# In-Situ Chemical Oxidation of Oil Sands Process Affected Groundwater

by

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## Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

## General Abstract

Development of oil sands mining in Athabasca basin, NE Alberta has resulted in generation of more than $1 \times 10^9$ $m^3$ of oil sands process-affected water (OSPW) mixed with fine tailings and currently stored in about 182 $km^2$ of tailings ponds. The OSPW has displayed acute toxicity to aquatic organisms due to the presence of a group of acid-extractable organics (AEOs), including aliphatic and cyclo-aliphatic carboxylic acids, termed naphthenic acids (NAs). Although slow aerobic degradation/aging processes in the tailings ponds reduces the toxicity of OSPW, AEOs in the oil sands process-affected groundwater (OSPGW) infiltrating into underlying sandy aquifers remain acutely toxic for decades. Subsequent transport of OSPGW towards surface water is one of the critical consequences of the on-site tailings storage. The main objective of this research was to investigate the potential for in situ chemical oxidation (ISCO) to mitigate toxicity of OSPGW. In order for effective application of ISCO of OSPGW three requirements must be met: 1) the oxidant must react with AEOs, 2) the ineffective oxidant consumption by aquifer components must be small, and 3) intimate contact between the injected oxidant and the AEOs in the aquifer within the time when the oxidant remains effective. Permanganate and un-activated persulfate were applied in this research.

A series of batch treatability testing were conducted on a variety of OSPW/OSPGW at temperatures ranging from 22 ˚C to 5 ˚C. The initial set of treatability experiments employed OSPW to evaluate the potential for oxidation of AEOs at 22 ˚C. Both permanganate and un-activated persulfate were able to degrade AEOs present in OSPW. Permanganate oxidation occurred mostly via molecular transformation with some residual dissolved organic carbon (DOC), whereas persulfate mineralized the AEO compounds. Characterization of oxidized samples revealed that permanganate degraded high Z number acids preferentially while persulfate initially reacted with smaller acids. The AEOs from oxidized OSPW showed essentially no Microtox toxicity.

The main goal of the next set of batch treatability experiments was to evaluate degradation of AEOs present in OSPGW, the potential in situ treatment target, at 22 ˚C. Again, both permanganate and persulfate effectively oxidized AEOs present in OSPGW and rendered the AEOs non-toxic, as judged by embryo-larval fathead minnow bioassays. Consistent with previous treatability experiments on OSPW, oxidation/detoxification of OSPGW by permanganate mostly occurred by molecule structural transformations while persulfate oxidation mineralized most AEOs. Interpretation of embryo-larval fathead minnow bioassay along with sample characterization by advanced mass spectrometry suggested that high Z number naphthenic acids have the greatest toxicity. As permanganate degrades higher Z number acids it quickly reduces the toxicity. It was also found that a decrease in carboxylic acid concentration, measured by FTIR, does not necessarily result in decreased toxicity.

Both permanganate and persulfate were able to degrade AEOs in OSPW and OSPGW at 22 ˚C. A series of batch test were conducted to investigate the capability of permanganate and persulfate to oxidize AEOs in OSPGW at the local aquifer temperature, 5 ˚C. At 5 ˚C, only permanganate oxidation reduced the toxicity of OSPGW. Persulfate was ineffective due to its limited reactivity with the more toxic AEOs. Neither permanganate nor persulfate showed any level of AEO mineralization, suggesting that oxidation mechanisms were temperature dependent. Similar to oxidation at 22 ˚C, toxicity mitigation was connected to degradation of high Z number acids by permanganate. This re-emphasizes that decrease in carboxylic acid concentration, measured by FTIR, does not necessarily reflect reduction of toxicity of OSPW/OSPGW. So, in order to ensure that any treatment results in the required mitigation in toxicity of AEOs, application of advanced AEO characterization in support of sensitive toxicity testing, such as with Pimephales promelas, is required.

A series of stop-flow column tests were conducted to mimic in situ oxidation of AEOs either using permanganate or persulfate at 5 ˚C in the presence of aquifer sediment. Permanganate degraded the toxic fraction of OSPGW in aquifer sediment at the local aquifer temperature of 5 ˚C. While aquifer material appears to activate persulfate resulting in higher rates of carboxylic acid degradation, it did not mitigate the acute toxicity of OSPGW.

Natural oxidant demand/interaction batch tests determined permanganate and persulfate consumption by non-target aquifer material at 22 and 5 ˚C was low. This suggests considerable dispersive mixing of oxidant with large volumes of acutely toxic OSPGW will occur while the oxidants are active.

Batch oxidation tests with OSPGW at 22 and 5 ˚C revealed that permanganate degraded the significant AEO/NA fraction at concentrations at least as low as 0.1 g $L^{-1}$. On the other hand, persulfate was not effective at 5 ˚C or at 15 ˚C even at concentrations as high as 10 g $L^{-1}$. This implies that contact between OSPGW and low concentrations of permanganate would still be effective after considerable dispersive dilution and some consumption by interaction with aquifer materials.

A series of simple simulations estimated that about 164000 $m^3$of a representative aquifer could be infused with at least 0.1 g $L^{-1}$ $KMnO_4$ following injection of 9000 $M^3$ of a 5 g $L^{-1}$ $KMnO_4$ solution. As an approximation, $KMnO_4$ was assigned no oxidant demand by the aquifer materials. The cost of oxidant was estimated to be $1.6 per $m^3$ of aquifer treated or $6.4 per $m^3$ of OSPGW treated, although overall project costs are likely 4- or 5-fold higher. The low oxidant demand of aquifers such as the WCSC and the capability of permanganate to remove sufficient acute toxicity when less than 50% of the AEOs are oxidized, makes ISCO using permanganate a promising technology to mitigate the acute aquatic toxicity of AEOs (or NAs) in OSPGW.

A pilot-scale permanganate injection trial in an aquifer impacted by OSPGW should be preformed to confirm permanganate ISCO efficacy and to optimize operations. A more comprehensive evaluation of physical and geochemical changes in the aquifer (permeability reduction due to $MnO_2$ precipitation, TDS increase, pH change, metal mobilization, etc.) should also be a priority.

## Acknowledgement

I owe perpetual appreciation to many people who generously concerned in helping me undertake this dissertation. I owe my deepest gratitude to my advisor, Professor Dr. James Barker for his learned advice, commitment and astute criticisms throughout my research. His passion for science, his positive attitude toward difficulties inherited in nature of research, and his willingness to teach has remarkably inspired and enriched my growth as a student and researcher. I am indebted specifically to Jim for his effort in developing my character as an independent researcher.

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I would like to thank my parents for their endless kindness, encouragements, and for their consistent effort in helping me develop confidence and intellectual abilities. I am deeply indebted to my wife, Golpira, who has never hesitated to offer her generous love and who has never doubted my abilities and has provided me the energy to attain my goals.

Despite all the assistance provided by my advisors and others, I am merely responsible for the content of the dissertation, including any errors or omissions which may unintentionally remain.

## Dedication

I am dedicating my dissertation to:

My wife, Golpira, for her supportive and encouraging attitude, and for her patience and comprehension.

My parents for their love, encouragement and guidance over my life.

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# Chapter 1:

# Introduction

## 1.1. General Background

Currently, oil sands mining in northeastern Alberta produces about 1 million b $d^{-1}$ of bitumen and upgraded crude oil (Government of Alberta, 2014). The processing of mined oil sands has resulted in the generation of more than 1 x $10^{9}$ $m^3$ of oil sands process water (OSPW) which has been retained in 182 $km^2$ tailings ponds (AESRD, 2013).

Fresh OSPW is slightly alkaline (pH 8-8.4) and contains sodium, chloride, bicarbonate, and sulfate as well as a highly complex mixture of dissolved and acid extractable organics (AEOs) (Allen, 2008). OSPW has displayed acute toxicity to a range of aquatic organisms. This toxicity was historically been attributed to a group of acid-extractable, aliphatic and cyclo-aliphatic mono-carboxylic acids, termed naphthenic acids (NAs) (MacKinnon and Boerger, 1986). The composition of OSPW varies with origin and age (Allen, 2008; Gamal El-Din et al., 2011). Fresh OSPW is the most acutely toxic but partially detoxifies due to natural processes such as aerobic biodegradation during retention in tailings ponds (MacKinnon and Boerger, 1986). Aged or mature OSPW which has been in ponds for decades is still acutely toxic to biota (Anderson et al., 2011) and contains recalcitrant AEOs that are only slowly degraded (Clemente and

Fedorak, 2005). Although slow aerobic degradation/aging processes in the tailings ponds reduces the toxicity of OSPW (MacKinnon and Boerger, 1986; MacKinnon and Costerton, 1994), AEOs in the OSPW infiltrating into the underlying sandy aquifers remain un-changed for decades (Scott et al., 2005) and some groundwater plumes are extending beyond tailings impoundments (Ferguson et al., 2009; Oiffer et al., 2009).

Several methods are being examined to treat OSPW in ponds and processing operations (e.g., biodegradation (Han et al., 2009), sorption onto granular activated carbon (Wong et al., 1996), nano-filtration (Peng et al., 2004), ozonation (Scott et al., 2008; Gamal El-Din et al., 2011), and oxidation by Fenton's reagent (Lu et al., 2010)). Of these, only biodegradation and in situ chemical oxidation (ISCO) hold potential for remediation of aquifers impacted by oil sands process effected groundwater (OSPGW). Currently, traditional controls such as cut-off walls and pump and treat systems have been considered in order to prevent OSPGW seepage into Athabasca River (Vincent-Lambert et al., 2011). Ex situ remediation of OSPGW would require long term expensive treatment facilities and groundwater extraction. Given the lack of significant natural attenuation such as sorption or biodegradation of AEOs in low temperature local groundwater, ISCO was pursued for this study. Potential ISCO treatment is attractive if detoxification of OSPGW can be accomplished with less expense and time.

ISCO technology has been utilized for remediation of aquifers contaminated by non aqueous phase liquids (NAPLs), especially petroleum hydrocarbons and chlorinated solvents (Li and Schwartz, 2004; Tsitonaki et al., 2010; Siegrist, 2011). Unlike ISCO treatment of residual NAPLs, oxidant must be dispersed in the aquifer to ensure maximum contact with dissolved AEOs. For effective, in situ remediation of OSPGW the

following requirements must be met: 1) the oxidant must persist in the aquifer and react with AEOs and 2) intimate contact between the injected oxidant and the AEOs in the OSPGW must be realized within the effective oxidant lifespan. The last issue depends on the hydrogeological processes of advection and dispersion for the required mixing. These are slow, weak processes (Payne et al., 2008) and so ISCO will require oxidants which remain effective for long period of time. This eliminates two commercial oxidants; peroxide and ozone. However, persulfate and permanganate are persistent oxidants (Huling and Pivetz, 2006; Siegrist, 2011) and used in this research to study in situ chemical oxidation of AEOs.

### 1.2. Research objectives

The current study investigated application of in situ chemical oxidation using the most commercially available persistent oxidants, permanganate and persulfate, for treating oil sands process affected groundwater infiltrated into the subsurface. The objectives of this study included:

1) To discover the potential for ISCO of oil sands process affected groundwater using permanganate and persulfate and to evaluate the changes in the composition of the acid extractable organics (AEOs) as well as toxicity mitigation due to oxidation (Chapter 2)
2) To examine reactivity of oil sands process affected groundwater with either permanganate or persulfate and to explore the relationship between changes in the make-up of acid extractable organics (AEOs) and the level of relative toxicity, measured by an organism native to the Athabasca basin (Chapter 3)

3) To evaluate the reactivity of oil sands process affected groundwater either with permanganate or persulfate at local aquifer temperature (5 ˚C) and to revalidate the relationship between changes in make-up of the AEOs and toxicity reduction (Chapter 4)
4) To estimate permanganate and persulfate oxidant consumption using representative aquifer material; to investigate the degradation of the toxic fraction of oil sands process affected groundwater in the presence of representative aquifer material at the aquifer temperature; and to evaluate the minimum oxidant concentration at which significant AEO degradation and as a result mitigation in toxicity occurs(Chapter 5)

### 1.3. Thesis organization

This dissertation has been organized based on four journal papers as chapters two to five. The research has been designed and conducted by Vahid Sohrabi unless it is mentioned in the following sections. This dissertation has been written by Vahid Sohrabi except as noted in the following sections.

