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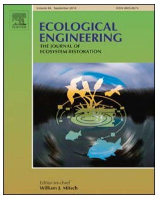

Treatment of oil sands process-affected waters using a pilot-scale hybrid constructed wetland

Maas Hendrikse[a,*], Daniel P. Gaspari[b], Andrew D. McQueen[a], Ciera M. Kinley[a], Alyssa J. Calomeni[a], Tyler D. Geer[a], Monique C. Simair[c], Kerry M. Peru[d], John V. Headley[d], John H. Rodgers Jr.[a], James W. Castle[b]

[a] Department of Forestry and Environmental Conservation, 261 Lehotsky Hall, Clemson University, Clemson, SC 29634, USA
[b] Department of Environmental Engineering & Earth Sciences, 455 Brackett Hall, Clemson University, Clemson, SC 29634, USA
[c] Contango Strategies Limited, LFK Biotechnology Complex, 15-410 Downey Road, Saskatoon, SK S7N 4N1, Canada
[d] Water Science and Technology Directorate, Environment and Climate Change Canada, 11 Innovation Blvd, Saskatoon, SK S7N 3H5, Canada

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ABSTRACT

Constructed wetland treatment systems (CWTSs) could provide a passive, low-energy strategy for mitigating risks associated with oil sands process-affected waters (OSPWs). Due to the large volumes (over 975 million m^3), heterogeneous composition, and acute and chronic toxicity of OSPW, passive and efficient treatment to decrease risks to biota will be necessary once operators obtain regulatory permission to discharge into aquatic receiving systems. The research objective was to design, assemble, and measure performance of a pilot-scale hybrid CWTS for treatment of OSPW. Constituents of concern (COCs) identified in OSPW included NAs, oil and grease, As, B, Cu, Pb, and Zn. Oxidizing conditions (net sediment redox > -50 mV) were promoted to allow aerobic degradation of organic constituents, and co-precipitation of arsenic with iron oxyhydroxides. Treatment of Cu, Pb, and Zn was targeted through precipitation with sulfides in reducing "micro-environments" in wetland sediments. Solar photocatalytic reactors (hybrid components) were used to remove recalcitrant organics. Performance was assessed using rates and extents of removal of COCs and changes in toxicity as indicated by *Ceriodaphnia dubia*. Mean total naphthenic acid fraction compound concentrations decreased from approximately 43 mg/L in untreated OSPW to 10 mg/L following a 16-d retention time in the hybrid CWTS. Mean As and Zn concentrations decreased from 0.026 mg/L and 0.129 mg/L in untreated OSPW to 0.011–0.014 mg/L and 0.052–0.062 mg/L in wetland outflows, respectively. Cu and Pb mass decreased by 13–26% in the CWTS; however, evaporative concentration masked removal (in terms of total metal concentrations). Toxicity (in terms of *C. dubia* survival and reproduction) of OSPW was eliminated following treatment. Results demonstrate that hybrid CWTSs can effectively degrade NAs and alleviate toxicity associated with metals and organics in OSPW.

1. Introduction

More than 975.6 million m^3 of oil sands process-affected water (OSPW) have been produced during bitumen extraction in the Athabasca oil sands (AOS) region of Alberta, Canada (Alberta Department of Energy, 2014). Oil sands operators store OSPW in tailings facilities for reuse in the bitumen extraction process (Shell Performance Report, 2016) and to comply with the current "zero discharge" policy (Alberta Environmental Protection and Enhancement Act, Section 23, 1993). OSPW is a complex mixture containing a variety of constituents including organics (i.e., naphthenic acids [NAs], residual bitumen), metals and metalloids, and suspended solids (Allen, 2008; McQueen et al., 2017a). Of these constituents, NAs have been identified as a primary source of aquatic toxicity (Verbeek et al., 1994; Morandi et al., 2015; Hughes et al., 2017a; McQueen et al., 2017a) with acute and chronic adverse responses measured for fish (Nero et al., 2006; Kavanagh et al., 2012), invertebrates (Zubot et al., 2012; Wiseman et al., 2013), vascular plants (Armstrong et al., 2009), and bacteria (Frank et al., 2008). OSPW contains classical NAs (generic chemical formula of $C_nH_{2n+z}O_2$), polyoxygenated NAs (e.g. $C_nH_{2n+z}O_x$), aromatic NAs, and sulfur and nitrogen containing heteroatom NAs which are collectively referred to as naphthenic acid fraction compounds (NAFC; Hughes et al., 2017b). Due to the persistence of NAs in OSPW under current storage conditions and the potential for toxicity to biota, NA concentrations must be decreased and forms of NAs degraded to less toxic forms prior to release to decrease

