show MFT flocculation results for Suncor MFT's and initial settling rate results of 5 wt% solids MFT.

Figure 2: MFT Flocculation Test using Suncor Test Method

Polymer functionalized activated carbon in a flocculation test using the Suncor Test method is shown in Figure 2. The images on the left and right demonstrate the cohesive nature of the flocculated solid when the flocculation is carried out using the polymerized activated carbon. The central image shows the water passed through the screen. The collected water is not as clear as that collected using a purely polymeric flocculent (image on the right in Figure 3) although this is likely impacted by the need to optimize the polymerized activated carbon flocculent dose. Indications from initial settling rate tests demonstrate that the water clarity is highly dependent on dose.

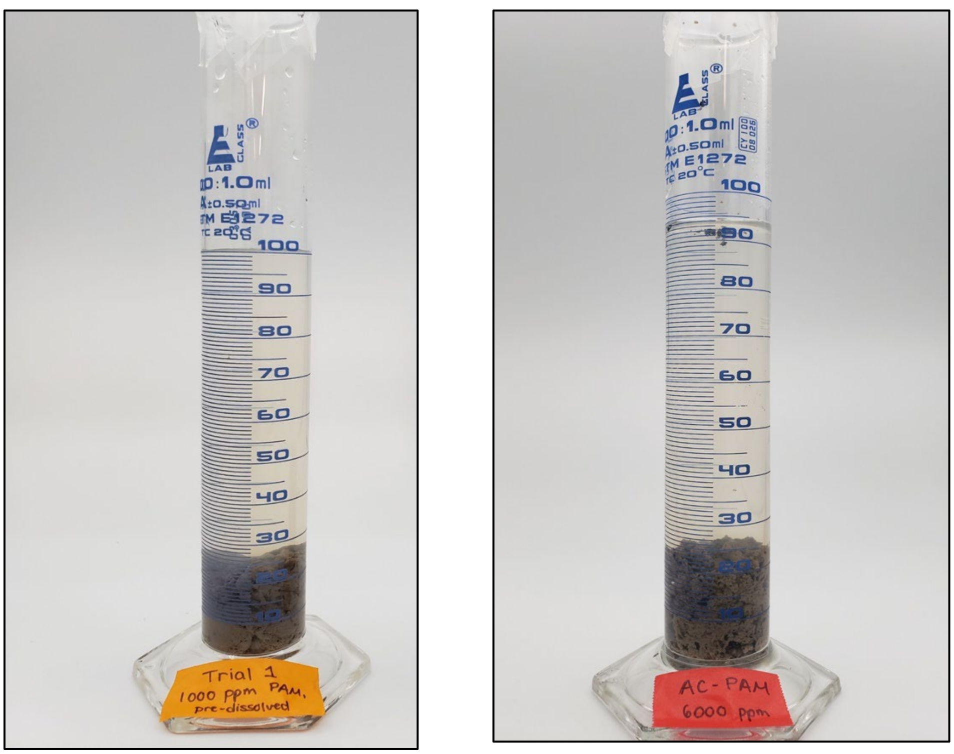

Figure 3: MFT Flocculation Test using Initial Settling Rate Test Method

Initial settling rate tests for flocculation of diluted MFT showing a comparison of PAM flocculent and PAM-Activated Carbon flocculent. The performance is very effective in both cases but the incorporation of activated carbon into the flocculant removes the need to pre-dissolve the polymer and provides the ability for the activated carbon to also act as an adsorbate for other species present in the MFT. Total quantity of polymer used is roughly equivalent in the two cases where the difference in ppm loading is due to the activate carbon inclusion.

Polymer functionalization of activated carbon has also been used to reduce chloride concentration OSPW. In this case Poly diallyl dimethylammonium chloride (pDADMAC) is bound to the activated carbon which provides charged nitrogen functionality capable for adsorbing chloride ions from solution. These pDADMAC-AC materials can be washed and recycled for multiple uses. Work is on-going to optimize the chloride adsorption capacity and adsorption kinetics and to evaluate the number of cycles over which the material will retain its efficacy.

LESSONS LEARNED

Notable lessons learned:

1. Economic and effective pore-size-distribution control of petroleum coke conversion into activated carbons. This is important for manipulating adsorption kinetics.
2. Developing polymerized activated carbons that require less energy to integrate flocculants into the MFT and enable effective MFT flocculation.
3. Developing polymerized activated carbons that enable adsorption of inorganics (e.g. chlorides) through ion exchange

PRESENTATIONS AND PUBLICATIONS

N/A

RESEARCH TEAM AND COLLABORATORS

Institution: Trent University

Principal Investigator: Dr. Andrew Vreugdenhil

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Andrew Vreugdenhil	Trent University	Professor, PI		
Oliver Strong (M.Sc.)	Trent University	Research Associate		
Kevin Scotland (Ph.D.)	Trent University	Post Doctoral Researcher		
Kyle Fisher	Trent University	Ph.D. Candidate	September, 2019	August, 2023
Elmira Nazari	Trent University	Ph.D. Candidate	September, 2018	August, 2022
Tyler Roy	Trent University	Ph.D. Candidate	January, 2020	December, 2024
Sarah Begin	Trent University	M.Sc. Candidate	September, 2020	August, 2022
Cole Dennis	Trent University	Research Assistant		

WJ0164 – SolarPass Demonstration for Mitigation of Volatile Emissions and Odour from Oil Sands Process-Affected Water

COSIA Project Number: WJ0164

Research Provider: H2nanO Inc.