The first chapter comprises a general introduction, objectives, contributions, and thesis organization.

Chapter two entitled “Potential for in situ chemical oxidation of acid extractable organics in oil sands process affected groundwater” was published in Chemosphere (Vol. 93, Issue 11, Nov. 2013, 2698–2703). This paper investigates the oxidation capacity of acid extractable organics of fresh oil sands process water either by permanganate or persulfate. The experiments were conducted and interpreted by this author, Vahid

Sohrabi. The whole text was written by Vahid Sohrabi, except the method for UPLC/QTOF analysis which was written by the second author, M.S. Ross. The manuscript was edited by M.S. Ross, J.W. Martin, and J.F. Barker.

Chapter three is entitled “Oxidation of acid extractable organic compounds in oil sands process affected groundwater either by permanganate or persulfate”. The experiments were conducted by and the manuscript written by Vahid Sohrabi, except the method for HPLC-Orbitrap-MS analysis which was written by A.S. Pereira. This chapter provides insight into oxidation of oil sands process affected groundwater and studies the impact of the AEO signature on toxicity of OSPGW. The toxicity testing was initially designed by Vahid Sohrabi and A. Bauer, a PhD candidate in the Biology Department, University of Waterloo. Toxicity testing was conducted by A. Bauer. A. Bauer provided useful interpretation of the toxicity testing results. The text was edited by A. Bauer, J.W. Martin, and J.F Barker.

Experiments as part of chapter four titled “Potential for in situ chemical oxidation of the toxic fraction of oil sands process affected groundwater at the local aquifer temperature” were designed and conducted by Vahid Sohrabi, who also wrote all but the method for HPLC-Orbitrap analysis which was written by A.S. Pereira. This chapter highlights the ability of permanganate and un-activated persulfate to degrade toxic constituents of oil sands process-affected groundwater (OSPGW) and reviews the impact of AEO signature on toxicity of OSPGW. The toxicity testing was designed by Vahid Sohrabi and A. Bauer. Bauer conducted toxicity testing on un-oxidized and oxidized samples and provided interpretation of toxicity testing results. The text was edited by A. Bauer, J.W. Martin, and J.F Barker.

Vahid Sohrabi conducted the experiments described in chapter five titled “Applicability of in situ chemical oxidation to remediate oil sands process affected water impacted aquifers” and wrote this chapter. J.P. Jones and J.F. Barker edited this chapter. This chapter provides an estimation of oxidant consumption by representative aquifer material from the Wood Creek Sand Channel, and discusses the oxidation of OSPGW when aquifer sediment was present at the local aquifer temperature of 5 ˚C. The minimum effective oxidant concentration at which AEOs in OSPGW were significantly degraded was estimated. This and the oxidant demand information was used to determine the volume of OSPGW that can be treated by a defined volume of injected permanganate solution.

Chapter six comprises the main findings and recommendations for future studies. Because of this manuscript thesis format, some information and references of chapter 2 to 5 are repeated.

# Chapter 2:

# Potential for in situ chemical oxidation of acid extractable organics in oil sands process affected water

## 2.1. Introduction

Canada has the third largest proven reserves of oil with 14% of global reserves (CAPP, 2013), 97% of which is in the oil sands of Alberta. In 2013, oil sands surface mining produced approximately 1.3 x $10^5$ $m^3$ $d^{-1}$ of bitumen (CAPP, 2013).

Hot-water extraction of bitumen from oil sands leads to an accumulation of the naturally-occurring, bitumen-derived, acid-extractable organics (AEOs) in oil sands process water (OSPW). The AEOs are responsible for the acute toxicity of OSPW (Verbeek et al., 1993). AEOs contain a prominent class of acids, namely naphthenic acids (NAs), which are a complex class of aliphatic and cycloaliphatic monocarboxylic acids, represented by the general formula $C_nH_{2n+z}O_2$, in which n and z represent the number of carbon atoms, and the number of hydrogen that are lost due to the presence of double bonds or rings in the molecule, respectively (Ross et al., 2012). Recent studies demonstrated that these classical NAs are only a fraction of the AEOs in OSPW and that molecules with a higher number of oxygen as well as sulfur and nitrogen atoms are present in the mixture (Pereira et al., 2013).

OSPW is retained in tailings ponds and is recycled back into the bitumen extraction process. It is estimated that about 830×$10^6$ $m^3$ of fluid fine tailings exist within tailing ponds covering more than 176 $km^2$ (AESRD, 2013). Clarification of tailings pond water

is extremely slow and, since all companies which mine oil sands agreed not to release any OSPW, the footprint of tailings ponds has grown steadily.

Infiltration of OSPW from tailings ponds and their retaining dykes into the subsurface and subsequent transport towards surface water is a consequence of this on-site tailings storage (Oiffer et al., 2009). Reduction in NA concentration and OSPW toxicity have been reported in experimental surface water ponds and wetlands over years of observation (MacKinnon and Boerger, 1986) due, at least in part, to aerobic biotransformation (Herman et al., 1994). NAs in groundwater appear to be somewhat recalcitrant to natural degradation (Scott et al., 2005; Oiffer et al., 2009), so with the continued growth in tailings being retained in potentially "leaky" tailings ponds and dykes, the potential need for technologies to remediate AEOs in groundwater is evident.

While process affected (PA) groundwater could conceivably be pumped out and treated *ex situ*, *in situ* treatment is attractive as it forgoes this expensive and often time consuming groundwater extraction (Adamson et al., 2011). Given the lack of significant sorptive retardation, or natural transformation of NAs, noted in the above groundwater studies, chemical degradation reactions are being pursued as a basis for *in situ* remediation of PA groundwater. Several oxidants have been examined to treat PA water in ponds and processing operations: e.g., ozone (Scott et al., 2008), UV/$H_2O_2$ (Afzal et al., 2012), Fenton's reagent (Lu et al., 2010), and activated persulfate (Drzewicz et al., 2012).

For *in situ* chemical oxidation (ISCO), the mixing of injected oxidant solution with PA groundwater is very slow (days to months) and so the oxidant must be both reactive

with AEOs and persistent in the aquifer (Brown, 2010). Chemical oxidation using ozone or peroxide is impractical in this case because these oxidants quickly decompose *in situ*. Activation is problematic *in situ* because of the short lifespan of radicals and the need to transport activators (e.g. $Fe^0$, peroxide) with the oxidant for months. This paper evaluates the potential for ISCO of PA groundwater, using the unactivated, persistent oxidants, persulfate and permanganate, which persist in the groundwater for weeks to months, to reduce AEOs and the associated acute toxicity of OSPW. Since maintaining activation *in situ* is problematic, only unactivated oxidants were investigated here. While most applications of persulfate have employed an activation agent (heat, pH, Fe(II), etc., (Drzewicz et al., 2012), recent research demonstrates that unactivated persulfate can still be effective, as in the *in situ* oxidation of fuel hydrocarbons (Sra et al., 2013).

The ISCO technology has been employed to remediate aquifers contaminated by many hazardous organic contaminants including petroleum hydrocarbons and chlorinated solvents (Siegrist et al., 2011). Our study is the first to examine the feasibility of ISCO for *in situ* remediation of groundwater containing OSPW. For effective *in situ* application three requirements must be met: 1) the oxidant must react with AEOs, 2) the proportion of ineffective oxidant consumption through interaction with aquifer components must be minimal, and 3) intimate contact between the injected oxidant and the AEOs in the PA groundwater must be realized within the timeframe of oxidant activity. The last issue depends on the hydrogeological processes of advection and dispersion for the required mixing of injected oxidant solution with PA groundwater. These are slow, weak processes (Payne et al., 2008) and so ISCO will require oxidants which remain effective for weeks at least. This requirement eliminates peroxide and ozone, but persulfate and

permanganate are sufficiently persistent (Siegrist et al., 2011). Preliminary laboratory studies by the authors have estimated that persulfate and permanganate will persist for months in sandy aquifer material (issue 2, above), while pilot scale field experiments are planned to evaluate issue 3, above. In this paper, we focused on the first issue: reactivity of these two persistent oxidants, employed without activation, with AEOs in PA groundwater. High resolution mass spectrometry was employed to confirm the oxidation process.

## 2.2. Materials and methods

### 2.2.1. OSPW

OSPW samples were collected from a siphon site at the South Tailings Pond on the Suncor property, 35 km northeast of Fort McMurray. The site is the discharge area of fresh tailings and OSPW into the pond. The OSPW samples were kept on ice and transferred to the University of Waterloo. Here, they were centrifuged at 10,000 rpm for 30 min to remove fine particles and then stored in 4-L amber jars. The initial carboxylic acid concentration, including NAs, was about 56.5±0.2 mg $L^{-1}$ (by Fourier Transform Infrared (FTIR), see 3. below). Table 2.1 shows major ion concentrations of OSPW used in this oxidation experiment.

Table 2.1. Major ion chemistry of OSPW, as measured by ICP-MS

| **Parameter (mg $L^{-1}$)** | **OSPW** |
|---|---|
| pH | 8.1-8.4 |
| Sodium | 751-792 |
| Calcium | 11-13 |
| Magnesium | 6-10 |
| Chloride | 430-473 |
| Bicarbonate | Not Analyzed |
| Sulphate | 325-380 |

### 2.2.2. Oxidation experiments

Analytical grade oxidants, potassium permanganate ($KMnO_4$, purity 99+%, A.C.S. reagent) and sodium persulfate ($Na_2S_2O_8$, Sigma Ultra, purity minimum 98%) were purchased from Sigma Aldrich. Two parallel experiments were conducted; one using permanganate and the other using persulfate. Oxidants were added to separate volumetric flasks with 12 L of OSPW and stirred for 90 min to ensure that oxidants were dissolved. The final concentrations were 5 and 10 g $L^{-1}$ of potassium permanganate and sodium persulfate, respectively. The final solutions were split into triplicate 4-L amber jars and a 4-L jar of centrifuged OSPW, without oxidant, was retained as an un-oxidized control. Jars were incubated in the dark, at room temperature (about 22 °C) and sampled periodically.

### 2.2.3. Sample preparation and analysis

Samples for all analyses, except dissolved organic carbon (DOC), were first acidified to pH~2, extracted with dichloromethane (DCM), and dried under nitrogen (Holowenko et al., 2002). This isolated the AEOs, including NAs, from residual oxidant. Specific preparation was then carried out for each analysis.

Potassium permanganate and sodium persulfate concentrations in water were measured by spectrophotometer (Milton Roy, Spectronic 20D) at various sampling times (APHA, 1995). The spectrophotometer was calibrated before and during concentration measurements using fresh standards prepared from the analytical grade oxidants. Samples were diluted by factors of 100 or 10 and analyzed at 525 and at 450 nm for permanganate and persulfate concentrations, respectively. Concentrations were

determined using the linear plot for standard solutions multiplied by the appropriate dilution factor.

Samples for DOC analysis were quenched by addition of saturated sodium bisulfite (Fisher Chemicals, S654-500) solution in order to stop the oxidation reaction (Forsey, 2004) and then stored in the dark at 4°C before analysis. Unoxidized controls were treated similarly. The reported DOC values are the average of two injections with ± 0.3 mg $L^{-1}$ reproducibility.

FTIR analysis was used for quantification of total carboxylic acid concentrations (including NAs) as per Jivraj et al. (1995) and Holowenko et al. (2001). Dried extracts were re-dissolved in 6-8 g of DCM and analyzed by FTIR. Quantification of NA concentration was done by comparing the absorbance peak heights of the C=O functional group at 1743 and 1706 $cm^{-1}$ for monomer and dimer compounds of commercial Merichem NA solutions (Merichem Chemicals and Refinery Services, Houston, TX) of known concentrations.

