Degradation and aquatic toxicity of naphthenic acids in oil sands process-affected waters using simulated wetlands

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Highlights

- Toxicity of oil sands process-affected waters associated with naphthenic acids (NAs).
- Examined NAs degradation and aquatic toxicity using simulated wetland microcosms.
- Microcosms successfully reduced total NAs concentrations, but process was incomplete.
- Persistent Microtox/C210 toxicity is likely associated with the residual NAs components.
- Acute toxicity of oil sands process-affected waters to rainbow trout was completely removed.

Abstract

Oil sands process-affected waters (OSPWs) produced during the extraction of bitumen at the Athabasca Oil Sands (AOS) located in northeastern Alberta, Canada, are toxic to many aquatic organisms. Much of this toxicity is related to a group of dissolved organic acids known as naphthenic acids (NAs). Naphthenic acids are a natural component of bitumen and are released into process water during the separation of bitumen from the oil sand ore by a caustic hot water extraction process. Using laboratory microcosms as an analogue of a proposed constructed wetland reclamation strategy for OSPW, we evaluated the effectiveness of these microcosms in degrading NAs and reducing the aquatic toxicity of OSPW over a 52-week test period. Experimental manipulations included two sources of OSPW (one from Syncrude Canada Ltd. and one from Suncor Energy Inc.), two different hydraulic retention times (HRTs; 40 and 400 d), and increased nutrient availability (added nitrate and phosphate). Microcosms with a longer HRT (for both OSPWs) showed higher reductions in total NAs concentrations (64–74% NAs reduction, \( p < 0.05 \)) over the test period, while nutrient enrichment appeared to have little effect. A 96 h static acute rainbow trout (Oncorhynchus mykiss) bioassay showed that the initial acute toxicity of Syncrude OSPW (LC50 = 67% v/v) was reduced (LC50 > 100% v/v) independent of HRT. However, EC20s from separate Microtox/C210 bioassays were relatively unchanged when comparing the input and microcosm waters at both HRTs over the 52-week study period (\( p > 0.05 \)), indicating that some sub-lethal toxicity persisted under these experimental conditions. The present study demonstrated that given sufficiently long HRTs, simulated wetland microcosms containing OSPW significantly reduced total NAs concentrations and acute toxicity, but left behind a persistent component of the NAs mixture that appeared to be associated with residual chronic toxicity.

1. Introduction

At the Athabasca Oil Sands (AOS) in northeastern Alberta, Canada, the caustic hot water extraction process described by Clark in 1932 is still used by some companies with surface mining operations to separate bitumen from oil sand ore (Clark and Pasternack, 1932). In current integrated surface mining operations at the AOS, approximately 2–2.5 m³ of fresh water is required to produce 1 m³ of synthetic crude oil (W. Zubot, Syncrude Canada Ltd., Edmonton, AB, Canada, personal communication). At production rates that are approaching one million barrels of oil per day, this results in the build-up of large inventories of liquid tailings, of which oil sands process-affected waters (OSPWs) is a major component and a significant stakeholder concern (MacKinnon, 1989; Holroyd and Simiervitsch, 2009). Previous toxicological investigations have shown that freshly produced OSPW, and OSPW contained within the active tailings system, are toxic to various aquatic organisms.
et al., 2010). However, in this research, the authors have decided to
within a given oil sands NAs mixture (Barrow et al., 2010; Grewer
that may or may not be more persistent than the “classical” NAs
2010). These components include heteroatomic species, polycyclic
better information on the refractory fractions of NAs has become
fact, the presence of additional components within oil sands NAs
associated reduction in aquatic toxicity of OSPW (Quagraine et al.,
2002). Complete microbial mineralization under natural conditions
do not appear to be occurring and a portion of the NAs mixture,
particularly the higher molecular weight NAs, appears to be resis-
tant to further degradation (Quagraine et al., 2005a). Even after a
period of 7–11 years, with no subsequent input of tailings material,
the total concentration of NAs in experimental ponds containing
fresh OSPW (50 mg L−1 NAs) did not decrease below 20 mg L−1
(Leung et al., 2001; Holowenko et al., 2002). However, Herman
et al. (1994) demonstrated that mineralization of oil sands NAs,
via microbial activity, was possible and that it corresponded to a
reduction in Microtox® toxicity. Some residual (i.e., chronic) toxicity
persisted, suggesting that this toxicity could be related to the
more persistent NAs. A clear relationship between the persistent
fraction of NAs and the associated persistent aquatic toxicity of
OSPW has not been established in wetland environments and re-
quires further investigation.
More recent studies have better demonstrated the pathways of
degradation of OSPW NAs and the limitations of natural processes
(Han et al., 2009). With improvements in analytical capabilities,
better information on the refractory fractions of NAs has become
available suggesting that these refractory constituents are more
associated with the presence of hydroxylated metabolites of degra-
dation than with molecular weight and ring structures alone. In
fact, the presence of additional components within oil sands NAs
mixtures that are not consistent with the “classical” definition of
NAs can make up a significant proportion of the total acid-extract-
able organic (AEO) fraction isolated from OSPW (Grewer et al.,
2010). These components include heteroatomic species, poly cyclic
aliphatic carboxylates, and other heterocyclic aromatic fractions
that may or may not be more persistent than the “classical” NAs
within a given oil sands NAs mixture (Barrow et al., 2010; Grewer
et al., 2010). However, in this research, the authors have decided to
retain the use of the term “naphthenic acids (NAs)” to represent
the broader definition of the AEO fraction, or oil sands naphthenic
acids. The pathway(s) of natural NAs degradation, including the
persistent components present within oil sands NAs mixtures, still
needs to be fully understood as options for reclamation are actively
being developed and deployed.
Reclamation landscapes using both lakes and wetlands offer a
strategy for the reclamation of OSPW at the AOS. Using small simu-
lated wetlands (laboratory microcosms), we evaluated the poten-
tial for NAs degradation, the influence of hydraulic retention time
(HRT) and nutrient enrichment on NAs degradation, and the asso-
ciated reduction in aquatic toxicity of OSPW generated by Syn-
crude Canada Ltd. (Suncrude) and Suncor Energy Inc. (Suncor).
Laboratory microcosms, under flow-through conditions, were used
to mimic wetland environments in order to better understand their
role in aquatic reclamation landscapes as opposed to the tradi-
tional detention ponds (without an inlet and outlet) used in previ-
ous field studies. A greater understanding of possible design and
management criteria to optimize such aquatic environments for
NAs remediation, and the associated rates of OSPW detoxification
(e.g., thresholds for naphthenic acids toxicity to aquatic biota), will
increase stakeholder confidence in performance goals within recla-
mation plans.