Industry Champion: Suncor Energy Inc.

Industry Collaborators: None

Status: In Progress

PROJECT SUMMARY

Tailings ponds in Canada's oil sands can be a source of fugitive emissions and odours, which could contribute to the greenhouse gas (GHG) emissions inventory of surface mining operations. These volatile and malodorous compounds can include methane, volatile organic compounds (VOCs), reduced sulphur compounds (RSCs) such as hydrogen sulphide, and ammonia. Managing fugitive emissions from the large tailings water area – including both froth treatment tailings (FTT) and mature fine tailings (MFT) – is a long-term and large-scale challenge.. A scalable, economical, and sustainable solution to reduce net emissions from tailings ponds and manage their accumulation is desirable for continuous improvement of mine operations and reducing odour and air quality impacts in the local environment.

This project targets hydrogen sulfide (H_2S), methane, and other VOCs emissions found in oil sands process-affected water (OSPW) and released from active tailings ponds. The objective is to achieve two key functions: (1) to reduce the rate of H_2S, methane and VOCs emissions and related odour from OSPW; and (2) to chemically transform the volatile and odorous compounds into less volatile forms in-situ without absorbents, consumable chemicals, or high electrical power input.

To achieve these objectives, H2nanO Inc. evaluated, optimized, and scaled its SolarPass™ Floating Reactive Barrier (FRB) technology for OSPW emissions management. H2nanO is a Canadian-owned cleantech innovator creating novel water and air emissions treatment technology, with operations in Alberta and Ontario. In collaboration with Suncor, H2nanO has designed and piloted this new, built-for-purpose technology called SolarPass FRB to mitigate fugitive emissions from tailings pond water. It is a first-of-kind in-situ, passive emissions capture and treatment process for water. SolarPass consists of buoyant photocatalysts that float at the water surface and can trap and oxidize emission compounds and gas bubbles before they are emitted. The SolarPass FRB system also includes deployment, containment, and environmental controls equipment installed in-pond to utilize the FRB material. The technology is powered by natural sunlight without additional chemical or energy input. SolarPass FRB addresses the scalability and fugitive emissions reduction needs of oil sands operators by combining these two high-value capabilities.

The 2021 project was the next phase of development following successful proof-of-concept and outdoor prototype treatment and emissions blocking studies completed from 2019 to 2020. Analytical, bench-scale studies validated that SolarPass FRB was capable of photocatalytically oxidizing all studied RSCs (including sulfide), methane, and VOCs (including BTEX and F1 hydrocarbons) to below detection, in addition to reducing their emission rates with and without sunlight exposure. The outdoor trials in Alberta, completed in 2020, demonstrated in both mass-balanced closed-tank systems and open-tank systems, that the SolarPass FRB treatment was successful in substantially reducing the magnitude of emissions compared to control samples, as well as demonstrating solar photocatalytic conversion of RSCs and VOCs into more soluble and inert by-products.

Building on this success, the 2021 project executed a scale-up deployment study of the SolarPass FRB system over a 400 m^2 stormwater lagoon at InnoTech Alberta in Vegreville (Figure 1). The objectives of the project were to: (1) demonstrate the SolarPass FRB deployment, containment, and collection process equipment; (2) evaluate the impact of environmental factors (wind, rain, etc.) at an order of magnitude increased scale; and (3) provide personnel training and process iteration in a simulation of on-site, in-tailings pond deployment and operations.

Figure 2 – SolarPass FRB scale-up module utilized for testing deployment, containment, environmental factors, and collection at InnoTech Alberta's Vegreville demonstration lagoon.

H2nanO and Suncor also utilized this demonstration period to refine and prepare engineering designs and operations plans for the next stage of pilot demonstration. This next phase is forecasted for completion at Suncor's Base Plant site in 2022.

PROGRESS AND ACHIEVEMENTS

The SolarPass FRB scale-up module test at InnoTech Vegreville successfully demonstrated its capabilities for increased in-pond deployment and coverage area. Between May to August 2021, H2nanO field operators deployed the 400 m^2 SolarPass FRB module into the test lagoon using H2nanO's proprietary SolarPass materials and process system designs. The project achieved its three objectives:

1. Deployment, containment, and collection unit operations following standard operating procedures and using a scaled version of the specified process equipment covered the lagoon surface with the SolarPass FRB module in multiple successful deployment and collection sequences across the test period. H2nanO refined process operations, generated data on observed unit operations rates, and improved specific of procedures with scaled exercise. The equipment was commissioned, operated, and removed from site in a rapid, flexible deployment, demonstrating suitability for both permanent and temporary deployments as necessary in future use cases for the SolarPass FRB system.

2. The SolarPass FRB system configuration was optimized during operation and observed to reach target coverage under typical and extreme wind and weather conditions (in comparison to typical tailings pond conditions). High intensity weather stress testing demonstrated that the system was resilient to maintain containment and naturally restore full coverage without intervention after weather abatement. The materials also maintained physical integrity across the test period, including among natural factors such as rain, nearby farming debris, and organic growth in the lagoon system.

3. H2nanO successfully completed the target personnel training and exercise of standard operating procedures with the SolarPass FRB unit cell required to inform planning and procedures for iterative scale up into the operating mine environment.

Overall, the SolarPass FRB scale up was a success and met and exceeded the technical objectives for its evaluation. These results – in combination with the treatment studies conducted outdoors in 2020 and refined through parallel lab work in 2021 – show a strong potential for effective tailings pond emissions mitigation and treatment of volatile compounds in-situ across large pond areas through the open water season. Implementation of the technology in the mine environment will be the next step in scale-up development.