Ultra-performance liquid chromatography quadrupole time-of-flight mass spectrometry (UPLC-QTOF/MS) analysis was also applied to characterize select control and oxidized samples based on the number of carbon atoms (n) and rings/double bonds (Z). The method is similar to that described by Ross et al. (2012). Dried extracts were reconstituted in 4 mL DCM, from which 80 µL was removed and added to a glass autosampler vial and allowed to evaporate to dryness in a fume hood. Samples were spiked with 50 µL of 8 µg $mL^{-1}$ $^{13}C$-tetradecanoic acid (internal standard), and diluted with 950 µLof 50:50 acetonitrile/$H_2O$. All samples were analyzed on a Waters Aquity

UPLC coupled to an AB Sciex Triple TOF 5600 MS. Samples were chromatographed on a Waters BEH Phenyl column (1.0 mm x 150 mm x 1.7 µm) at a flow rate of 110 µL $min^{-1}$ and a column temperature of 65 °C. The mobile phase consisted of 10 mM ammonium acetate in water (A solvent) and 10 mM ammonium acetate in 60:40 methanol/acetonitrile (B solvent). The initial condition was 99% B held for 2 min, ramped to 60% B in 1 min (3 min total time), then ramped to 70% B in 4 min (7 min total time), then ramped to 95% B in 6 min (13 min total time), held at 95% B for 1 min, returned to 1% B and re-equilibrated for 6 min (20 min total time). The Z = 0 compounds were present in the blank samples, as previously described by Ross et al. (2012), and so are not reported here.

### 2.2.4. Toxicity bioassay

Finally, Microtox toxicity testing based on Environment Canada method EPS/RM/24 was applied to assess toxicity changes in the AEOs extract by oxidation. Unfortunately, the actual oxidized water could not be assayed as the residual oxidant would be toxic to organisms and so only the oxidant-free, extracted acids (AEOs) were tested. The samples for Microtox toxicity testing were prepared by dissolving the dried AEOs in 0.05 N NaOH (EMD Millipore, SX0590-1), followed by pH adjustment to 8 by adding 0.1 N NaOH or 1% $H_2SO_4$ (Fisher Scientific, 95-98%). The Microtox assay was then performed by Aquatox Laboratory in Guelph, Ontario. The prepared solutions were serial diluted with deionized water and each dilution added to a cuvette containing Vibrio fischeri bacteria. The light reader (Model 2055 Toxicity Analyzer) was adjusted so that the reading for a non-toxic control was 80 or more after 10 min of reconstitution. For samples where 50% inhibition of light emission was not attained, the endpoint is not

considered to have been reached and the toxicity of the sample is not defined as per Environment Canada regulation. However, we used the light inhibition versus concentration as an estimate of relative toxicity of the extracted AEOs. In total, 10 samples were tested: two un-oxidized non-extracted controls, two un-oxidized extracted controls, three extracted, persulfate-oxidized samples from day 58, and three extracted, permanganate-oxidized samples also from day 58.

## 2.3. Results and discussion

### 2.3.1. Total carboxylic acid concentration

The concentration of total carboxylic acids which includes NAs, measured by FTIR, decreased to < 1 mg $L^{-1}$ and 4.1±0.2 mg $L^{-1}$ in the presence of persulfate (10 g $Na_2S_2O_8$ $L^{-1}$) and permanganate (5 g $KMnO_4$ $L^{-1}$), respectively, over the 111 d experiment (Fig. 2.1).

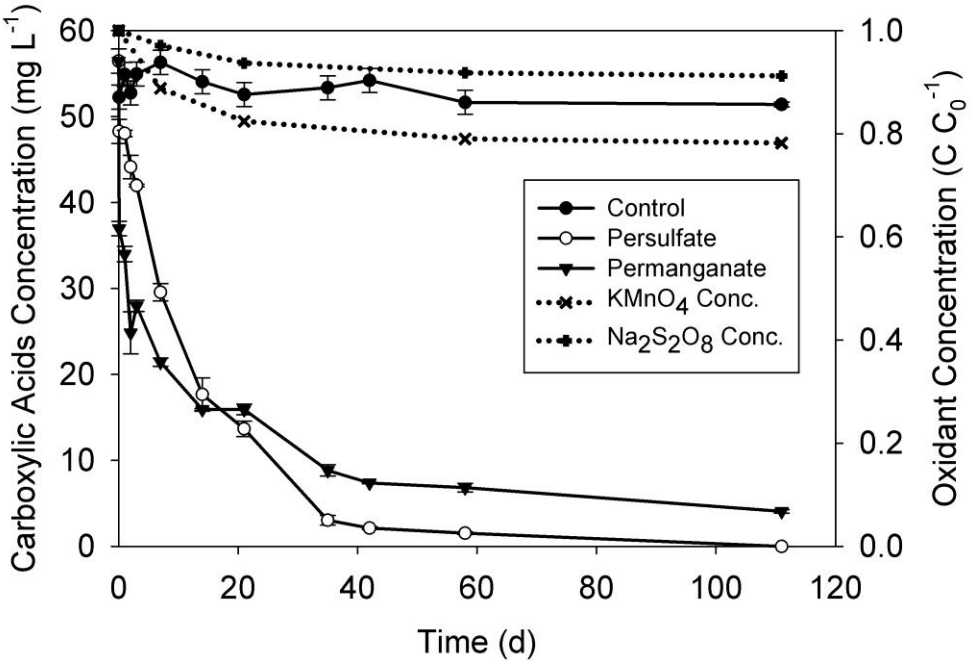


Fig. 2.1. The total carboxylic acid concentration during the oxidation experiment, as determined by FTIR. (three measurements with error bars based on the 95% confidence limit). Dotted lines are oxidant concentrations (C) relative to the initial concentrations ($C_0$). The $C_0$ for potassium permanganate and sodium persulfate concentrations were 5 and 10 g $L^{-1}$, respectively.

The control microcosm concentrations showed no significant decline, with the final concentration of 51.7±0.5 mg $L^{-1}$. Up to day 15, total carboxylic acid oxidation by permanganate was greater, but by day 35, persulfate had removed more acids than permanganate. The oxidants remained near their initial concentrations, confirming their persistence in OSPW (Fig. 2.1).

### 2.3.2. Characterization

Un-oxidized controls, permanganate and persulfate oxidized samples from day 2 and one persulfate oxidized sample from day 7 were characterized by UPLC/QTOF to see if a significant change in the NA distribution resulted from partial oxidation. The use of

high resolution MS provided data for NAs (i.e. compounds with two oxygen atoms), as well as oxidized NAs (i.e. compounds with three oxygen atoms in their structure). Plots of the NA profiles are shown in Fig. 2.2 and plots of the oxidized NAs are shown in Fig. 2.3.

The UPLC/QTOF NA profiles (Fig. 2.2) reveal that oxidation by persulfate and permanganate resulted in altered NA distribution patterns. In the un-oxidized control (Fig. 2.2.a), $C_{13}$ to $C_{19}$ compounds constituted about 90% of the NAs, mostly distributed in Z = -12 (48%), Z = -6 (18%), Z = -4 (12%), and Z = -10 (8%) homologues. It was observed that permanganate removed most of the NAs by day 2 (Fig. 2.2.b), but preferentially removed the more abundant, higher molecular weight NAs ($C_{16}$-$C_{22}$) relative to $C_{12}$-$C_{13}$ NAs. Oxidation by permanganate for 2 d resulted in essentially complete removal of Z = -10 and -12 NAs, and significant reduction in Z = -4 to -8 NAs (Fig. 2.2.b). Little change in the Z = -2 series was seen.

Persulfate also appeared to degrade most NA homologues by day 2 (Fig. 2.2.c). By day 2, persulfate was more successful in reducing $C_{12}$–$C_{14}$ members than permanganate (Fig. 2.2.b), but was less successful at reducing the $C_{15+}$ and the Z = -10 and -12 homologues than permanganate. However, by day 7 (Fig. 2.2.d) persulfate had degraded essentially all the NAs to below detection limits.

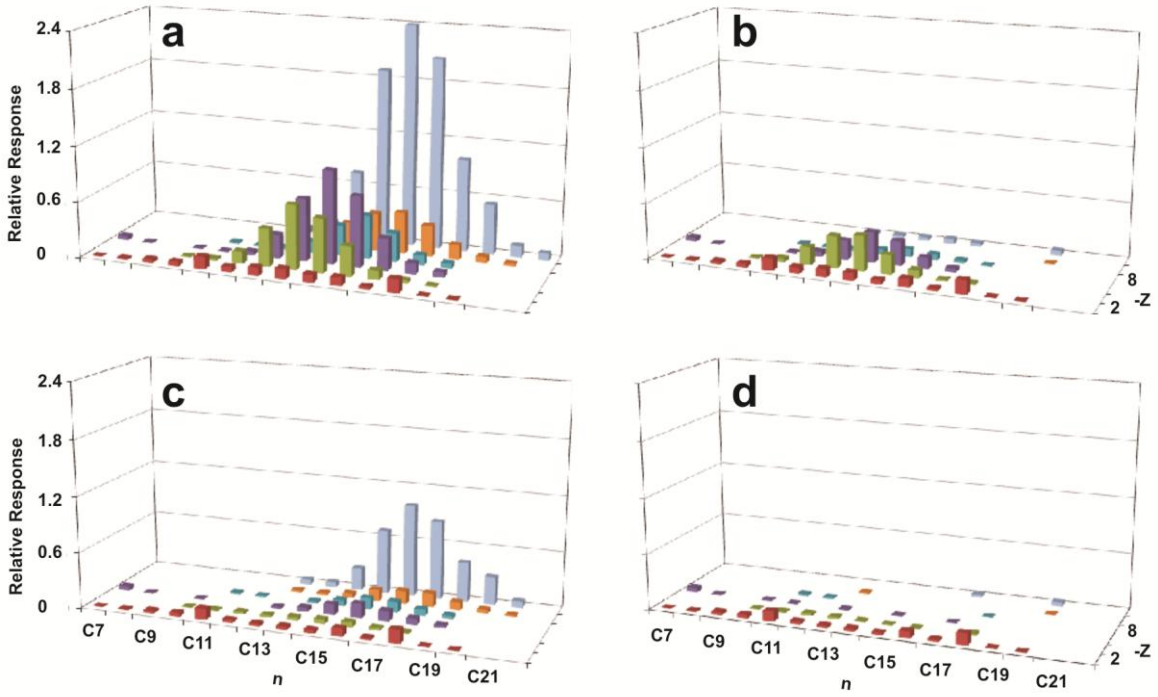


Fig. 2.2. Three dimensional plots of compounds with two oxygen atoms in un-oxidized and oxidized samples analyzed by UPLC/QTOF. a) un-oxidized control, b) permanganate, day 2, c) persulfate, day 2, and d) persulfate, day 7. The analyte areas are normalized by the area of the internal standard.

Initially (2 d) permanganate preferentially oxidized higher Z number, oxidized NAs (three-oxygen acids, Fig. 2.3.b) in comparison with persulfate (Fig. 2.3.c). In 2 d persulfate had essentially no impact on the three-oxygen NAs, but had reduced all oxidized NAs by day 7. One reason for permanganate's better performance initially might be the presence of C=C double bonding in NAs with higher Z numbers and in oxidized NAs which makes them susceptible to permanganate attack (Singh and Lee, 2001; Petri et al., 2011). However, persulfate removed more NAs by day 58 (97 versus 87%) as well as by day 111 (100 versus 93%), the end of the experiment.

