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# Fate and behavior of oil sands naphthenic acids in a pilot-scale treatment wetland as characterized by negative-ion electrospray ionization Orbitrap mass spectrometry

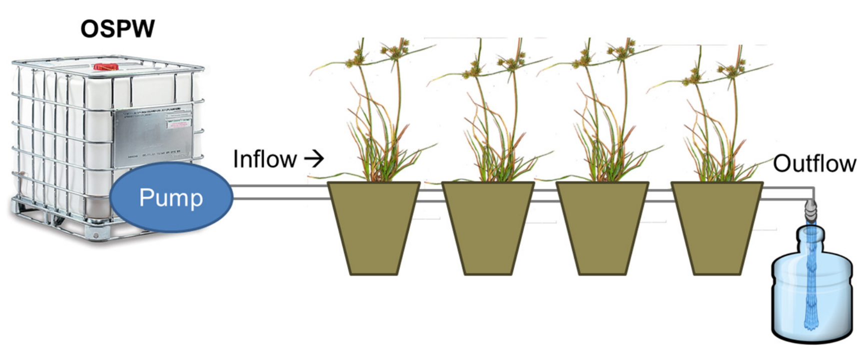
Chukwuemeka Ajaero [a,b,*], Kerry M. Peru [b], Monique Simair [c], Vanessa Friesen [c], Gwen O'Sullivan [d], Sarah A. Hughes [e], Dena W. McMartin [a,f,*], John V. Headley [b]

[a] Environmental Systems Engineering, University of Regina, Regina, Saskatchewan, 3737 Wascana Parkway, S4S 0A2, Canada
[b] Watershed Hydrology & Ecology Research Division, Water Science & Technology Directorate, Environment & Climate Change Canada, 11 Innovation Boulevard, Saskatoon, Saskatchewan S7N 3H5, Canada
[c] Contango Strategies Limited, 15-410 Downey Road, Saskatoon, Saskatchewan S7N 4N1, Canada
[d] Department of Earth & Environmental Science, Mount Royal University, 4825 Mount Royal Gate SW, Calgary, AB T3E 6K6, Canada
[e] Shell Health – Americas, One Shell Plaza, 910 Louisiana, Houston, TX 77002, USA
[f] Department of Civil, Geological and Environmental Engineering, 57 Campus Drive, University of Saskatchewan, Saskatoon, Saskatchewan S7N 5A9, Canada

## HIGHLIGHTS

- The removal rate of the naphthenic acids (NAs) species followed first-order kinetics.
- The non-aerated wetland system preferentially removed NAs species of higher carbon numbers.
- Constructed wetlands showed practical prospect for the treatment of OSPW-NAs.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Large volumes of oil sands process-affected water (OSPW) are generated during the extraction of bitumen from oil sands in the Athabasca region of northeastern Alberta, Canada. As part of the development of treatment technologies, molecular characterization of naphthenic acids (NAs) and naphthenic acid fraction compounds (NAFC) in wetlands is a topic of research to better understand their fate and behavior in aquatic environments. Reported here is the application of high-resolution negative-ion electrospray Orbitrap-mass spectrometry for molecular characterization of NAs and NAFCs in a non-aerated constructed treatment wetland. The effectiveness of the wetlands to remove OSPW-NAs and NAFCs was evaluated by monitoring the changes in distributions of NAFC compounds in the untreated sample and non-aerated treatment system. After correction for measured evapotranspiration, the removal rate of the classical NAs followed approximately first-order kinetics, with higher rates observed for structures with relatively higher number of carbon atoms. These findings indicate that constructed wetland treatment is a viable method for removal of classical NAs in OSPW. Work is underway to evaluate the effects of wetland design on water quality improvement, preferential removal of different NAFC species, and reduction in toxicity.



* Corresponding author.
*E-mail address:* dena.mcmartin@usask.ca (D.W. McMartin).

