



SURFACE AND GROUNDWATER MANAGEMENT IN THE OIL SANDS INDUSTRY

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GEORGE DIXON, UNIVERSITY OF WATERLOO

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BACKGROUND

Water plays a central role in open pit mining of Canadian oil sands (Figure 1). Vast quantities of water from the Athabasca River are used and recycled for processes such as extracting bitumen (heavy, thick form of crude oil) from sand. Bitumen extraction and upgrading processes generate wastewater (known as process-affected water) that contains elevated levels of constituents that are toxic to aquatic organisms including: naphthenic acids (NAs), salts, polycyclic aromatic compounds, metals and others.

Since process-affected water is toxic to aquatic organisms, it cannot be safely discharged into the Athabasca River and needs to be temporarily stored on-site in previously mined pits or tailings ponds. Once mining operations have ceased, the site will be reclaimed using dry and wet landscape strategies. Wet strategies include placement of process-affected water and/or tailings to create shallow wetlands in some areas and large end pit lakes in previously mined pits. Eventually, this network of reclaimed wetlands and lakes will be connected to the watershed.

Understanding the chemical nature and effects of NAs is one of the greatest challenges for wastewater management in the oil sands. There are concerns that NAs in process-affected water could hinder the environmental health of aquatic reclamation options or escape into the Athabasca River. Insufficient past monitoring by outdated and inaccurate analytical methods has provided little valuable data to make scientific evaluations of safety and risk.

The multi-disciplinary team brought together for this research, which was funded in part by Canadian Water Network, developed and executed a wide range of projects to address knowledge gaps in the chemistry of NAs and the fate and effects of these compounds in aquatic environments. Projects were conducted under laboratory-based conditions and/or field-based conditions to address environmental issues associated with wastewater storage (e.g. oil sands tailings ponds) or the use of wastewater in reclamation (e.g. experimental wetlands and ponds constructed in 1980s and 1990s).

The research conducted covers a broad range of questions relevant to wastewater management in the oil sands from environmental assessment to remediation. The following examples highlight some of the studies conducted, the findings and the significance of these findings for wastewater management and regulatory agencies (Table 1).

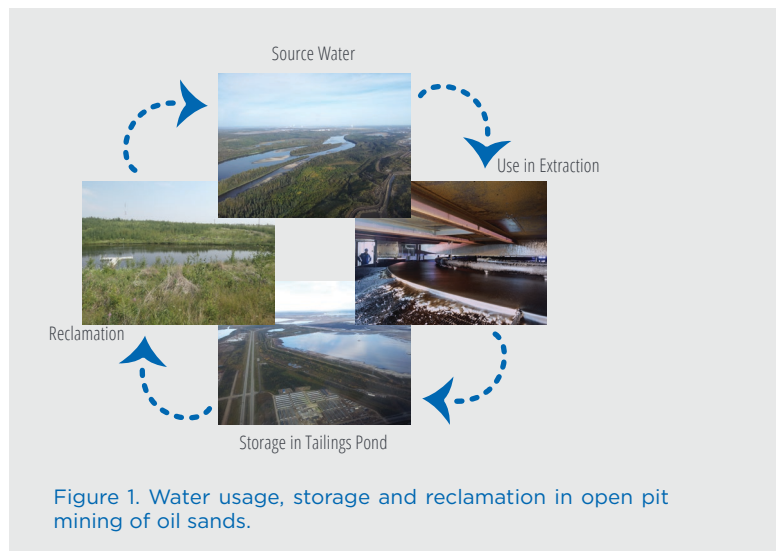


Table 1. Research Questions

RESEARCH CATEGORY	RESEARCH QUESTIONS
Concentration and Composition	What compounds are in the acid-extractable fraction of oil sands process-affected water?
Fish Toxicology	What are the effects of process-affected water on sensitive life stages of fish such as reproduction?
Ecosystem Function	What are the effects of process-affected water and tailings on food web compartments and carbon flow?
Transport and Fate in Groundwater	Is there seepage of process-affected water into groundwater from tailings ponds? Is there biodegradation of NAs in groundwater?
Remediation Options	What techniques can be applied to remediate process-affected water?

CONCENTRATION AND COMPOSITION OF PROCESS-AFFECTED WATER

WHAT COMPOUNDS ARE IN THE ACID-EXTRACTABLE FRACTION OF OIL SANDS PROCESS-AFFECTED WATER?

< 50% of compounds in oil sands process-affected water are naphthenic acids

composition of this fraction. Using electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR MS) to analyze acid-extractable fractions of oil sands tailings ponds and other water samples, researchers determined that classical NAs and oxy-NAs (NAs that have undergone mild oxidation) only account for <50% of total abundance of compounds in acid-extractable fractions.