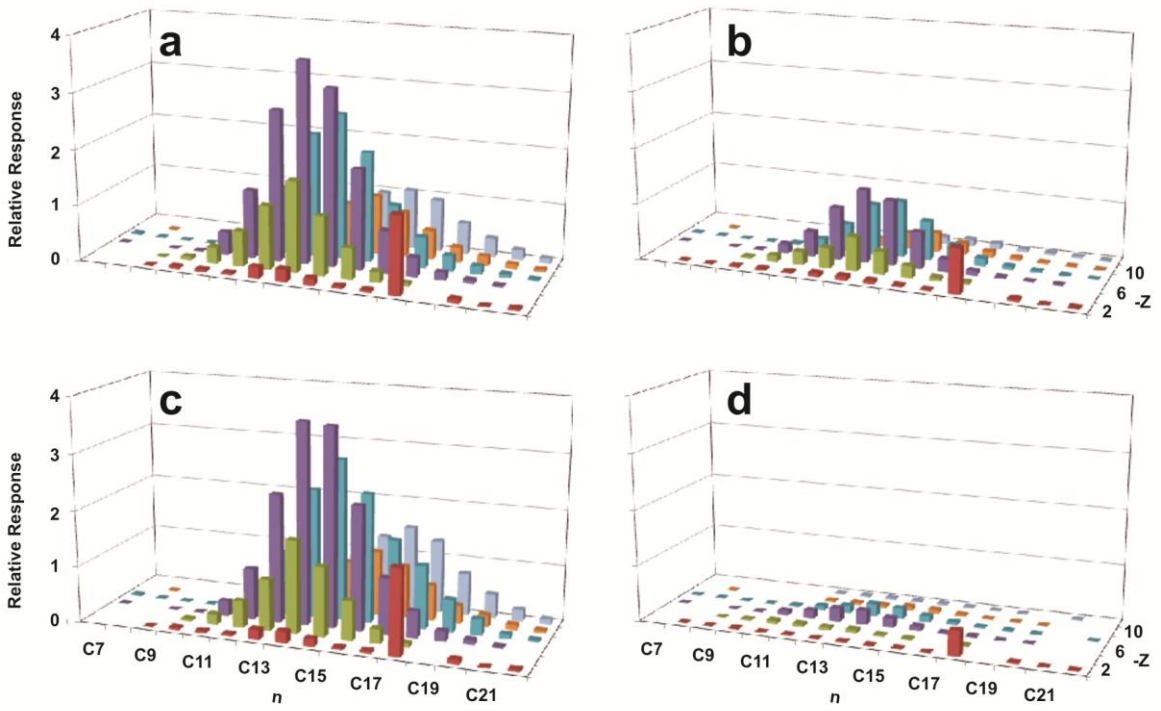


Fig. 2.3. Three dimensional plots for compounds with three oxygen atoms in un-oxidized and oxidized samples analyzed by UPLC/QTOF. a) un-oxidized control, b) permanganate, day 2, c) persulfate, day 2, and d) persulfate, day 7. The analyte areas are normalized by the area of the internal standard.

### 2.3.3. Toxicity bioassay

Both persulfate and permanganate were able to decrease the concentration of total carboxylic acids (Fig. 2.1) and to change the distribution pattern of NAs (Fig. 2.2) and oxidized NAs (Fig. 2.3) present in OSPW. This suggests that chemical oxidation with either persulfate or permanganate could reduce the toxicity of OSPW.

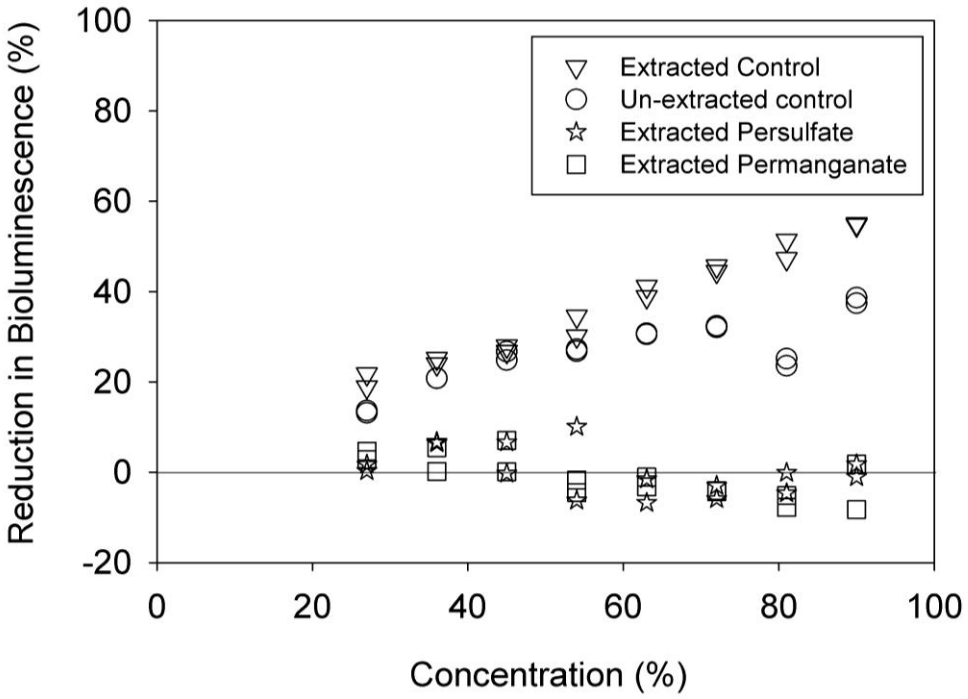


Fig. 2.4. Microtox toxicity testing results for two non-extracted, non-oxidized controls, two extracted non-oxidized controls, three extracted permanganate oxidized samples (58 d), and three extracted persulfate oxidized samples (58 d). The effect is the reduction of light emitted after 15 minutes compared to the light emitted by non-toxic solutions. Concentrations are the % of sample water in the solution actually tested. For example, a 25% concentration sample has been diluted 3:1 (75%) with deionized water.

To investigate if oxidation mitigated the toxicity of NAs to aquatic organisms, the Microtox toxicity assay, which has been used widely in the oil sands industry (Clemente and Fedorak, 2005; Scott et al., 2008; Frank et al., 2008), was applied to both extracted and non-extracted unoxidized control and oxidized extracts from day 58 of the experiment. It was necessary to extract all oxidized water samples to remove any residual oxidant before the Microtox assay was applied.

Both the extracted and un-extracted controls showed an increasing dose-response effect in the Microtox test (Fig. 2.4). Only one sample, an extracted un-oxidized control,

showed toxicity at the level of $EC_{50}$ at 83% of the original concentration (i.e., about 44 mg total carboxylic acids /L). Oxidized samples showed less effect when compared to either non-extracted or extracted control samples for all dilutions. In fact, there was no detectable toxicity for AEOs following persulfate and permanganate oxidation. While the Microtox is not a highly sensitive method for assessing the toxicity of OSPW, the current results confirm that the oxidation reduced the toxicity, and more sensitive assays should be investigated in future trials.

### 2.3.4. DOC concentration

While extracted oxidized samples showed less toxicity than either extracted or non-extracted un-oxidized samples, it was considered that toxic oxidation by-products might not be extracted by the DCM. Therefore, DOC concentrations were measured to see if oxidation might have left potentially toxic (but un-extracted) organic by-products in the water samples. The changes in DOC and total carboxylic acid concentrations over 111 d are shown in Fig. 2.5. There was no significant change of total carboxylic acids (Fig. 2.5.a) and DOC (Fig. 2.5.b) concentrations of un-oxidized control samples. The oxidized samples showed 93% (permanganate) and essentially 100% (persulfate) removal of total carboxylic acids by day 111 (Fig. 2.5.a). However, permanganate-oxidized samples still had 67% of the initial DOC whereas persulfate oxidation had only about 6% of the initial DOC by day 111 (Fig. 2.5.b). This suggests that while permanganate oxidation removed most of the total acids (Fig. 2.1), it yielded significant organic by-products that persisted over this 111 day experiment. The composition and toxicity of the residual DOC from permanganate oxidation is unknown. On the other hand, persulfate oxidation resulted in more complete mineralization of the NAs/AEOs.

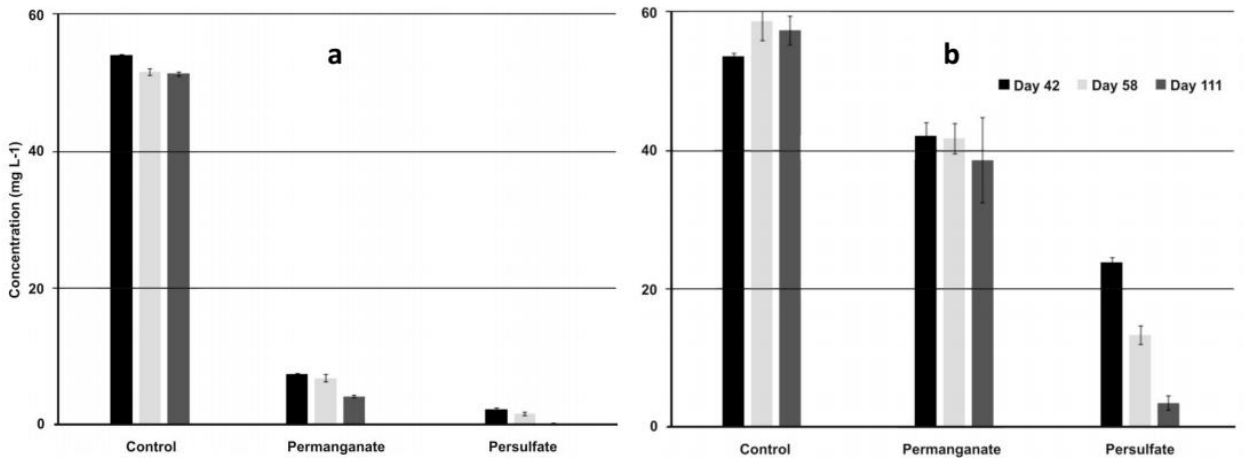


Fig. 2.5. NA concentrations (a) and DOC (b) of un-oxidized control, permanganate and persulfate oxidized samples for days 42, 58, and 111.

### 2.4. Summary

Un-activated persulfate and permanganate oxidation removed 100 and 93% of the carboxylic acids from OSPW over 111 d, respectively, in batch experiments at room temperature. Less than 10% of the persulfate and about 20% of the permanganate were consumed by day 58, indicating both oxidants were persistent and so potentially useful for ISCO of oil sands PA groundwater. Characterization of the traditional, two-oxygen NA mixture using UPLC/QTOF analysis revealed that both oxidants were able to transform NAs, likely with somewhat different oxidation mechanisms. The mechanisms of persulfate oxidation are complex (Anipsitakis and Dionysiou, 2004; Tsitonaki et al., 2010) and are not clarified here. Ongoing research with persulfate and permanganate using single NAs is underway which may clarify the oxidation mechanisms.

Although Microtox toxicity testing was not sufficiently sensitive, persulfate and permanganate oxidation appears to have reduced the toxicity of extracted AEOs including NAs. More sensitive species such as fathead minnow will be used to estimate the toxicity changes in ongoing experiments. The DOC analyses suggested that

persulfate and permanganate initially transformed NAs, but that persulfate mineralized much more of the intermediate by-products (94 versus 33%) by day 111. Complete mineralization of organic compounds leaves no residual toxicity and so, at least to this point, persulfate is the preferred oxidant for *in situ* oxidation of oil sands process affected groundwater.

# Chapter 3:

# Oxidation of acid extractable organic compounds in oil sands process-affected groundwater by permanganate or persulfate

## 3.1. Introduction

Oil sands mining in northeastern Alberta currently produces about 1 million b $d^{-1}$ of bitumen and upgraded crude oil (Government-of-Alberta, 2014). Following surface mining, the oil sands ore is crushed, mixed with heated water and sodium hydroxide and hydro-transported to an extraction plant. Bitumen is recovered and the tailings, a mixture of sand, silt, clay, residual bitumen, and oil sands process water (OSPW), is transferred to tailings ponds. Fresh OSPW is slightly alkaline (pH 8-8.4) and contains sodium, chloride, bicarbonate, and sulfate as well as a highly complex mixture of dissolved, acid extractable organics (AEOs) (Allen, 2008). Although 80-95% of the water used in the extraction is recycled from tailings ponds (CAPP, 2014), freshwater must still be imported from the Athabasca River, and by 2013 tailings ponds covered 182 $km^2$ (AESRD, 2013). Eventually, OSPW will be returned to the environment, either following long-term storage, treatment, or by groundwater seepage (Oiffer et al., 2009).