LESSONS LEARNED

The H2nanO SolarPass™ FRB technology has been engineered and demonstrated preparedness for on-site deployment operation. In the 2021 study, the project team learned:

- The SolarPass technology is capable of being deployed into, contained within, and collected from a large area (400 m^2) unit cell using established process equipment designs. The unit cells can be easily configured to the pond area and shape, including alterations after initial deployment.
- The SolarPass FRB materials maintained the target coverage of the pond area under environmental conditions similar to those at Suncor Base Plant site and the materials and system were completely collected from the lagoon without residual impact. In extreme weather conditions, the technology containment and surface coverage was maintained.
- During initial deployment, re-configuration of the system containment area, or following sustained high winds the SolarPass FRB materials, without operator intervention, naturally spreads to level and re-covers the system surface area.
- Photocatalytic testing was not conducted in the lagoon due to use of existing accumulated stormwater. However, the SolarPass FRB materials maintained a high physical integrity across the duration of the months long trial.

PRESENTATIONS AND PUBLICATIONS

Gu, F. *SolarPass™ Floating Reactive Barrier: Sunlight-activated emissions & odour reduction for tailings ponds.* 2021 Mine Water Release Science Workshop. December 1, 2021. Virtual.

RESEARCH TEAM AND COLLABORATORS

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Rodney Guest	Suncor Energy Inc.	Director, Closure Environmental Integrity Mining and Upgrading	-	-
Hafez Massara	Suncor Energy Inc.	Development Specialist Water Technology, Upstream	-	-
Trevor Bugg	Suncor Energy Inc.	Tailings Specialist, Tailings Engineering	-	-
Elizabeth Wells	Suncor Energy Inc.	Contact Engineer, Treated Tailings	-	-
Frank Gu	H2nanO Inc.	Chief Executive Officer	-	-
Zac Young	H2nanO Inc.	Chief Operating Officer	-	-
Matthew Kerwin	H2nanO Inc.	Lead Process Engineer	-	-
Jim Davies	InnoTech Alberta	Scientist	-	-
Mark Belec	InnoTech Alberta	Technical Lead, Industrial Sensors Technology & Informatics Division	-	-

WJ0174 – Development of a Passive, Plant-Based Naphthenic Acid Remediation Technology for Treatment of Oil Sands Process-Affected Water

COSIA Project Number: WJ0174

Research Provider: University of Calgary, Northern Alberta Institute of Technology (NAIT)

Industry Champion: Canadian Natural

Industry Collaborators: Imperial

Status: Year 2 of 3

PROJECT SUMMARY

Surface mining of bitumen in the Canadian oil sands results in the accumulation of oil sands process-affected water (OSPW). This research project is aimed at determining the capacity of selected upland plant species and their associated microbes to remove organics from OSPW in an irrigated soil environment. This treatment approach builds on numerous examples of successful water treatment strategies that use an irrigated plantation approach but is tailored to OSPW. It takes advantage of the natural genetic diversity and extensive metabolic capacity of plants and microbes to remediate contaminated environments. An upland plant-based approach such as this could be applied on a large scale using a gravity-based water distribution system capable of irrigating large volumes of OSPW through plant root systems on a sloped landscape lined with a clay or geotextile base.

The organic fraction of OSPW is comprised of thousands of different compounds that include recalcitrant forms of naphthenic acids (NAs). The benefit of using this approach is that native plant species provide diverse genetic complexity that has the potential to enhance NA remediation. We will screen for the most promising plant species and native genotypes for growth and remediation in an OSPW irrigated environment.

The specific objectives of this research are to:

1. Screen natural genotypes of diverse plant species and genotypes to determine their suitability and capacity for growth in an OSPW irrigated environment and their ability to take up NAs. (Phase 1)
2. Perform greenhouse mesocosm experiments with the selected genotypes from Phase 1 to determine the effectiveness of communities of plants and microbes to reduce toxicity and remove NAs from OSPW. (Phase 2)

PROGRESS AND ACHIEVEMENTS

Phase 1 – Screen for species/genotypes suitable for growth under OSPW stress conditions and establishing assays for NA removal ability

Phase 1 was executed in three distinct components. In phase 1A we optimized our plant genotype screening approach to integrate screening for OSPW toxicity as well as other key environmental extremes (flooding and drought). In phase 1B, we screened genotypes from 3 genera (*Calamagrostis canadensis*, *Solidago canadensis*, and *Salix* spp. including *Salix interior*). A total of 64 genotypes with a short list of 14 genotypes were selected for phase 1C (refer to Figure 1 for a visual example). In addition, 20 genotypes from 6 additional species (*Populus balsamifera*, *Populus tremuloides*, *Cornus sericea*, *Carex aquatilis*, *Elymus trachycaulus* and *Phragmites australis*) were also included in phase 1C though they were not pre-screened in phase 1B as there were too few individually viable genotypes for comparisons. Phase 1C, which compares the ability of individual genotypes and species in their ability to treat OSPW, is ongoing. Of note, while we initially worked with plant material from 15-20 individual genotypes per species (experiment wide), we have observed strong patterns in individual genotypes, within certain species, in their ability to vegetatively propagate. This was especially true for *Carex aquatilis* and *Populus balsamifera* (Figure 2). On the other extreme, *Calamagrostis canadensis*, *Solidago canadensis* and *Salix interior* tended to show a high degree of readiness to vegetatively propagate, regardless of genotype.