These findings sparked the development of a wide variety of improved analytical techniques that are candidates to replace existing methods. Improved measurement of the concentration and composition of acid-extractable organics in the environment and determining the toxicity of known concentrations is central to the assessment of environmental risk and the protection of aquatic life in natural and reclaimed systems. Consensus on the best method(s) to analyze this complex mixture will provide consistent and reliable data on concentration and composition of acid-extractable organics to improve monitoring and regulatory practices.

Organic compounds in oil sands process-affected water can be separated into acid and base-neutral fractions; the acid-extractable fraction is known to cause acute toxicity.

In past decades, the acid-extractable fraction was thought to be comprised of mainly classical NAs and there have been few analytical methods available to determine the chemical

FISH TOXICOLOGY

WHAT ARE THE EFFECTS OF PROCESS-AFFECTED WATER ON SENSITIVE LIFE STAGES OF FISH SUCH AS REPRODUCTION?

Measures of fish health (survival, growth and reproduction) are highly valued indicators for assessing environmental risk of oil sands reclamation. While acute (lethal) toxicity may subside after an extended aging period in reclaimed systems, sublethal effects to fish growth and reproduction may be an ongoing issue that could lead to declining fish populations.

Naphthenic acids greater than 25 mg/L and conductivity greater than 2000 $\mu\text{S}/\text{cm}$ negatively impact fish reproduction.

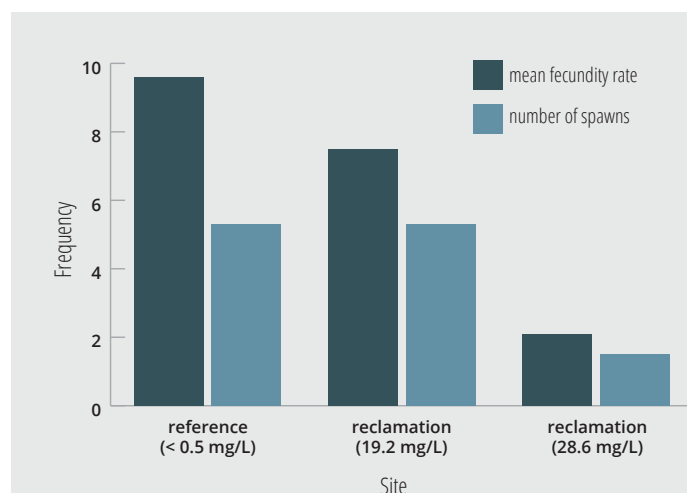


Figure 2. Effects of aged oil sands process-affected waters on fathead minnows. NA concentration, mg/L in brackets. (Figure based on data from Kavanagh et al. 2011).

To assess the effects of aged oil sands process-affected water on fish reproduction, fathead minnows were exposed to different aged process-affected waters from a variety of experimental oil sands reclamation under laboratory conditions. Often there were reductions in sex steroid levels, male secondary sexual characteristics, mean fecundity rate (number of eggs per female per day) and/or number of spawns depending on the source and quality of the aged process-affected water (Figure 2).

Based on the water quality of the complex mixture of constituents found in process-affected water, it was determined that levels of NAs greater than 25 mg/L and conductivity greater than 2000 $\mu\text{S}/\text{cm}$ would not support fish reproduction.

Due to the complex mixture of constituents found in process-affected water, it is difficult to isolate the effects of NAs from other constituents such as salts; therefore researchers extracted the NAs from process-affected water and exposed these extracts to fathead minnows to determine their impact on reproduction. Researchers found reduced egg production, male secondary sexual characteristics and sex steroid levels at 10 mg/L of NA extract.

Some of these effects were lessened in the presence of salt (NaHCO_3) at concentrations similar to oil sands process-affected water. Further studies of larval fathead minnows indicate that 700 mg/L NaHCO_3 reduced the acute and chronic effects of the NA extract.

The findings of this study have significant implications for future large-scale reclamation (e.g. end pit lakes). The knowledge gained from these studies helps to define the upper limits of NAs and salts in reclamation that could support fish populations and emphasize the need to reduce NA concentrations in reclamation. This information contributed to the development of the End Pit Lakes Guidance Document (2012).

ECOSYSTEM FUNCTION

WHAT ARE THE EFFECTS OF PROCESS-AFFECTED WATER AND TAILINGS ON FOOD WEB COMPARTMENTS AND CARBON FLOW?