A challenge for tailings reclamation is that OSPW has displayed acute toxicity to a range of aquatic organisms (Frank et al., 2008). This toxicity was historically attributed to a group of acid-extractable, aliphatic and cyclo-aliphatic mono-carboxylic acids, termed naphthenic acids (NAs) (MacKinnon and Boerger, 1986). These compounds can

be represented by the general formula $C_nH_{2n+z}O_2$, whereby n is the number of carbon atoms and Z is an even negative integer assigned for the number of hydrogen atoms that are missing due to double bonds or rings (Brient et al., 1995; Grewer et al., 2010). However, recent application of ultra-high resolution mass spectroscopy has indicated that in addition to NAs, many other organic acids are also present in the AEO mixture such as poly-oxygenated compounds ($O_x$), sulfur (e.g. $SO_x$, $S_2O_x$) and nitrogen ($NO_x$) containing acids (Headley et al., 2009, Barrow et al., 2010, Pereira et al., 2013). To date, no studies have demonstrated which of these compounds are the most toxic.

The composition of OSPW varies with origin and age (Allen, 2008; Gamal El-Din et al., 2011). Fresh OSPW is the most acutely toxic but partially detoxifies during retention in tailings ponds due to natural processes which might include aerobic biodegradation (MacKinnon and Boerger, 1986). Nevertheless, aged OSPW which has been in ponds for decades is still toxic to fish (Anderson et al., 2011) and contains recalcitrant AEOs that are only slowly degraded (Clemente and Fedorak, 2005). Remediation of this mature OSPW, which might infiltrate into groundwater and form oil sands process affected groundwater (OSPGW) (Frank et al., 2014), is the main focus of this chapter.

Several potential treatments for OSPW detoxification have been reported including aerobic biodegradation (Clemente and Fedorak, 2005), adsorption, and chemical oxidation (Scott et al., 2008; Martin et al., 2010). Sohrabi et al. (2013) found positive results for chemical oxidation of OSPW at 22 ˚C using permanganate and un-activated persulfate to degrade AEOs and to mitigate their toxicity. This suggests that these persistent, unactivated oxidants might permit in situ chemical oxidation of oil sands process affected groundwater (OSPGW). Since OSPGW may include a higher

proportion of recalcitrant and toxic AEOs, chemical oxidation of this water, using permanganate and un-activated persulfate is examined in this paper. In the previous study, characterization of oxidized samples by ultrahigh resolution mass spectrometry revealed that permanganate and persulfate initially attacked different NA fractions; permanganate oxidized high Z number acids, while persulfate oxidized the low molecular weight NA fraction. Here, we again applied ultrahigh resolution mass spectrometry tool to oxidized samples in an effort to reveal differences in NAs, and the broader AEO mixture, in both OSPGW and OSPW. Sohrabi et al. (2013) used a standard aquatic toxicity test, Microtox, but recommended a more sensitive test to better evaluate the toxicity of treated and untreated AEOs. The differences in AEO patterns of permanganate- and persulfate-oxidized OSPW samples, as observed previously, raised the idea of evaluating the relative toxicity of AEOs, from OSPW and OSPGW sources, after different oxidation treatments. Thus, embryo-larval bioassays were conducted using *Pimephales promelas* to track changes in toxicity of oxidized samples in comparison with un-oxidized OSPGW and OSPW.

### 3.2. Materials and methods

#### 3.2.1. OSPW and OSPGW

The OSPW and OSPGW samples were collected from the Suncor lease, 35 km northeast of Fort McMurray, AB, Canada. Fresh OSPW was collected at the discharge point to an active tailings pond, while OSPGW was collected from a monitoring well at an old tailings structure. OSPW was kept refrigerated prior the experimentation. The OSPW and OSPGW were centrifuged (10,000 rpm) for 30 min to remove suspended solids before oxidation experiments. Initial total carboxylic acid concentrations,

measured by Fourier Transform Infrared (FTIR) spectroscopy, were 60.1±1.3 and 46.9±0.3 mg $L^{-1}$ for centrifuged OSPW and OSPGW, respectively. Table 3.1 shows major ion chemistry of OSPW and OSPGW samples.

Table 3.1. Major ion chemistry of OSPW and OSPGW, as measured by ICP-MS

| **Parameter (mg $L^{-1}$)** | **OSPW** | **OSPGW** |
|---|---|---|
| pH | 8.1-8.4 | 8-8.2 |
| Sodium | 751-792 | 280-292 |
| Calcium | 11-13 | 37-61 |
| Magnesium | 6-10 | 1-2 |
| Chloride | 430-473 | 18-19 |
| Bicarbonate | - | 1000-1040 |
| Sulphate | 325-380 | <0.5 |

### 3.2.2. Chemical reagents

Potassium permanganate ($KMnO_4$, purity 99+%, A.C.S. reagent) and sodium persulfate ($Na_2S_2O_8$, Sigma Ultra, purity 98+ %) were purchased from Sigma Aldrich and used as received. A saturated solution of analytical grade sodium bisulfite ($NaHSO_3$, Fisher Chemicals, S654-500) was used to quench the oxidation reaction when collecting samples from experimental treatments at different times (Forsey, 2004).

### 3.2.3. Oxidation experiments

Permanganate and persulfate were used in parallel oxidation experiments with both OSPGW and OSPW at 22 ˚C. Each oxidant was spiked into its own 12 L jug of OSPW/OSPGW and stirred until the oxidant was dissolved. The initial concentrations for potassium permanganate and sodium persulfate in the OSPW/OSPGW solutions were 5 and 10 g $L^{-1}$, respectively, both about 10 times in excess of that required for stoichiometric mineralization of a $C_{20}$ NA with ~ 50 mg $L^{-1}$ concentration by either of

these two oxidants. Each OSPW-oxidant solution was immediately split into triplicate, 4-L amber jar reactors. A 4-L container for each of centrifuged OSPW and OSPGW, without oxidant, was retained as a control and was sampled at each episode. All reactors were stored in the dark at room temperature (~ 22 ˚C) and were sampled at time zero and 2 h and 2, 7, 21, 45, 75, and 120 d after set up.

### 3.2.4. Sampling and analyses

Potassium permanganate and sodium persulfate concentrations were analyzed by spectrophotometry (Thermo Scientific GENESYS 10S Bio UV/Visible Spectrophotometer, 6 cell) as per APHA (1995). The spectrophotometer was calibrated before and during analysis using fresh standards prepared from the analytical grade oxidant. Samples were diluted by appropriate factors and analyzed at 525 and at 450 nm for permanganate and persulfate concentrations, respectively. Oxidant concentrations were determined by comparing the sample readings with the linear plot for standard solutions multiplied by the corresponding dilution factor.

Samples for DOC analysis were quenched by addition of saturated sodium bisulfite (Fisher Chemicals, S654-500) solution (Forsey, 2004) and then stored in the dark at 4 ˚C before analysis. Unoxidized controls were treated similarly. The wet combustion method was then used for DOC measurements using a Shimadzu TOC-L Total Organic Carbon Analyzer with TNM-L Total Nitrogen Measuring Unit. The oxidation temperature for organic carbon in high temperature furnace was 680 ˚C. The reported DOC values are the average of two analyses with ±0.7 mg $L^{-1}$ reproducibility.

Samples for total carboxylic acid concentration measurement, mass spectral characterization, and toxicity testing were acidified to pH ~ 2, extracted with dichloromethane (DCM), and dried under a stream of nitrogen gas (Holowenko et al., 2002). These steps isolated the acid-extractable organics (AEOs), including NAs, from residual oxidant which would otherwise interfere in these assays. Semi-quantitative FTIR analysis was used to measure total carboxylic acid concentrations, including NAs, as per Jivraj et al. (1995) and Holowenko et al. (2001). The method was described by Sohrabi et al. (2013).

High performance liquid chromatography orbitrap mass spectrometry (HPLC-Orbitrap-MS) analysis was also applied to characterize select control and oxidized samples. HPLC separation was performed using an ARIA MX transcend system (Thermo Fisher Scientific, San Jose, CA, USA) on a Hypersil Gold column (50 x 2.1 mm, 1.9 µm particle size; Thermo Fisher Scientific, San Jose, CA, USA) at 40 °C. Flow rate was 0.5 mL min-1 and an injection volume of 5µL was used. The mobile phases consisted of (A) 0.1% acetic acid in water and (B) 100 % methanol. The mobile phase composition was 5% B for 1 min, followed by a linear gradient ramp to 90% B at 10 min, to 99% over 5 min, and returning to 5% B in 1 min, followed by a 4 min hold prior to the next injection. The Orbitrap Elite mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) was operated with an ESI source at 350°C in negative mode and the spray voltage set to 5 KV. The sheath, aux, and sweep gas flow at 30, 10 and 5 (arbitrary units), respectively, capillary temperature at 300 °C, and S-Lens RF level at 65%. The resolving power was set to a nominal resolving power of 240,000 at full width half-maximum at m $z^{-1}$ = 400, and using a full maximum ion time of 200 ms. Mass calibration and tuning was done

externally by direct infusion of a standard mixture of caffeine, the peptide MRFA (sequence, Met-Arg-Phe-Ala), and Ultramark 1600 in $H_2O$ acetonitrile$^{-1}$ 50:50 (v v$^{-1}$), covering a range from m z$^{-1}$ = 138 to 1722. Mass spectral data were collected at 2 full scans per second between 100-1000 m z$^{-1}$ using automatic gain control. Data acquisition and analysis was performed with Thermo Xcalibur 2.0 software.

### 3.2.5. Toxicity bioassay

Toxicity testing consisted of static-renewal embryo-larval fathead minnow bioassays in accordance with Environment Canada toxicity testing protocols (EPS 1/RM/22). Fathead minnow (*Pimephales promelas*) embryo were obtained from Aquatox Testing & Consulting (ON, Canada). Stock test solutions were prepared using AEO extracted from each chemical treatment, and then re-dissolved in 0.05 M NaOH to 100 mg L$^{-1}$. Stock solutions were then diluted to appropriate concentrations using control water which consisted of 50% Milli-Q water and 50% University of Waterloo well water. All exposures were repeated in triplicate and included at least 8 test solutions (100 mg total carboxylic acid L$^{-1}$ maximum), a water control, vehicle control (0.05 M NaOH), and positive control (ACROS commercial acid, Sigma-Aldrich®, Oakville, ON). Ten embryos were selected for each solution and placed in a 100-mL beaker (VWR, Mississauga, ON) with at least 1 mL of solution per embryo. All test solutions were renewed daily and maintained at pH 8±0.2 and 25±1 ˚C with a 16:8 h light:dark photoperiod in a Conviron® model E7H plant growth chamber (Conviron®, Winnipeg, MB). Mortality and hatch length endpoints were measured twice daily. Hatch length was measured to 0.5 mm for live, non-deformed larvae at hatch using a dissecting microscope.

Mortalities for each treatment were represented by a 7 d $LC_{50}$, calculated using a Spearman-Karber statistical analysis in Excel. Threshold concentrations for hatch length were calculated as the geometric mean of the no-observed effect concentration (NOEC) and lowest-observed effect concentration (LOEC) as compared against water controls. The NOEC and LOEC were determined using non-parametric statistical analysis (Kruskal-Wallis and Mann-Whitney U tests) and performed using SPSS® (v 21).