Figure 1. Visual illustration of phase 1B screening result at the conclusion of the 8-week trial where plants were exposed to flooding (F), regular watering (R) or drought (D) conditions while being irrigated with OSPW. Four out of fourteen genotypes of *Solidago canadensis* are shown in the images below, where genotypes 1 and 2 ranked the highest while genotypes 11 and 18 ranked the lowest in terms of overall ability to thrive over the range of conditions.

Figure 2. Visual illustration of genotypic variation in ability to vegetatively propagate from an unrooted cutting in *Populus balsamifera*. The numbering on the block denotes individual plant genotypes. Note that the stem cutting tips were painted with black tree paint to reduce desiccation during early propagation.

Phase 2 – Greenhouse mesocosm studies using selected plant species/genotypes

Replicated greenhouse mesocosm systems have been developed and tested. Substrate, water flow, nutrient addition and sampling regimes are optimized. Using *Salix interior* as the test plant species in preliminary experiments, these irrigated subsurface flow systems demonstrated a significant reduction in OSPW toxicity (as determined by biomimetic extraction, BE-SPME) and >40% reduction in AEO concentration in recirculating passes after a one-week period. Temperature, evapotranspiration, plant biomass, redox, pH, toxicity (BE-SPME and aquatic organism), water quality, and high-resolution mass spectrometry are some of the measurements used in the mesocosm testing regime. Implementation of selected plants from the Phase 1 experiments in mesocosm experiments are planned in the next funding year.

LESSONS LEARNED

Phase 1 experiments have demonstrated that the selection of specific stress-tolerant genotypes will be critical for the development of effective OSPW phytoremediation technologies. Additionally, practical aspects such as ease of propagation will be an important parameter for genotype selection, as field-scale implementation of this technology will require resilient, easy to grow genotypes that will have high rate of survivability. Phase 2 experiments performed to date have demonstrated that our closed-loop greenhouse mesocosm setup is a tractable and effective approach for testing the ability of upland plant species to reduce toxicity and remove organics from OSPW under variable treatment conditions.

PRESENTATIONS AND PUBLICATIONS

N/A

RESEARCH TEAM AND COLLABORATORS

Institution: University of Calgary

Principal Investigator: Doug Muench

Name	Institution or Company	Degree or Job Title	Degree Start Date (For Students Only)	Expected Degree Completion Date or Year Completed (For Students Only)
Doug Muench	University of Calgary	Professor		
Thomas Oldenburg	University of Calgary	Adjunct Professor		
Amanda Schoonmaker	Northern Alberta Institute of Technology	NSERC Industrial Research Chair		
Heather Kaminsky	Northern Alberta Institute of Technology	NSERC Industrial Research Chair		
Andrea Sedgwick	Northern Alberta Institute of Technology	Ledcor Applied Research Chair in Oil Sands Environmental Sustainability		
Chibuike Chigbo	Northern Alberta Institute of Technology	Research Associate, PhD		
Simon Sun	Northern Alberta Institute of Technology	Research Associate, MSc		
Kaela Walton-Sather	Northern Alberta Institute of Technology	Research Assistant		
Mitchell Alberts	University of Calgary	PhD Student	2018	2022
Camryn Charriere	University of Calgary	MSc Student	2021	2023
Katelyn Grado	Northern Alberta Institute of Technology	Student research assistant	2019	2021
Marie-Pierre Ouellet-Pariseau	Grande Prairie Regional College	Student research assistant	2019	2021
Alyssa Loutan	Northern Alberta Institute of Technology	Student research assistant	2019	2021

WJ0181 – Calcite Technology Assessment

COSIA Project Number: WJ0181

Research Provider:

Industry Champion: Teck

Industry Collaborators: None

Status: Complete

PROJECT SUMMARY

This project includes 4 different scopes of work during 2021 as described below:

1. Calcite Remediation through Physical Excavation and Channel Reconstruction

The Creek 1 Stream Remediation Trial is intended to evaluate physical excavation and channel reconstruction as a calcite remediation technology. The objectives of this trial are to:

- Remediate approximately 260 m of a highly concreted section of Creek 1 by excavating calcite.
- Re-establish a natural and ecologically functioning channel in terms of morphology and aquatic habitat.
- Monitor construction, remediation, and ecological recovery.

This project was designed to evaluate physical excavation and channel reconstruction through the collection of two sources of information:

- Permitting, design, engineering, construction, and logistical considerations evaluated through project execution and engagement with stakeholders and subject matter experts in fish biology, construction, geomorphology, and remediation/stream rehabilitation; and
- Ecological recovery will be evaluated through pre- and post-remediation monitoring by Minnow Environmental using a Before-After-Control-Impact (BACI) approach.

2. Development of Passive Calcite Precipitation Technology as a Method for Calcite Control

In 2020/2021, cascade systems were evaluated as a passive or semi-passive method to prevent calcite precipitation in the Location 1. Cascade systems consist of two components – a cascade which is designed to off-gas CO2, followed by a precipitator channel to precipitate calcite in a controlled space rather than downstream in the natural receiving environment, while also mitigating metal constituents of concern (COCs) through calcite co-precipitation. The overall objective of this project was to optimize the design and size of a cascade system for real-world constraints to prevent calcite precipitation in a natural receiving environment. Test work aimed to answer the following key questions:

- What full-scale design and configuration of a cascade system results in the most efficient CO2 removal and calcite precipitation?
- What are the CO2 removal and calcite precipitation rates in the optimized design?
- How does flow variability impact system performance?
- What are the footprints, geometries, and dimensions of a full-scale cascade system capable of preventing calcite precipitation in a natural downstream receiving environment that can accommodate representative full-scale flow variability?