Wetlands provide important ecosystem services, such as carbon storage, water retention and purification, and biological diversity. Previous studies have identified many types of aquatic invertebrates and plants that colonize experimental oil sands reclamation wetlands, but little is known about how these reclamation wetlands function. To bridge this knowledge gap, investigators examined major food web compartments (benthic invertebrates, plants, etc.) and processes (microbial production, primary production, etc.) in reclamation wetlands; key elements for assessing carbon flow in functioning ecosystems.

Wetlands that ranged in age from 2 to 20 years were sampled to determine if aging could mitigate the effects of process-affected water and tailings on various biological compartments. Compared to younger oil sands-affected wetlands (≤ 7 years), older oil sands-affected wetlands (>8 years) tended to be more similar to reference wetlands in terms of biomass for many food web compartments. However, the effect of age was not statistically significant, and several important differences remained. Oil sands-affected wetlands had lower submerged aquatic plant biomass, biomass and diversity of predatory invertebrates, and microbial production compared to reference wetlands. Natural aging processes in oil sands-affected wetlands over a 20-year time span had not fully restored ecosystem function to levels equivalent to reference wetlands.

Level of ecosystem function in oil sands- affected wetlands is not equivalent to reference wetlands.

The co-occurrence of elevated salinity with NAs in oil sands-affected wetlands makes it difficult to relate the observed toxicity of oil sands-affected wetlands to a particular constituent. In aged wetlands, there is some degradation of NAs, but there is still residual salinity, which is also an important regulator of aquatic plant community composition and possibly carbon production. Wetland reclamation should consider the type of waste material used in reclamation and the effect this material will have on salinity levels during dry and wet periods as it pertains to aquatic plant development.

The findings of this study have significant implications for future wetland reclamation. The knowledge gained on long-term effects of ecosystem function in oil sands-affected wetlands aids in the development of guidance documents for future wetland reclamation.

TRANSPORT AND FATE OF PROCESS-AFFECTED WATER IN GROUNDWATER

IS THERE SEEPAGE OF PROCESS-AFFECTED WATER INTO GROUNDWATER FROM TAILINGS PONDS?

One of the challenges associated with storage of oil sands process-affected water in tailings ponds is the potential for this wastewater to seep into groundwater and flow to surface water. Identifying flow pathways that lead from groundwater to surface water is important due to the potential effects of process-affected water on aquatic biota residing in these receiving environments.

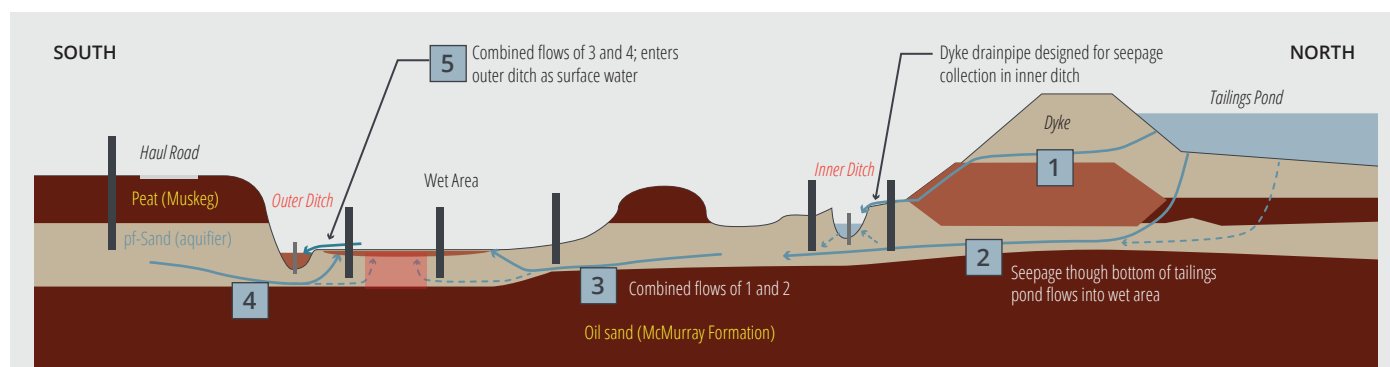


Figure 3. Potential flow pathways of groundwater and surface water in a seepage collection system of a tailings pond (modified from Yasuda et al., 2010).

Using measurements of chemical tracers and hydraulic conditions, and tools such as groundwater models, investigators were able to identify potential flow pathways of process-affected water originating from a tailings pond (Figure 3).

IS THERE BIODEGRADATION OF NAPHTHENIC ACIDS IN GROUNDWATER?