### 3.3. Results and discussion

#### 3.3.1. Total carboxylic acid concentration

Oxidation of OSPGW and OSPW, using either persulfate or permanganate was investigated in parallel treatments. Nominal starting concentrations for permanganate and persulfate were 5 and 10 g $L^{-1}$, respectively, and these showed only 20% and 10% decreases, respectively, by the end of 120 d. Concentrations of total carboxylic acids over 120 d are shown in Fig. 3.1 for all treatments. Total carboxylic acid concentrations in un-oxidized controls of OSPGW and OSPW decreased only minimally (12%, 8%, respectively), whereas much greater declines were observed with both oxidants in both OSPGW and OSPW. Permanganate degraded ~50 % of the total carboxylic acids in the first 2 d, for both OSPGW and OSPW, followed by slower reactivity with ~25% more degradation by day 21, and finally minimal reactivity for the rest of the experiment. In comparison, persulfate did not show a strong effect on total carboxylic acids in the first 2 d, but subsequent carboxylic acid degradation accelerated until day 45, by which time 85% were degraded, followed by minimal further degradation up to 120 d. From a practical point of view, this suggests that with sufficient mixing of injected oxidant and

OSPGW in situ, a significant fraction of the OSPGW AEOs can be degraded in the presence of these oxidants at 22 ˚C.

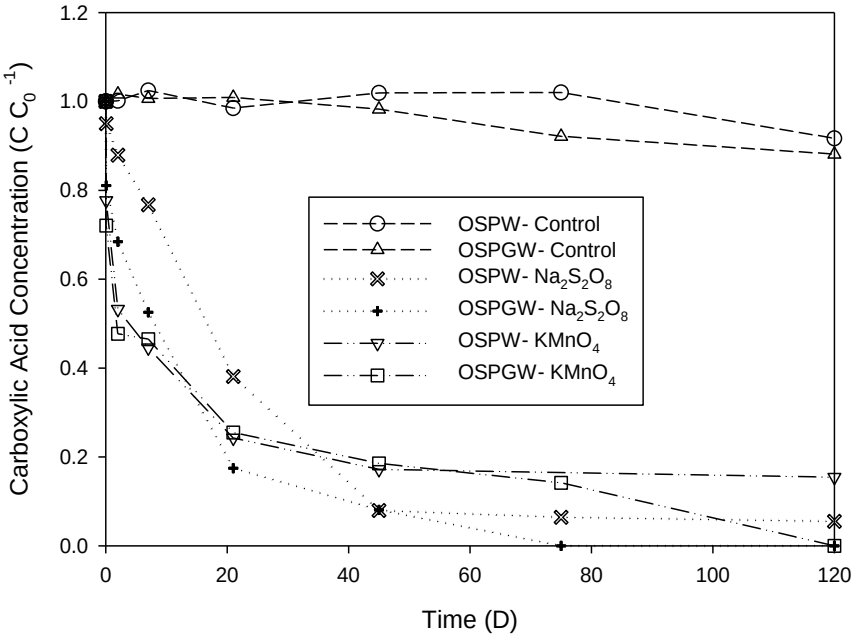


Fig. 3.1. The total carboxylic acid concentration changes over 120 d oxidation of OSPGW and OSPW samples by persulfate and permanganate at 22 ˚C. All concentrations are shown relative to initial un-oxidized control concentrations ($C_0$, 46.9±0.3 and 60.1±1.3 mg $L^{-1}$, respectively). Error bars derived from triplicate analyses are generally within the symbol.

As will be discussed in Section 3.3.3, analysis by HPLC-Orbitrap-MS revealed that the higher Z number NA homologues (i.e. those with more rings or double bonds) were most susceptible to rapid permanganate oxidation. Interestingly, these are also the most resistant to biodegradation (Han et al., 2009), thus their rapid degradation here is a promising result for future remediation. Saturated cyclic or acyclic acids should not be susceptible to permanganate oxidation, whereas carbon-carbon double bonds are (Siegrist, 2011), thus it is likely that these acids contain many double bonds or aromatic rings.

### 3.3.2. DOC concentration

The changes in DOC (Fig. 3.2) provide interesting insight into the oxidation of AEOs. The DOC analysis measures the total organic carbon content, including carbon in dissolved total carboxylic acids and other organic compounds. Consistent with carboxylic acid concentration measurements, un-oxidized controls of OSPGW and OSPW samples showed minimal decrease in DOC concentration over 120 d.

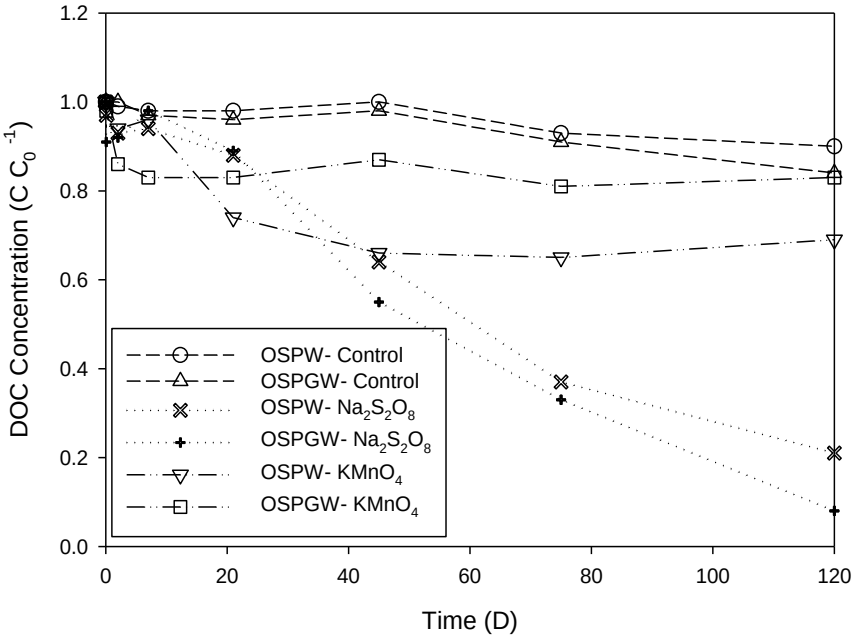


Fig. 3.2. DOC concentrations ($C_t$) relative to initial un-oxidized control concentrations ($C_0$). The initial DOC concentrations for un-oxidized OSPGW and OSPW samples were 49.4±0.7 and 64.3±0.4 mg $L^{-1}$, respectively. Error bars derived from triplicate analyses are generally within the symbol.

By day 120, persulfate removed more than 80% of the DOC in both OSPGW and OSPW, whereas permanganate removed only ~20 to 30% of the DOC. While both oxidants removed > 80% of the total carboxylic acids (including NAs), the persistence of DOC during permanganate oxidation suggests that carboxylic acid oxidation by permanganate occurred mainly by structural transformation (e.g. degradation to smaller

acids, or more oxidized species), not mineralization. During persulfate oxidation, an initial lag period in DOC reduction (e.g. up to 20 d), compared to carboxylic acid degradation (Fig. 3.1), suggests some structural transformation of dissolved organics, but mineralization processes dominated in the subsequent period up to 120 d.

### 3.3.3. Detailed Characterization by HPLC-Orbitrap-MS

Distribution plots of NAs (i.e. carboxylic acids containing only two oxygen atoms), characterized by HPLC-Orbitrap-MS (Pereira et al., 2013) are shown in Fig. 3.3. These plots show a qualitative profile of the NA mixture in each sample based on the relative response of various species by carbon number (x-axis) and Z number (different colored bars). The height of the bars represents the abundance of each homologue in the NA mixture, relative to a common internal standard. In comparison with OSPW, the OSPGW has a greater abundance of lower Z NAs (e.g. Z= -2, -4, -6), and a lower abundance of higher Z acids. After only 2 d, however, both permanganate treated samples (Panel b1 and e1) appeared similar, as did both persulfate treated samples (Panel c1 and f1), and all samples showed marked changes to the NA profiles in this short time. By 21 d, the permanganate treated samples showed only traces of residual NAs. Similarly, by 21 d the persulfate treated samples showed continued degradation of NAs, and changes to the NA profile were evident.

To better illustrate the changes in the NA mixture occurring during oxidation, the ratio of each congener to the initial unoxidized abundance was calculated and organized based on C and Z numbers (Fig. 3.4). Oxidation of OSPW by permanganate altered the NA distribution pattern, generally decreasing (shown as green) the higher Z number acids and increasing (shown as red) the amount of aliphatic (Z = 0) and single ring (Z = -2)

NAs (Fig. 3.4.A1, A2). For example, after 2 d of oxidation of OSPW by permanganate, NAs with 7 and 8 carbons and no rings or double bonds (Z = 0), showed 31 and 15 fold increases, respectively. Similarly, NAs with 7 carbons and one double bond or ring (Z = -2) increased 37 times, suggesting that these are being formed as oxidation by-products. Further oxidation of OSPW by permanganate (21 d) decreased the relative abundances of most NAs, even aliphatic (Z = 0) and single ring (Z = -2) acids, but some compounds, mostly Z = 0 (e.g. 9-13 carbons) still increased enormously (Fig. 3.4.A2). This suggests that higher Z number NAs were cleaved by permanganate treatment and aliphatic and single ring acids were generated. These smaller acids were then possibly cleaved to produce still-smaller acids that could not be monitored by this mass spectrometry method, but which would nevertheless be measured as DOC (Fig. 3.2). Permanganate oxidation of OSPGW degraded essentially all NA congeners (Fig. 3.4.B1, B2) with somewhat less generation of Z = 0 and -2 acids. Again, similar to OSPW the permanganate oxidation of OSPGW reduced total acid concentrations as measured by FTIR (Fig. 3.1); still a few aliphatic and single ring NAs (Z = 0, -2) were generated as by-products.

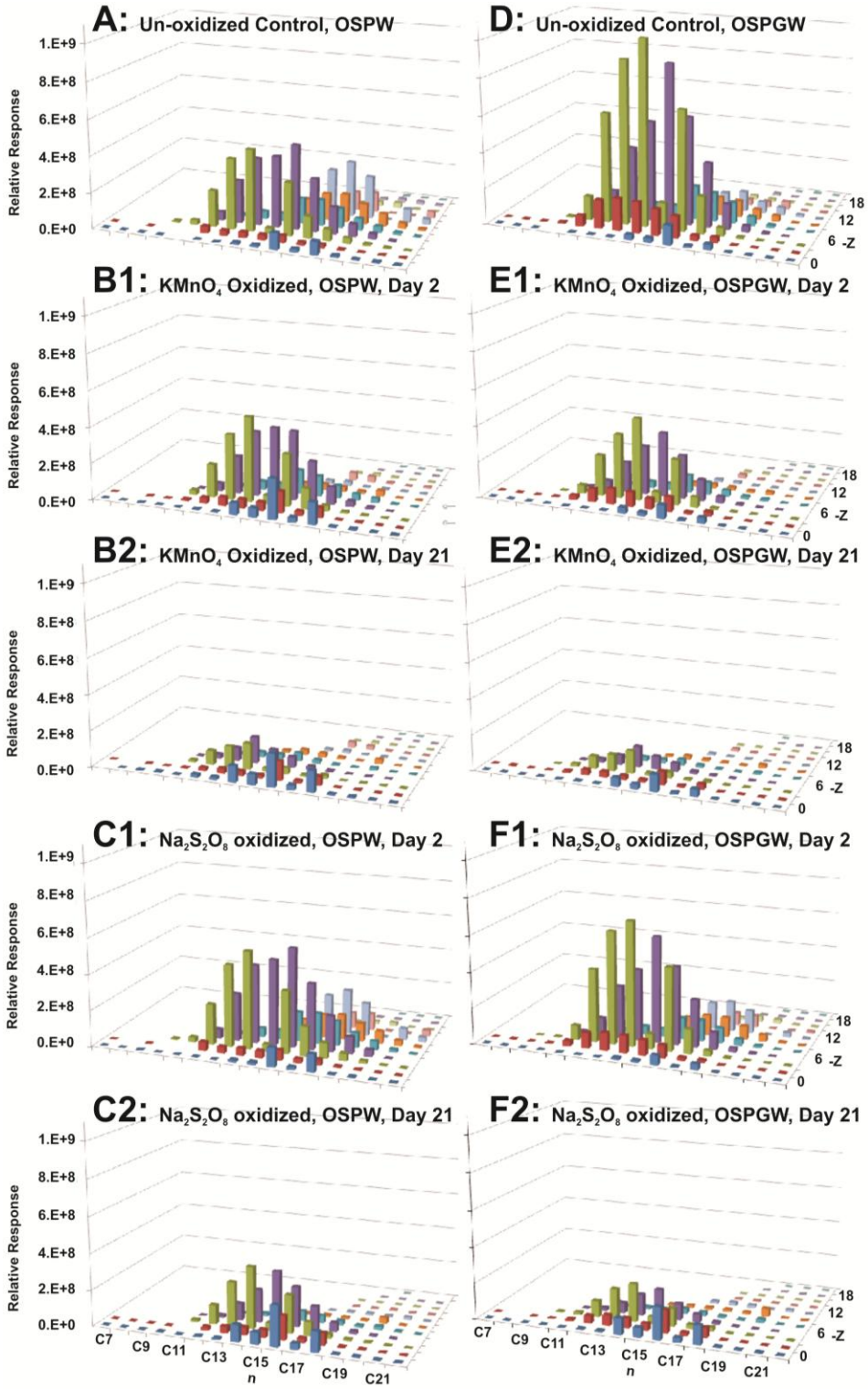


Fig. 3.3. Three dimensional plots of classical carboxylic acids with two oxygen atoms (NAs) in OSPGW and OSPW samples oxidized with permanganate and persulfate at 22 ˚C.