3. Evaluation of Calcite Remediation via Softened Water

The effectiveness of softened water to dissolve calcite was evaluated as a potential method to chemically remediate calcite deposits. In theory, the softened water, which is undersaturated with respect to calcium and alkalinity, will have a propensity to dissolve calcite rock and uptake ions.

Through scoping-level tests, the project simulated a water softening technology (i.e., membrane separation) by blending and evaluating different volume ratios of municipal water and mine-impacted water (MIW) to estimate dissolution rates. The objectives of the tests were to answer the following key questions:

- Which ratios of soft water (municipal water) and MIW suggest a potential for calcite dissolution/remediation, based on calcium, alkalinity, conductivity, and pH changes over time?
- What is the estimated rate of calcite dissolution for each ratio?
- What is the top performing ratio of municipal water and MIW in terms of calcite remediation timelines?
- What are the acute toxicity effects associated with mixing soft water with MIW?

Water was recirculated at simulated creek conditions through artificial channels filled with site-sourced calcite rocks. MIW and calcite from Creek 2 were used for this test work as a case study. The intent of the design was to follow a plug of water as it was continuously circulated through calcite-filled channels until a simulated creek distance of 3 km was achieved. Calcite dissolution rates were determined by sampling the outfall water over the course of the tests and determining water quality changes over time, with the sample intervals converted to simulated downstream distances.

4. Technology screen of chemical and biological calcite management technologies

This technology screen was undertaken to evaluate calcite management technologies for implementation within the Location 1. Previously, a technology screen for calcite management technologies was completed by Teck Applied Research and Technology in 2019. This technology screen is intended to capture any emerging chemical and/or biological calcite management technologies since the previous report, as well as to assessment all known chemical and biological technologies to determine if further consideration is warranted, either through bench-scale, pilot testing or optimization of current field-scale practices.

PROGRESS AND ACHIEVEMENTS

Major results for the different work scopes are below:

- For work scope 1, the work did not progress past the planning stage as there were uncertainties regarding the permitting process.
- Decoupling the CO2 stripping and calcite precipitation steps offers design optimization ability for the cascade and precipitator systems, minimizes maintenance challenges, and capital and operating costs.

- The hydraulic analysis identified theoretical ideal performance of the precipitator system and realistic ways to influence the calcite precipitation process, mass transfer, precipitation kinetics, and hydrodynamic parameters.

- The test program indicated that to produce water capable of dissolving calcite outside the uncertainty of experimental and creek flows, 90–95% soft water would be required, with a dissolved calcium concentration of 33 mg/L and total alkalinity (as $CaCO_3$) of 41 mg/L, or less. With 90% soft water, which yielded the highest dissolution rate in this test program, treatment would require an estimated 3 to 16 years to remediate 1,000 tonnes of calcite. Toxicity testing on rainbow trout and daphnia magna indicated that blending up to 90% soft water with MIW caused no acute toxicity effects.

- The report identified multiple technologies and evaluated them based on the criteria defined.

LESSONS LEARNED

- Permitting of field trials for stream remediation requires significant time and effort due to the large number of uncertainties.

- The cascade is not a required unit operation to improve calcite precipitation. The team will advance the project focusing only on the precipitator design.

- Water softening seems to be a viable option to remove calcite precipitates from the stream.

- The highest ranked technology for calcite prevention was antiscalants, while the highest ranked chemical/biological technology for calcite remediation was MaxH2O desalters.

PRESENTATIONS AND PUBLICATIONS

No public reports or presentations.

RESEARCH TEAM AND COLLABORATORS

N/A

APPENDIX – INDEX BY TOPIC AND ALPHABETICALLY

INDEX (BY TOPIC)

Summary Report Title	Project Number	Topic	SOURCE REPORT 2021	2020	2019	2018
Best Practices						
Mining Best Practices Report for Alternate Water Sourcing and Salinity Management	WJ0061	Best Practices				2018
Overburden Dewatering Effectiveness Study	WJ0099	Best Practices				2018
Standardize Measurement and Quantification Techniques	WE0027.1	Best Practices				2018
Mine Depressurization Water						
Mine Depressurization Water Management - Phase II and III	WJ0145	Mine Depressurization Water			2019	
Mine Depressurization Water Management -Phase II and III	WJ0063	Mine Depressurization Water			2019	
Mining Depressurization Water Treatment to Create Acid and Caustic	WJ0152	Mine Depressurization Water		2020		
Mine Water Return						
Regional Substance Loading Allocation Study	WE0009	Mine Water Return				2018
River Ecosystem Health Assessment Using Pilot Facility - Feasibility Study	WE0013	Mine Water Return				2018
Salt Load Model	WE0010	Mine Water Return				2018
Natural and Anthropogenic Inputs to the Athabasca Watershed						
Athabasca River Project: Creation of Artefacts During Sample Filtration	WE0077	Natural and Anthropogenic Inputs to the Athabasca Watershed	2021			
Bioavailability and Bioaccessibility of Trace Elements in Natural and Industrial Particles of the Lower Athabasca River Watershed	WE0072	Natural and Anthropogenic Inputs to the Athabasca Watershed	2021	2020		
Current Knowledge of Oil Sands Process-Affected Water Seepage from Tailings Ponds and its Environmental Influence in Northeastern Alberta	WE0059	Natural and Anthropogenic Inputs to the Athabasca Watershed				2018