2. Materials and methods

2.1. Experimental design

Two sources of OSPW (Suncrude and Suncor) were used to
charge and recharge flow-through, simulated wetland microcosms
in the laboratory. Two exposure times were used to create wetland
systems with a short (40 d) and long (400 d) hydraulic retention
time (HRT). Nutrient levels were also modified by the addition of
mineral forms of nitrogen (NaNO3) and phosphorus (Na2HPO4) to
provide a low (no added nutrients) and high (~1 mg L−1 N and
~150 μg L−1 P) nutrient loading. The resulting matrix of test condi-
tions allowed for the evaluation of basic factors possibly linked to
enhanced biodegradation of NAs and associated reduction in aqua-
tic toxicity. Laboratory microcosms were constructed to simulate a
simplistic wetland habitat similar to those that could be used in
the reclamation of OSPW at the AOS. An array of indigenous micro-
obial communities present in the input OSPW and in the sediments
from a local wetland (both added to the microcosms) were the
main sources of microbial activity in each system. Overall there
were 12 different treatment scenarios, tested in triplicate, resulting
in a total of 36 microcosms (Appendix A).

Microcosms were evenly spaced on shelves in a controlled-
environment chamber at the Toxicology Centre, University of Sas-
katchewan (Saskatoon, SK, Canada). Input waters for the 12 treat-
ments were placed in 10 L (long HRT) and 20 L (short HRT) high
density polyethylene plastic containers located above the experi-
mental microcosms. A Masterflex® multi-channel peristaltic pump
(Cole–Parmer Canada Inc., Montreal, QC, Canada) was used to con-
tinually pump the 12 treatment waters to their respective tripli-
cate microcosms at two different rates to achieve the arbitrarily
selected 40 d (short) and 400 d (long) HRTs. The 10-fold difference
in flow rates were achieved using two different sizes (3.1 and
0.8 mm I.D.) of Masterflex® high performance precision pump Ty-
gon® tubing. Microcosms with a short HRT were recharged at a rate
of 18 mL h−1 and microcosms with a long HRT were recharged at a
rate of 1.8 mL h−1, resulting in a residence time of about 40 and
400 d, respectively. Nitrogen and phosphorus, in the form of so di-
salts (5 mg L−1 NaNO3 and 0.64 mg L−1 Na2HPO4), were added to the
input water containers of the six treatments with nutrient enrich ment. All input water containers were covered with
black plastic, and the tubes conducting the water to the micro-
cosms were wrapped with duct tape to minimize light exposure
and biological activity until the input water reached the test
time.

Environmental variables such as dissolved oxygen (DO) concen-
tration, pH, temperature, and photoperiod were maintained at lev-
eels intended to promote microbial activity. The DO concentration
in each microcosm was maintained between 2 and 8 mg L−1 by
low and constant aeration. Microcosm pH was monitored regularly
and on average was stable between 8.7 to 8.9, and 7.7 to 8.0, for
those containing OSPW and control waters, respectively (Appendix
B; Table B.1). The temperature of the test chamber was maintained
at 25 ± 1°C. Additional fluorescent light bulbs, with a spectral
range of 350–750 nm, were attached to the shelves directly above
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