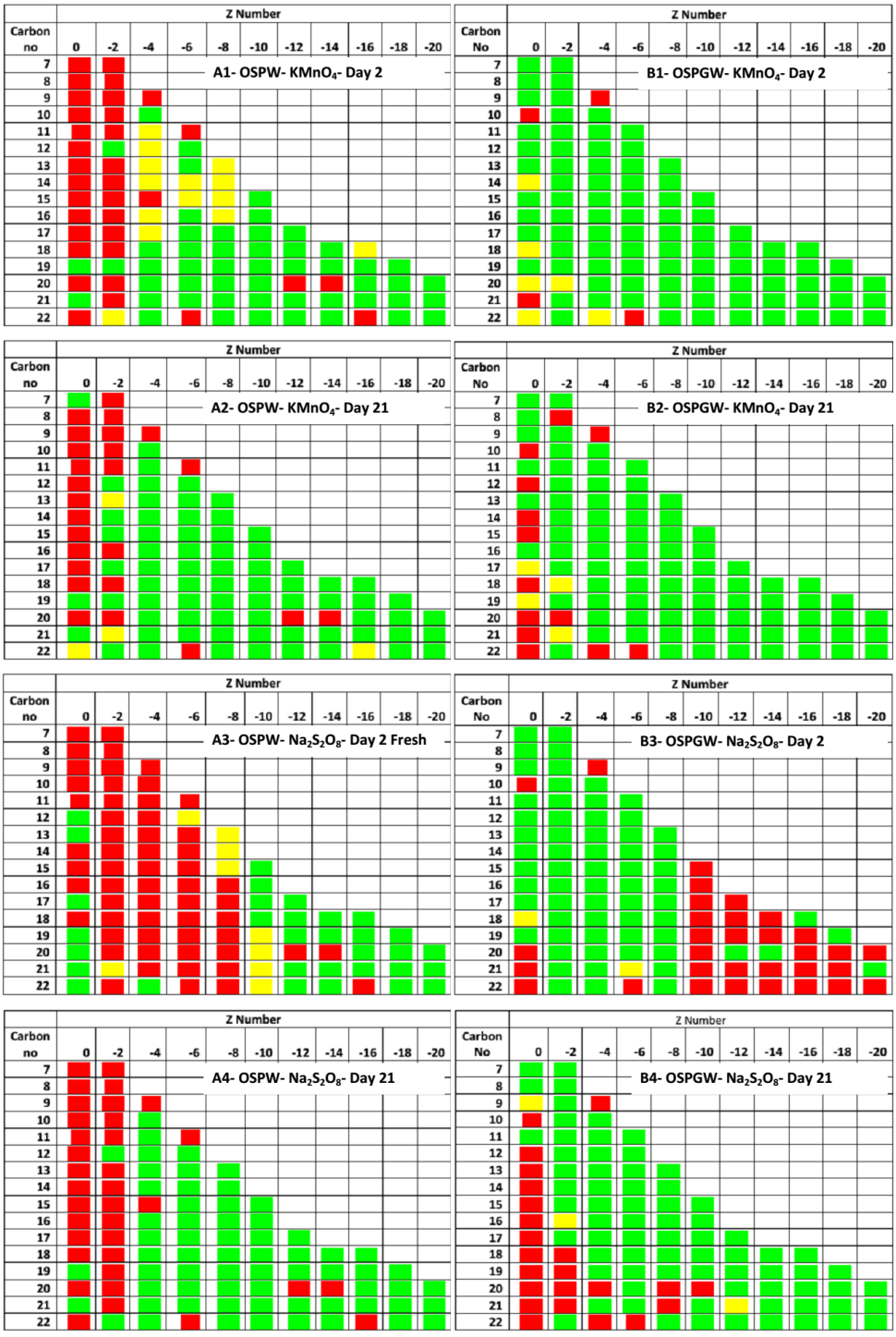


Fig. 3.4. Changes in relative abundances of congeners ($C_t$ / $C_0$) in NA mixture due to oxidation. Series A and B are related to OSPW and OSPGW, respectively. The colors green, yellow, and red are referred to as decrease, no change, and increase in abundance of each congener relative to its abundance in un-oxidized control, respectively.

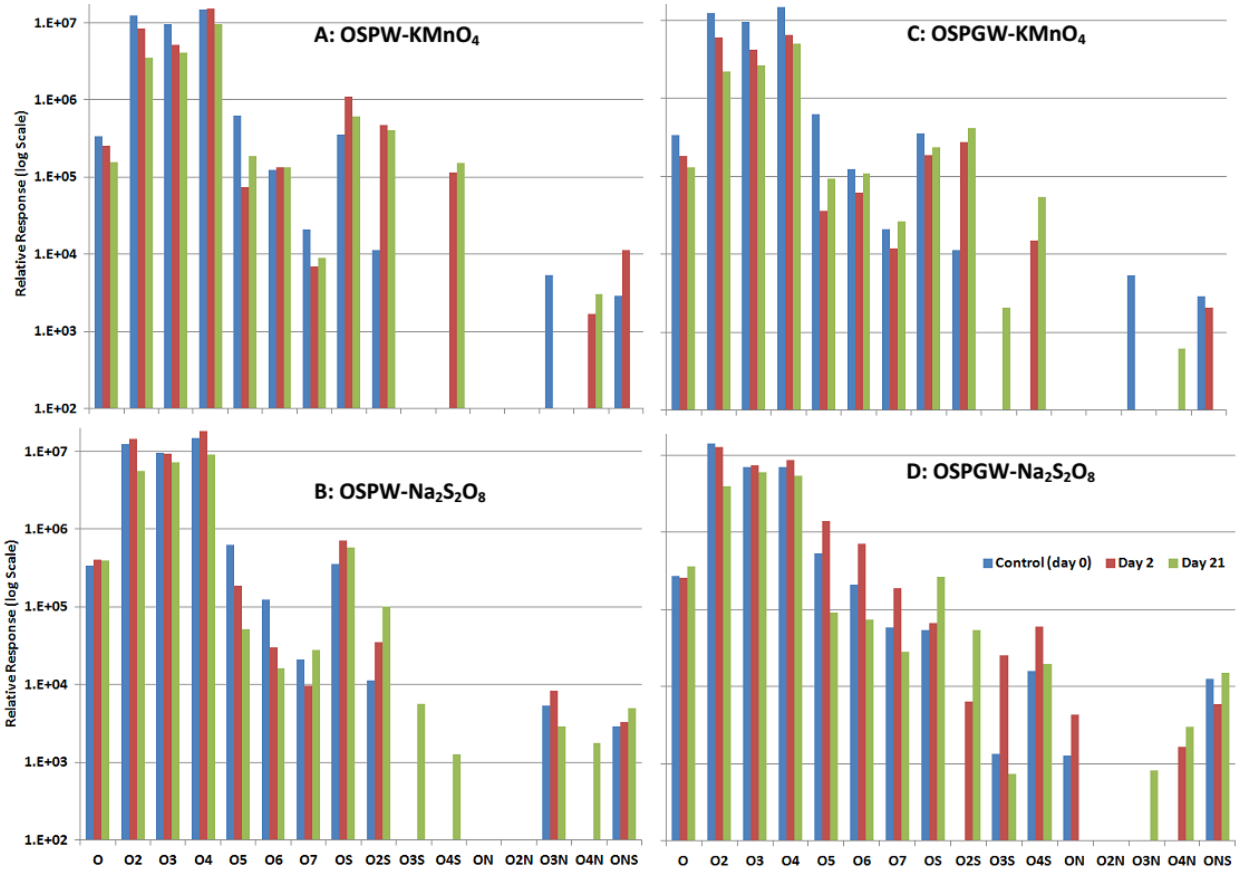


Fig. 3.5. Changes in total abundance of DOC components over the first 21 days, as classified by heteroatom groups of various oxygen (O), sulfur (S), and nitrogen (N) containing species in OSPW and OSPGW following persulfate treatment (B, D) or permanganate treatment (A, C) as characterized by negative ion HPLC-Orbitrap-MS. For example, the $O_2$ group represents total abundance of NAs.

As with permanganate oxidation, 2 d of oxidation of OSPW by persulfate resulted in only slight decreases in higher Z number classes (e.g. Z = -16, -18, and -20), and increases in relative abundances of a few NAs with lower Z (Fig. 3.3.C1). Further oxidation by persulfate (day 21) removed higher Z number classes but dramatically increased the relative abundances of some smaller acids (e.g. $C_7$-$C_{16}$ in Z = 0, and $C_7$-$C_{11}$ in Z = -2). For instance, NAs with 7 carbons and Z = 0 or Z = -2 showed approximately 33 and 7 fold increases in their relative abundances by day 21,

respectively. In contrast, 2 d of oxidation of OSPGW by persulfate resulted in small decreases in the relative abundances of smaller NAs, and increases for larger NAs with high Z numbers (Fig. 3.4.B3). The former may be formed as oxidation by-products from other reactive heteroatomic class species detected by negative ion HPLC-Orbitrap-MS (e.g. $O_3$, $O_4$, OS) (Fig. 3.5), and or other neutral molecules that were not monitored in the current work (e.g. positive ion mass spectrometry of OSPW reveals many neutral species) (Pereira et al., 2013). However, further oxidation (21 d) degraded most NAs in the mixture (Fig. 3.4.B4). Relative abundances of mid to high carbon number NAs (Z = 0 homologues) showed dramatic increase which may be due to degradation of larger NAs, or of other OSPW heteroatomic species. For instance, Z = 0 NAs with 19 and 21 carbon atoms increased in relative abundance approximately 21- and 27-fold by day 21, respectively, compared to day 2.

As discussed, species other than NAs were also monitored in this work by negative ion HPLC-Orbitrap-MS (Fig. 3.5). The chemical identity of these species is unknown, only their elemental composition is reported here, but their detection in this mode of analysis suggests they contain an acidic proton and are therefore all organic acids (carboxylic, sulfonic, phenolic, amines or amides, for example). For example, the $O_2$ species shown in Fig. 3.5 represents the total response of NAs (which by definition have 2 oxygen atoms). Over 21 d, total NAs were more greatly diminished in the permanganate treatment, relative to persulfate treatment, consistent with detailed profiles for NAs shown in Fig. 3.3. Like the NAs, most other classes of compounds were simultaneously degraded, but were sometimes transiently increased (as by-products) on day 2. A few exceptions were some classes of compounds that were increased at day 21, relative to

day 0 or 2, specifically the $SO_x$ classes. Unfortunately we did not monitor these compounds at later time points.