Summary Report Title	Project Number	Topic	2021	2020	2019	2018
Impact of Climate Change on Surface Water and Groundwater Resources in the Athabasca River Basin	WE0063	Natural and Anthropogenic Inputs to the Athabasca Watershed		2020	2019	
Impacts of Atmospheric Dust Deposition on the Speciation of Trace Elements in Snowmelt and Peatland Surface Waters	WE0018	Natural and Anthropogenic Inputs to the Athabasca Watershed				2018
Metals vs Minerals:Water Quality in the Lower Athabasca River	WE0057	Natural and Anthropogenic Inputs to the Athabasca Watershed	2021	2020	2019	2018
Natural vs Anthropogenic Inputs: Water Quality in the Lower Athabasca River	WJ0017	Natural and Anthropogenic Inputs to the Athabasca Watershed		2020	2019	2018
OP-FTIR Optical Remote Sensing Field Measurement of VOC & GHG Emissions	WJ0064	Natural and Anthropogenic Inputs to the Athabasca Watershed			2019	
Surveying Conductive Anomalies within the Athabasca River	WJ0146	Natural and Anthropogenic Inputs to the Athabasca Watershed			2019	
OSPW Chemistry and Toxicity						
Analytical and Toxicological Evaluation of Bioavailable Naphthenic Acids from Oil Sands Process-Affected Water and Groundwater Using Biomimetic Extraction - Solid Phase Microextraction	WJ0113	OSPW Chemistry and Toxicity				2018
Development of a Passive Sampler-Based Framework	WJ0109	OSPW Chemistry and Toxicity			2019	
Development of a Passive Sampler-Based Framework	WJ0147	OSPW Chemistry and Toxicity		2020	2019	
Development of a Passive Sampler-Based Framework for Derivation of Water Quality Benchmarks for Oil Sands Process-Affected Water	WJ0045	OSPW Chemistry and Toxicity			2019	2018

Summary Report Title	Project Number	Topic	2021	2020	2019	2018
Development of Microbial Fuel Cell Biosensor for Detection of Naphthenic Acids	WJ0116	OSPW Chemistry and Toxicity	2021	2020	2019	2018
Investigations of the Bioaccumulation Potential of Dissolved Organics in Oil Sands Process-Affected Water: A Review	WE0049	OSPW Chemistry and Toxicity				2018
Literature Review and Evaluation of Dissolved Chloride for Treated Oil Sands Process Affected Water (OSPW) Return	WE0037	OSPW Chemistry and Toxicity				2018
Oil Sands Process-Affected Water (OSPW) Typology	WE0011	OSPW Chemistry and Toxicity				2018
Protecting the Athabasca River Basin: Bacterial Biosensors for Detection and Bioremediation of Oil Sands Process-Affected Water (OSPW)	WJ0168	OSPW Chemistry and Toxicity	2021			
The Base Mine Lake Toxicity Identification and Evaluation Study	WJ0025	OSPW Chemistry and Toxicity				2018
Toxicity of Ozone -Treated and Untreated OSPW	WE0016	OSPW Chemistry and Toxicity				2018
Vanadium Toxicity to Aquatic Organisms Representative of the Athabasca Oil Sands Region	WJ0024	OSPW Chemistry and Toxicity				2018
Pit Lakes						
Base Mine Lake Monitoring and Research Program	WJ0121	Pit Lakes	2021	2020	2019	2018
Literature Review and Proposed Study Design in Support of the Proposed 2022/23 Demonstration Pit Lake Mesocosm Study	WE0083	Pit Lakes	2021			
Literature Review of Global Pit Lakes	WJ0135	Pit Lakes		2020		
Mesocosm Research in Support of Pit Lakes	WJ0013	Pit Lakes	2021	2020	2019	

Summary Report Title	Project Number	Topic	2021	2020	2019	2018
Suncor Lake Miwasin - Demonstration Pit Lake	WJ0091	Pit Lakes	2021	2020	2019	
Regional Water Projects						
Athabasca River Watershed Project	WE0006	Regional Water Projects				2018
Regional Water Management Initiative	WE0005	Regional Water Projects				2018
Water Treatment						
Alternative Mine Rock Stockpile Construction Methods	WJ0042.08	Water Treatment	2021			
Application of Ceramic Nanofiltration Mambranes for Water Treatment in Oil Sands Mines	WJ0014	Water Treatment		2020	2019	
Calcite Remediation using Acid Addition	WJ0032.1	Water Treatment		2020		
Calcite Remediation using Cascades	WJ0032.2	Water Treatment		2020		
Calcite Technology Assessment	WJ0181	Water Treatment	2021			
Calcite Treatment Technology Review	WJ0029	Water Treatment			2019	
Carbonix Activated Carbon Project	WJ0139	Water Treatment	2021	2020	2019	
Clean Water Return Demonstration Pilot - Phase 1	WJ0132	Water Treatment	2021	2020	2019	
Co-mingling of Mine Rock and Tailings to Minimize Oxidation and Mobilization of Constituents of Interest	WJ0042.10	Water Treatment	2021			
Constructed Wetland Treatment System: Summary	WJ0067	Water Treatment				2018
Cultivating the Uncultivatibles in the Canadian Oil Sands	WE0041	Water Treatment			2019	
Cultivating the Uncultivatibles in the Canadian Oil Sands	WE0055	Water Treatment				2018
Demonstration of Biochar and Ash to Sequester Zn & Cd (2019YE)	WJ0042.01	Water Treatment			2019	
Demonstration-Scale Constructed Wetland	WJ0142	Water Treatment				2018