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[*] Corresponding author.
E-mail address: maash@g.clemson.edu (M. Hendrikse).

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potential risks for biota in aquatic receiving systems. Hybrid constructed wetland treatment systems (CWTSs) provide a passive or semi-passive strategy for treating the considerable volumes of OSPW stored on oil sands leases (McQueen et al., 2017a) and can contribute to reclamation goals of mining leases (e.g., attaining equivalent land use capabilities of pre-mined landscapes; CEMA, 2014).

CWTSs have been effective for treating complex mixtures such as refinery effluents (Gillespie et al., 2000; Huddleston et al., 2000) and produced waters (Murray-Gulde et al., 2003; Kanagy et al., 2008) using naturally occurring transfer (e.g. sorption, precipitation, settling) and transformation processes (e.g. photolysis, oxidation/reduction, biodegradation; Rodgers and Castle, 2008). Compared to other naturally occurring wetland processes (e.g. anaerobic degradation, sorption, photolysis), aerobic degradation of NAs in OSPW is a relatively rapid transformation process, with calculated half-lives of 44 d–240 d (Han et al., 2008); however, these rates may be too slow to meet mine closure deadlines. To efficiently and effectively treat NAs, hybrid components (i.e., mechanical, chemical, or physical devices) will likely be necessary in CWTS for OSPW. Solar photocatalytic (PC) reactors have shown promise as a hybrid component, achieving 47–93% removal of NAs after a 12 h photoperiod (approximately 1.3–2.3 MJ/m^2 cumulative ultraviolet [UV] insolation) as a final treatment step in other CWTS designs (McQueen et al., 2017b). Solar photocatalysis may provide additional benefits when incorporated prior to aerobic degradation if constituents that increase light attenuation (e.g., oil and grease, suspended solids) are removed in an early treatment step. Research by Martin et al. (2010), Gamal El-Din et al. (2011), and Hwang et al. (2013) suggested that degradation of higher molecular weight NAs by advanced oxidation processes (e.g., ozonation) prior to biodegradation increased subsequent aerobic degradation rates by increasing the relative abundance of more labile NA species. The premise of the present research is that by incorporating solar photocatalysis in sequence with CWTS treatment processes targeting NAs (i.e., aerobic degradation), wetland performance for treating NAs can be increased (i.e., NA removal rate and extent and decreases in toxicity).

A robust CWTS design is necessary to treat OSPW, as composition varies based on ore type, ore quality, the method of extraction, and the age of the processed water (i.e., extent of recycling; Mikula, 2013). An effective CWTS is supported by a design basis that considers the: 1) expected ranges of constituent concentrations in OSPW, 2) outflow goals (targeted constituent concentrations and toxicity) of treated OSPW, 3) wetland biogeochemical conditions and targeted transfer and transformation processes, and 4) site specific climate data of the AOS region (e.g., temporal availability, temperature, rainfall, evapotranspiration) that may influence the performance of the CWTS. The initial step in the design process is thorough characterization of the impaired water (i.e., OSPW) in terms of its physical, chemical, and toxicological properties. Importantly, these characterization data provide the expected range of concentrations for the design basis. Constituent concentrations in exceedance of regional water quality criteria (WQC) and toxicological endpoint values (e.g., LC_{50}s, EC_{50}s) are identified as constituents of concern (COCs). Numeric and narrative WQC (e.g., no toxics in toxic amounts, no visible sheen present) also serve as treatment performance and outflow goals for the CWTS. The next step in this process-based design approach is the use of strategic literature reviews, bench-scale experiments, and theoretical modeling (e.g., Eh-pH diagrams) to identify transfer and transformation processes capable of achieving treatment performance goals for COCs. Macrofeatures (i.e., vegetation, hydrosoil, and hydroperiod) are incorporated during assembly of the pilot-scale CWTS based on their ability to promote biogeochemical conditions required for treatment processes (Rodgers and Castle, 2008).