While partial aerobic degradation of NAs in process-affected water was demonstrated previously in laboratory and surface water studies, few studies have investigated subsurface water where anaerobic conditions are more common.

Naphthenic acids do not biodegrade in groundwater; therefore, there may be a need to manage and treat groundwater that may be contaminated by tailings seepage in order to protect surface water environments.

Researchers found that in a shallow sand aquifer there was no significant biodegradation of NAs in a mildly anaerobic plume, despite a long residence time of > 20 years. In the absence of biodegradation of NAs in groundwater, any flow of groundwater into surface waters could have negative impacts on biota in these receiving environments.

Determining the transport and fate of process-affected water in these systems has prompted research on treatment options (e.g. in situ chemical oxidation, reactive barriers in aquifers, wetlands in discharge zones) to aid long term wastewater management of groundwater plumes. Increasing salinity in groundwater plumes and the potential negative impact on aquatic vegetation is of particular concern due to water recycling practices and the use of ore that contains saline porewater.

REMEDICATION OPTIONS

WHAT TECHNIQUES CAN BE APPLIED TO REMEDIATE PROCESS-AFFECTED WATER?

Laboratory and field assessments of aquatic biota in aged oil sands process-affected water from experimental reclamation ponds and wetlands indicate that slow in situ biodegradation over time is not sufficient to eliminate chronic toxicity, even though there is no longer evidence of acute toxicity.

Chronic toxicity is thought to be caused by persistent NAs that are not easily degraded by natural microbial populations. Using advanced oxidation treatment methods (ozonation) to remove persistent NAs and advanced analytical methods (ultra performance liquid chromatography/high resolution mass spectrometry; UPLC-HRMS) to detect a wide range of parent and oxidized NAs, researchers were able to accelerate the removal of NAs from oil sands process-affected water.

Mild ozonation followed by microbial degradation accelerates removal of naphthenic acids.

The combination of mild ozonation of oil sands process-affected water, followed by inoculation and degradation by native microbes, appears to be a promising approach to aid in the removal of NAs and the reduction in toxicity based on bacterial toxicity testing (Microtox). Additional testing using a suite of aquatic biota is required to assess the effects of degradation products in this complex mixture.

The findings of this study and other related studies provide potential technologies to address the issue of chronic toxicity that currently remains in oil sands reclamation

after decades of aging. The implementation of treatment methods prior to reclamation to reduce toxicity attributed to acid-extractable organics will improve the water quality and the sustainability of aquatic ecosystems in future reclaimed wetlands and end pit lakes.

**FOR MORE INFORMATION, PLEASE CONTACT GEORGE DIXON, UNIVERSITY OF WATERLOO,
DGDIXON@UWATERLOO.CA**

REPORT AUTHORED BY ANDREA FARWELL, UNIVERSITY OF WATERLOO

RESEARCH TEAM

GEORGE DIXON, Department of Biology, University of Waterloo

JIM BARKER, Department of Earth Sciences, University of Waterloo

PHIL FEDORAK, Department of Biological Sciences, University of Alberta

JONATHAN MARTIN, Department of Laboratory Medicine & Pathology, University of Alberta

JAN CIBOROWSKI, Department of Biological Science, University of Waterloo

NIELS BOLS, Department of Biology, University of Waterloo

LUCILLA LEE, Department of Biology, Wilfred Laurier University

BARBARA BUTLER, Department of Biology, University of Waterloo

GLEN VAN DER KRAAK, College of Biological Science, University of Guelph

ULRICH MAYER, Department of Earth and Ocean Sciences, University of British Columbia

CARL MENDOZA, Department of Earth and Atmospheric Sciences, University of Alberta

DAVID RUDOLPH, Institute for Groundwater Research, Earth Sciences, University of Waterloo

CAROL PTACEK, Department of Earth Sciences, University of Waterloo

NEIL THOMSON, Department of Civil Engineering, University of Waterloo

KEVIN DEVITO, Department of Biological Sciences, University of Alberta

JONATHAN PRICE, Geography, University of Waterloo

JAMES SMITH, School of Geography and Earth Sciences, McMaster University

KEVIN BIGGAR, Civil and Environmental Engineering, University of Alberta

KRISTIN SCHIRMER, Department of Cell Toxicology, Helmholtz-Zentrum für Umweltforschung-UFZ

MOHAMED GAMAL EL-DIN, Civil and Environmental Engineering Department, University of Alberta

JOHN GIBSON, Isotope Hydrology, National Water Research Institute

JEAN BIRKS, Integrated Resource Management, Alberta Research Council

MICHAEL POWER, Department of Biology, University of Waterloo

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PHOTO CREDITS

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