Summary Report Title	Project Number	Topic	2021	2020	2019	2018
Treatment System for Oil Sands Process-Affected Water (OSPW)						
Development of a Passive, Plant-Based Naphthenic Acid Remediation Technology for Treatment of Oil Sands Process-Affected Water	WJ0174	Water Treatment	2021			
H2nanO Treatment of Oil Sands Process-Affected Water (OSPW)	WJ0096	Water Treatment			2019	2018
In Pit Treatment - Beam treatment Summary(2020YE)	WJ0042.05	Water Treatment	2021	2020		
In Situ Pit Lake Treatment	WJ0050	Water Treatment		2020		
Industrial Research Chair in Oil Sands Tailings Water Treatment - First Term	WJ0035	Water Treatment			2019	
Industrial Research Chair in Oil Sands Tailings Water Treatment - Second Term	WE0025	Water Treatment	2021	2020	2019	2018
Microbiology Program - MiniPilots for Nitrate and Selenium Removal (2019YE)	WJ0042.02	Water Treatment			2019	
Napthenic Acid Degradation by Gamma Irradiation	WJ0150	Water Treatment			2019	
Nickel Cobalt Non-tank Based Treatment	WJ0042.09	Water Treatment	2021			
Nickel Cobalt Tank Based Treatment	WJ0042.06	Water Treatment	2021	2020		
Organics Treatment of Oil Sands Process-Affected Water (OSPW)	WE0014	Water Treatment				2018
Quenching of AOP Ozone and Peroxide Residual using Sodium Sulfite (2019YE)	WJ0042.04	Water Treatment			2019	
SolarPass Demonstration for Treatment of Dissolved Organics in Water	WJ0164	Water Treatment	2021	2020	2019	
Spray Evaporators for Treatment of Dissolved in Water	WL0088	Water Treatment			2019	

Summary Report Title	Project Number	Topic	2021	2020	2019	2018
Spray Evaporators for Water Management	WJ0055	Water Treatment			2019	
Statistical Evaluation of Microbiology Ecology Data to Operational Data(2019YE)	WJ0042.03	Water Treatment			2019	
Tailings Water Treatment Plant Engineering Design Specifications	WJ0051	Water Treatment			2019	
Weep Berm Technology Review	WJ0042.07	Water Treatment	2021	2020		
Wetland Treatment of Oil Sands Process-Affected Water	WJ0046	Water Treatment	2021	2020		2018
Watershed Modeling						
Evaluation of a Surface Water Modelling Framework for Athabasca River Water Quality Assessment	WE0040	Watershed Modeling		2020		

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Summary Report Title	Project Number	Topic	2021	2020	2019	2018
Alternative Mine Rock Stockpile Construction Methods	WJ0042.08	Water Treatment	2021			
Analytical and Toxicological Evaluation of Bioavailable Naphthenic Acids from Oil Sands Process-Affected Water and Groundwater Using Biomimetic Extraction - Solid Phase Microextraction	WJ0113	OSPW Chemistry and Toxicity				2018
Application of Ceramic Nanofiltration Mambranes for Water Treatment in Oil Sands Mines	WJ0014	Water Treatment		2020	2019	
Athabasca River Project: Creation of Artefacts During Sample Filtration	WE0077	Natural and Anthropogenic Inputs to the Athabasca Watershed	2021			
Athabasca River Watershed Project	WE0006	Regional Water Projects				2018
Base Mine Lake Monitoring and Research Program	WJ0121	Pit Lakes	2021	2020	2019	2018
Bioavailability and Bioaccessibility of Trace Elements in Natural and Industrial Particles of the Lower Athabasca River Watershed	WE0072	Natural and Anthropogenic Inputs to the Athabasca Watershed	2021	2020		
Calcite Remediation using Acid Addition	WJ0032.1	Water Treatment		2020		
Calcite Remediation using Cascades	WJ0032.2	Water Treatment		2020		
Calcite Technology Assessment	WJ0181	Water Treatment	2021			
Calcite Treatment Technology Review	WJ0029	Water Treatment			2019	
Carbonix Activated Carbon Project	WJ0139	Water Treatment	2021	2020	2019	
Clean Water Return Demonstration Pilot - Phase 1	WJ0132	Water Treatment	2021	2020	2019	
Co-mingling of Mine Rock and Tailings to Minimize Oxidation and Mobilization of Constituents of Interest	WJ0042.10	Water Treatment	2021			
Demonstration of Biochar and Ash to Sequester Zn & Cd (2019YE)	WJ0042.01	Water Treatment			2019	
Demonstration-Scale Constructed Wetland Treatment	WJ0142	Water Treatment				2018