Rates and extents of COC removal and changes in toxicity of OSPW to sensitive aquatic organisms are lines of evidence for CWTS performance. Removal of acute toxicity associated with NAs in OSPW has been observed despite no significant changes in total NA concentrations (Armstrong et al., 2009; Toor et al., 2013; McQueen et al., 2017b). To accurately characterize NA exposures, it is necessary to measure the distribution of NAFCs in OSPW, in addition to total NA concentrations (which are a function of the analytical method used; Hughes et al., 2017b). Since other transfer (e.g., sorption, volatilization) and transformation processes (e.g., photolysis) do not significantly contribute to the removal of NAs, total NA concentrations and changes in NAFC distributions can also be used as lines of evidence that aerobic degradation and photocatalysis are occurring. Therefore, NA speciation by Orbitrap-mass spectrometry (Orbitrap-MS) was used to confirm changes in NAFC distributions (Hughes et al., 2017a). Toxicity experiments provide a line of evidence supporting the "no toxics in toxic amounts" narrative WQC following treatment by the developed hybrid CWTS, reinforce data from analytical measurements of constituent bioavailability, and account for potential matrix effects of constituents in OSPW (e.g., synergism, additivity, antagonism; USEPA, 1991). *Ceriodaphnia dubia* are aquatic invertebrate organisms that are relatively sensitive to constituents in OSPW (Zubot et al., 2012; McQueen et al., 2017a, 2017b), play an important role in aquatic food chains, and are widely distributed in freshwater throughout Canada (ECCC, 2007).

The overall objective of this research was to measure performance of a pilot-scale hybrid CWTS for treatment of OSPW sourced from the Athabasca Oil Sands region in Alberta, Canada. Specific objectives were to 1) design and assemble a pilot-scale CWTS incorporating a hybrid component to treat COCs in OSPW, and 2) measure performance of the pilot-scale hybrid CWTS in terms of rates and extents of COC removal in treated OSPW and changes in toxicity to *C. dubia* (mortality and reproduction).

2. Materials and methods

2.1. Source water

OSPW used in this study was obtained in November 2015 from the Muskeg River Mine External Tailings Facility (MRM-ETF), which was operated by Shell Canada Limited. The MRM-ETF is located approximately 60 km north of Fort McMurray in Alberta, Canada, and contained approximately 94 million m^3 of OSPW in the year the sample was collected (Shell Performance Report, 2016). In addition to OSPW, MRM-ETF received inputs precipitation, surface water runoff, groundwater extracted from aquifers located within and below oil sands deposits, waters produced during pre-mining preparation activities, waters collected from seepage ponds and ditches, and connate water. Approximately 40,000 L of OSPW were transported to Clemson, SC, USA in two stainless steel tanker trailers. Transported OSPW was transferred to 3780-L high density polyethylene (HDPE) tanks upon arrival and stored outdoors at a secure research facility.

2.2. Pilot-scale hybrid constructed wetland treatment system design

2.2.1. Chemical analysis for oil sand process-affected water characterization and performance monitoring

The following chemical analyses were used to characterize OSPW and to measure constituent concentrations necessary to calculate removal extents, percent removal, and rate coefficients. Physical, chemical, and toxicological characterization was performed for samples of OSPW (n = 3–4) collected from 3780-L HDPE tanks.

2.2.1.1. Water characteristics, nutrients, cations, and anions. Water characteristics, nutrient concentrations, and cation and anions concentrations in OSPW were analyzed using methods in *Standard Methods for Examination of Water and Wastewater* (APHA, 2012). Water characteristics including pH (Method 4500-H^+ B), dissolved oxygen (DO; Method 4500-O G), specific conductivity (Method 2510B), alkalinity (Method 2320B), hardness (Method 2340C), total suspended solids (TSS; Method 2540 D), total dissolved solids (TDS;