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## 1. Introduction

Oil sand process-affected water (OSPW) is a complex mixture having naphthenic acids (NAs) as the primary acid component (Grewer et al., 2010; Headley et al., 2013b). Classical NAs are complex mixtures of saturated aliphatic, cyclic and alkyl- substituted carboxylic acids (Grewer et al., 2010; He et al., 2010; Kannel and Gan, 2012), they are represented by the general formula; $C_nH_{2n+z}O_2$ where n is the carbon number and z is a negative even integer that indicates hydrogen deficiency due to formation of rings or double bonds. In addition, OSPW contains naphthenic acid fraction compounds (NAFCs) a class of compounds that includes the oxidized NAs (oxy-NAs) with more than two oxygen atoms, hydroxylated species, nitrogen-containing and sulfur-containing species, aromatic and unsaturated compounds (Headley et al., 2013a). These compounds together with the classical NAs, constitutes NAFCs. The concentration of NAFCs in OSPW is between 20 and 120 mg/L depending on the geology of the ore, age of tailing, extraction technique and analytical method employed (Clemente and Fedorak, 2005; Allen, 2008). Recent studies have identified classical NAs among the environmental constituents of concern (COC) in OSPW primarily because of their toxicity (McQueen et al., 2017a, 2017b). The toxic effects of OSPW was observed in aquatic plants (Armstrong et al., 2008), fish (Kavanagh et al., 2012; Marentette et al., 2015) and invertebrates (Anderson et al., 2012). The environmental concerns associated with OSPW such as toxicity and lack of feasible remediation approach are the primary reasons why OSPW is not permitted for discharge and impounded in tailings ponds (Madill et al., 2001; Headley and McMartin, 2004; Giesy et al., 2010). However, as a part of their regulatory approvals, improvement in water quality prior to return is mandatory for oil sands operators (Shell Canada Ltd, 2014; Hughes et al., 2017b). Recent studies have confirmed classical NAs as the primary toxic constituent in OSPW (Morandi et al., 2015; Hughes et al., 2017a). This development has given rise to extensive research on the treatment of OSPW with classical NAs as the principal treatment target.

A number of treatment techniques including nanofiltration (Kim et al., 2012; Kim et al., 2013; Alpatoa et al., 2014), coagulation/flocculation (CF) (Mohamed et al., 2008; Pourrezaei et al., 2011; Iranmanesh et al., 2014), biodegradation (Whitby, 2010; Misiti et al., 2013; Yue et al., 2015) and advanced oxidation processes (AOP) utilizing ozone (Perez-Estrada et al., 2011; Afzal et al., 2015), UV light (McMartin et al., 2004; Afzal et al., 2012), and transition metal catalyst (Mishra et al., 2010; Leshuk et al., 2016) have been shown to degrade NAs. The limitations associated with these techniques include: membrane fouling in nanofiltration techniques (Peng et al., 2004), generation of more toxic transformation compounds associated with AOP (Afzal et al., 2012), the cost of large quantity of coagulant and flocculants required to achieve effective removal and further treatment of the solid waste generated in CF technique (Quinlan and Tam, 2015). NAs removal using microbes has been shown to be slow, half-lives of 12.8–13.6 years (Han et al., 2009). However, biotechnology such as constructed wetland treatment (CWT) which is designed based on scientific principals and with site-specific considerations may expedite transformation rates allowing for timely treatment of OSPW wastewater. Constructed wetlands are currently gaining acceptance as an alternative treatment technology because of low environmental impacts and relatively inexpensive operational costs. Constructed wetlands have been extensively applied in the treatment of industrial wastewaters including petroleum industry wastewater (Vymazal, 2010), water polluted by organic compounds (Yousaf et al., 2011; Ho et al., 2012; Al-Baldawi et al., 2015) and mitigation of acid mine drainage (Nyquist and Greger, 2009; Clyde et al., 2016).