Summary Report Title	Project Number	Topic	2021	2020	2019	2018
System for Oil Sands Process-Affected Water (OSPW)						
Evaluation of a Surface Water Modelling Framework for Athabasca River Water Quality Assessment	WE0040	Watershed Modeling		2020		
H2nanO Treatment of Oil Sands Process-Affected Water (OSPW)	WJ0096	Water Treatment			2019	2018
Impact of Climate Change on Surface Water and Groundwater Resources in the Athabasca River Basin	WE0063	Natural and Anthropogenic Inputs to the Athabasca Watershed		2020	2019	
Impacts of Atmospheric Dust Deposition on the Speciation of Trace Elements in Snowmelt and Peatland Surface Waters	WE0018	Natural and Anthropogenic Inputs to the Athabasca Watershed				2018
In Pit Treatment - Beam treatment Summary(2020YE)	WJ0042.05	Water Treatment	2021	2020		
In Situ Pit Lake Treatment	WJ0050	Water Treatment		2020		
Industrial Research Chair in Oil Sands Tailings Water Treatment - First Term	WJ0035	Water Treatment			2019	
Industrial Research Chair in Oil Sands Tailings Water Treatment - Second Term	WE0025	Water Treatment	2021	2020	2019	2018
Investigations of the Bioaccumulation Potential of Dissolved Organics in Oil Sands Process-Affected Water: A Review	WE0049	OSPW Chemistry and Toxicity				2018
Literature Review and Evaluation of Dissolved Chloride for Treated Oil Sands Process Affected Water (OSPW) Return	WE0037	OSPW Chemistry and Toxicity				2018
Literature Review and Proposed Study Design in Support of the Proposed 2022/23 Demonstration Pit Lake Mesocosm Study	WE0083	Pit Lakes	2021			
Literature Review of Global Pit Lakes	WJ0135	Pit Lakes		2020		
Mesocosm Research in Support of Pit Lakes	WJ0013	Pit Lakes	2021	2020	2019	

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Metals vs Minerals:Water Quality in the Lower Athabasca River	WE0057	Natural and Anthropogenic Inputs to the Athabasca Watershed	2021	2020	2019	2018
Microbiology Program - MiniPilots for Nitrate and Selenium Removal (2019YE)	WJ0042.02	Water Treatment			2019	
Mine Depressurization Water Management - Phase II and III	WJ0145	Mine Depressurization Water			2019	
Mine Depressurization Water Management -Phase II and III	WJ0063	Mine Depressurization Water			2019	
Mining Best Practices Report for Alternate Water Sourcing and Salinity Management	WJ0061	Best practices				2018
Mining Depressurization Water Treatment to Create Acid and Caustic	WJ0152	Mine Depressurization Water		2020		
Napthenic Acid Degradation by Gamma Irradiation	WJ0150	Water Treatment			2019	
Natural vs Anthropogenic Inputs: Water Quality in the Lower Athabasca River	WJ0017	Natural and Anthropogenic Inputs to the Athabasca Watershed		2020	2019	2018
Nickel Cobalt Non-tank Based Treatment	WJ0042.09	Water Treatment	2021			
Nickel Cobalt Tank Based Treatment	WJ0042.06	Water Treatment	2021	2020		
Oil Sands Process-Affected Water (OSPW) Typology	WE0011	OSPW Chemistry and Toxicity				2018
OP-FTIR Optical Remote Sensing Field Measurement of VOC & GHG Emissions	WJ0064	Natural and Anthropogenic Inputs to the Athabasca Watershed			2019	
Organics Treatment of Oil Sands Process-Affected Water (OSPW)	WE0014	Water Treatment				2018
Overburden Dewatering Effectiveness Study	WJ0099	Best Practices				2018
Protecting the Athabasca River Basin: Bacterial Biosensors for Detection and Bioremediation of Oil Sands Process-Affected Water (OSPW)	WJ0168	OSPW Chemistry and Toxicity	2021			

Summary Report Title	Project Number	Topic	2021	2020	2019	2018
Quenching of AOP Ozone and Peroxide Residual using Sodium Sulfite (2019YE)	WJ0042.04	Water Treatment			2019	
Regional Substance Loading Allocation Study	WE0009	Mine Water Return				2018
Regional Water Management Initiative	WE0005	Regional Water Projects				2018
River Ecosystem Health Assessment Using Pilot Facility - Feasibility Study	WE0013	Mine Water Return				2018
Salt Load Model	WE0010	Mine Water Return				2018
SolarPass Demonstration for Treatment of Dissolved Organics in Water	WJ0164	Water Treatment	2021	2020	2019	
Spray Evaporators for Treatment of Dissolved in Water	WL0088	Water Treatment			2019	
Spray Evaporators for Water Management	WJ0055	Water Treatment			2019	
Standardize Measurement and Quantification Techniques	WE0027.1	Best Practices				2018
Statistical Evaluation of Microbiology Ecology Data to Operational Data (2019YE)	WJ0042.03	Water Treatment			2019	
Suncor Lake Miwasin - Demonstration Pit Lake	WJ0091	Pit Lakes	2021	2020	2019	
Surveying Conductive Anomalies within the Athabasca River	WJ0146	Natural and Anthropogenic Inputs to the Athabasca Watershed			2019	
Tailings Water Treatment Plant Engineering Design Specifications	WJ0051	Water Treatment			2019	
The Base Mine Lake Toxicity Identification and Evaluation Study	WJ0025	OSPW Chemistry and Toxicity				2018
Toxicity of Ozone -Treated and Untreated OSPW	WE0016	OSPW Chemistry and Toxicity				2018
Vanadium Toxicity to Aquatic Organisms Representative of the Athabasca Oil Sands Region	WJ0024	OSPW Chemistry and Toxicity				2018
Weep Berm Technology Review	WJ0042.07	Water Treatment	2021	2020		
Wetland Treatment of Oil Sands Process-Affected Water	WJ0046	Water Treatment	2021	2020		2018