The appropriate selection of the environmental conditions, soil and vegetation types can promote removal processes such as oxidation, sedimentation, microbial transformation, photolysis and plant uptake of organic contaminants in treatment wetlands (Rodgers Jr. and Castle, 2008; Haakensen et al., 2015). The biological communities (plant and microorganisms) and the substrate in the constructed wetland play central roles in the removal of contaminants. Biodegradation has been identified as the primary biotransformation mechanism responsible for the removal of organic contaminants in wetlands (Truu et al., 2009; Faulwetter et al., 2009; Meng et al., 2014).

Microbial communities present in the wetland environment enhance the degradation of organic contaminants (Knight et al., 1999; Pham et al., 2011; Horner et al., 2012; Zhang et al., 2012; Toor et al., 2013a; McQueen et al., 2017b). Constructed wetlands with porous mineral substrate media attained ~90% removal of organic compounds in petroleum (Salmon et al., 1998). Among the transfer and transformation pathways studied, microbial degradation and plant uptake were responsible for the removal of 60% of the contaminants and sorption and volatilization accounted for <10% and <25% reduction, respectively (Salmon et al., 1998). Natural and CWT technologies have been shown to remediate OSPW (Gulley and Klym, 1992; Bendell-Young et al., 2000; Crowe et al., 2002; Mackinnon et al., 2001) including between 35 and 70% removal of NAs (Bishay et al., 1995). A recent study, based on laboratory-scale CWT, by Toor et al. (2013a), found that NAs can be degraded from Athabasca OSPW.

Estimation of the concentration changes over time in a treatment process is a useful tool for the evaluation of the efficiency of the treatment strategy employed and provides valid information on the treatment time required to achieve minimum threshold of the contaminant degradation (Islam et al., 2014). Kinetic study of OSPW-NAs treatment can help provide better understanding of the degradation processes (Headley et al 2010; Islam et al., 2014). Most of the information on the influence of structural composition on rate of removal of NAs in treatment wetlands is based on bench-scale applications using high performance liquid chromatography-mass spectrometry (MS) Toor et al., 2013b). The applications of ultra-high-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) and high-resolution Orbitrap- MS with high accuracy in mass assignments of numerous polar compounds has been highly successful for compositional determination of petroleum derived samples (Marshall and Hendrickson, 2008). Performance and feasibility of the weak anion exchange solid phase extraction (WAX SPE) method for the selective isolation of NAFCs, particularly NAs from OSPW incubated with wetland plants and their further characterization by ultra-high-resolution negative electrospray (ESI) FT-ICR-MS have been reported earlier (Ajaero et al., 2017). Recently the application of high and ultra-resolution mass spectrometry has revealed the composition of the NAFC compounds in OSPW to include oxidized acid species, sulfur, and nitrogen containing compounds (Barrow et al., 2009; Grewer et al., 2010; Headley et al., 2011). These invaluable tools have made molecular level characterization of the diverse components in OSPW attainable (Martin et al., 2008; Grewer et al., 2010). The application of ESI enables accurate determination of molecular composition of NAFCs and successful assignment of carbon and double bond equivalent (DBE) numbers from spectra data (Grewer et al., 2010). The optimization of treatment design for contaminant removal in wetlands requires a detailed knowledge of their chemical constituents.

The present study reported herein is the first study to evaluate the feasibility of OSPW-NAFCs transformation in CWT using high-resolution negative-ion electrospray Orbitrap-MS for detailed understanding of their fates and behavior in the system. In this work, the effectiveness of CWT in the transformation of NAFCs was evaluated in a non-aerated wetland design using high-resolution Orbitrap-MS. We observed that under non-aerated wetland conditions, increased carbon number in NAFCs resulted in more effective transformation. Comprehensive characterization and distribution of classical NA classes and NAFC oxidation states through wetland treatment suggests that classical NAs transformation pathway is mainly by biodegradation rather than sorption or volatilization mechanisms. Conditions found in the real world may not always be simulated in pilot-scale study. However, investigations