Mechanisms for oxidation of organic acids have previously been discussed. A fraction of organic acids in OSPW are unsaturated or aromatic (Ross et al., 2012; Rowland et al., 2012; Frank et al., 2014), and permanganate is reactive with carbon-carbon double bonds based on the availability of reactive $\pi$ electrons (Clar, 1972; Hosoya, 1990). Permanganate reaction at double bonds may result in decomposition of the organic molecule or addition of hydroxy or carbonyl functional groups (Ladbury and Cullis, 1958; Fatiadi, 1987; Singh and Lee, 2001). The higher the Z number, the higher the likelihood that double bonds are present in the NA structure. Reaction of permanganate with carbon-carbon double bonds in high Z number NAs might be the case (Fig. 3.4 A1, -A2, -B1, and -B2). Although reactivity of saturated aliphatic compounds with C-C single bonds with permanganate is limited due to the lack of $\pi$ electrons, the presence of functional groups such as hydroxyl may enhance reactivity with permanganate (Arndt, 1981). Partial oxidation of branched aliphatic carboxylic acids by permanganate at tertiary C-H has also been suggested (Wiberg and Fox, 1963) which could be a possible reaction scenario. Permanganate reaction with saturated carboxylic acids via alpha hydrogen removal is also possible. The presence of an alkyl substitution on a benzene ring increases the reactivity with permanganate, as demonstrated in a previous study in which toluene and xylene were reactive with permanganate, while benzene was not (Waldemer and Tratnyek, 2006). Similarly, AEOs may be altered due to the presence of alkyl substitutions on their rings. The FTIR analysis (carboxylic acid concentrations) suggests removal of C=O (a form of decarboxylation) from carboxylic acid structures

during oxidation by permanganate because of the reduction in absorbance at 1743 and 1706 $cm^{-1}$ (Fig. 3.1). OSPW contains an organic fraction with sulfur and nitrogen in their molecule structures (Grewer et al., 2010; Pereira et al., 2013). Degradation of compounds with electron attracting substituent such as nitrogen and sulfur is likely by permanganate (Gould 1959). In support of this possibility, plots shown in Fig. 3.4 reveal changes in abundances of sulfur bearing species during oxidation by permanganate.

Persulfate reaction with organic acids is more complex than permanganate as a number of activated species may be involved (Ocampo, 2009; Tsitonaki et al., 2010; Drzewicz et al., 2012). Similar to permanganate, a decrease in C=O peaks, measured by FTIR, could be have resulted from decarboxylation of carboxylic acids by persulfate. Decarboxylation seems viable only when the sulfate radical is present in the solution (Tanner and Osman, 1987; Drzewicz et al., 2012). With a mildly basic pH (~ 8.2), no transition metal ions were likely available in OSPW to activate persulfate but some organic compounds, such as phenols (Ahmad et al., 2013) and some carboxylic acids (Ocampo, 2009) present in OSPW may activate persulfate. A brief colorimetric test using ferric chloride (NPCS-board-of-consultants-&-engineers, 2007) revealed the presence of phenolic compounds in OSPW and OSPGW and so autocatalytic activation of persulfate may have occurred.

### 3.3.4. Toxicity bioassay

Previous studies have indicated that AEOs, specifically carboxylic acids, were the main (but not only) source of toxicity of OSPW (Dokholyan and Magomedov, 1983; MacKinnon and Boerger, 1986; Verbeek et al., 1993). However, a decrease in carboxylic acid concentration does not necessarily result in decreased toxicity, as

previous studies suggest that carboxylic acids with diverse molecular weights have different levels of toxicity (Holowenko et al., 2002; Frank et al., 2008). In order to evaluate the impact of oxidation on the toxicity of the AEO mixtures, extracted un-oxidized AEOs from OSPGW and OSPW, as well as extracted oxidized samples from days 2 and 21 were selected for toxicity testing. The embryo-larval bioassay using *Pimephales promelas* (fathead minnows) was selected because it has been used with OSPW as it is sensitive to carboxylic acids (Peters et al., 2007; Kavanagh et al., 2011; He et al., 2012). Additionally, unlike previous toxicity analyses using marine bacteria (Microtox®) exposed to OSPW, fathead minnow are indigenous to the oil sands region of Alberta, and therefore represent an ecologically relevant species. $LC_{50}$ values were compared to evaluate the relative toxicity reduction of each oxidation treatment (Fig. 3.6) and combined with mass spectral characterization provided valuable insight into the relative toxicity of different carboxylic acid fractions. Unless specified elsewise, “toxicity” in Chapters 3 to 5 refers to embryo-larval bioassay using *Pimephales promelas* (fathead minnows).

The toxicity testing identified that the AEOs in both OSPGW and OSPW were toxic (Table 3.2). That is, the AEOs in un-oxidized samples were present at concentrations sufficient to cause significant embryo-larval mortality. The OSPGW had an initial carboxylic acids concentration of 47 mg $L^{-1}$, but had an $LC_{50}$ of only about 18 mg $L^{-1}$. The OSPW had a carboxylic acid concentration of about 60 mg $L^{-1}$ while the $LC_{50}$ was only 28 mg $L^{-1}$.

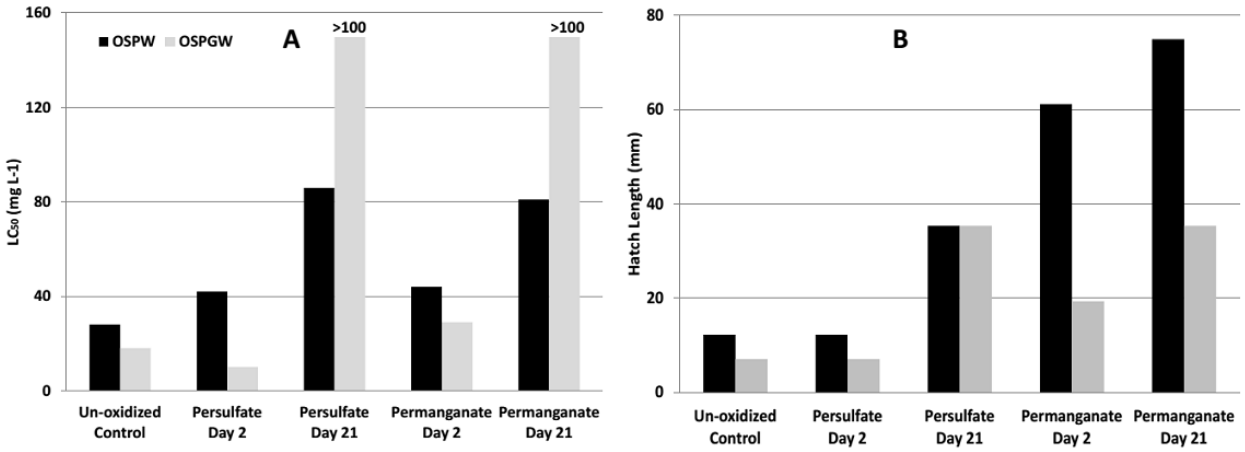


Fig. 3.6. A: $LC_{50}$'s of un-oxidized controls and permanganate and persulfate oxidized AEOs for days 2 and 21, B: Hatch length threshold effects concentrations of the un-oxidized control and days 2 and 21 of permanganate and persulfate oxidized AEOs from OSPGW and OSPW oxidation experiments at 22 ˚C.

For OSPGW, persulfate decreased total carboxylic acid concentration by 34% from 47 to 31 mg $L^{-1}$ in 2 d but toxicity increased, with a 44% reduction in $LC_{50}$ from 18 mg $L^{-1}$ to 10 mg $L^{-1}$. In this period, decreases in abundances of smaller NAs in Z = 0 and -2 and increases in some of the high C and Z number NAs occurred (Fig. 3.4.B3). Further oxidation by day 21 detoxified OSPGW, based on an $LC_{50}$ over 100 mg $L^{-1}$. This was accompanied by increases in high C number NAs, in Z = 0 & -2 homologues and removal of high Z number NAs (Fig. 3.4.B4). The high $LC_{50}$ value for day 21 suggests that the remaining acids in the mixtures are far less toxic than acids present in the un-oxidized extract. The results of both the 2 and 21 d tests are consistent with the high Z number, but not necessarily with high C number, NA fractions being the major source of toxicity in the AEOs of OSPGW.

Oxidation of OSPW using persulfate resulted in reduced toxicity (increased $LC_{50}$ values, Table 3.2), commensurate with decreased total carboxylic acid concentrations (by FTIR)

and altered NA signatures. After 2 d of persulfate oxidation, the concentration of carboxylic acids in OSPW decreased minimally to 53 mg $L^{-1}$ and the toxicity of the residual acids was reduced with an $LC_{50}$ of 42 mg $L^{-1}$. It appears that although persulfate rapidly degraded only a small proportion of carboxylic acids, they might include the most toxic fraction present in OSPW sample. Reviewing Fig. 3.4.A3 and -A4 indicates increases in lower C and Z number NAs (in red), while higher Z number acids decreased (in green). Although carboxylic acid concentration analysis by FTIR did not change much, high Z acids decreased, while small Z number and smaller acid molecules NAs increased (Fig. 3.4.A3). This illustrates that the level of toxicity does not simply reflect the concentration of total carboxylic acids.

Table 3.2. Carboxylic acid concentration versus $LC_{50}$ of OSPW and OSPGW for un-oxidized control, and days 2 and 21 persulfate and permanganate oxidized samples. **Bold** values indicate cases where the $LC_{50}$ is below the measured total carboxylic acid concentration after oxidation.

| | **OSPW** | | **OSPGW** | |
|---|---|---|---|---|
| **Water Sample** | **NA Conc. (mg $L^{-1}$)** | **$LC_{50}$ (mg $L^{-1}$)** | **NA Conc. (mg $L^{-1}$)** | **$LC_{50}$ (mg $L^{-1}$)** |
| Un-Oxidized Control | 60 | 28 | 47 | 18.3 |
| Permanganate Day 2 | 32 | **44** | 22 | **29** |
| Persulfate Day 2 | 53 | 42 | 31 | 19 |
| **Permanganate Day 21** | 15 | **81** | 12 | **>100** |
| **Persulfate Day 21** | 23 | **86** | 8 | **>100** |

Further oxidation by persulfate reduced the toxicity of the remaining acids to an $LC_{50}$ value of > 80 mg $L^{-1}$. Because the carboxylic acid concentration is only ~22 mg $L^{-1}$ (Fig. 3.1), persulfate effectively rendered the acids in OSPW significantly less toxic than un-

oxidized controls after 21 d. Oxidation resulted in more fragmentation of acids with mid and high Z numbers (in green) with by-products accumulating in Z = 0 and -2 (in red) (Fig. 3.4.A4). These changes in the distribution of AEOs are likely associated with the reduced toxicity.

Oxidation of OSPGW by permanganate for 2 d decreased carboxylic acid concentration to 22 mg $L^{-1}$ and reduced the toxicity of the sample ($LC_{50}$ = 29 mg $L^{-1}$). Permanganate reduced the abundances of most congeners including small C number acids as well as high Z number acids (Fig. 3.4.B1). Further oxidation by day 21, resulted in $LC_{50}$ > 100 mg $L^{-1}$ and a decrease in abundance of most acids, including high Z number acids (Fig. 3.4.B2).

After only 2 d of oxidation of OSPW by permanganate, total carboxylic acid concentrations decreased to 32 mg $L^{-1}$, now with an $LC_{50}$ of 44 mg $L^{-1}$. That is, the NA mixture was rendered significantly less toxic. The high Z number acids dramatically decreased and low C number acids in the Z = 0 and -2 fractions increased (Fig. 3.4.A1). Twenty one d of oxidation decreased the carboxylic acid concentration to 15 mg $L^{-1}$ and increased the $LC_{50}$ to > 80 mg $L^{-1}$. By day 21, the smaller and mid Z number acids had also decreased. Simultaneously, the relative abundances of a few aliphatic acids (Z = 0) increased, perhaps being breakdown products of higher Z acids (Fig. 3.4.A2). Reviewing the carboxylic acid signatures of permanganate oxidized samples of days 2 and 21 and comparing them to toxicity results again suggests that high Z number acids may have a greater contribution to toxicity than lower Z number acids, and that smaller molecular weight acids are not as toxic as was previously thought using Microtox® assays (Holowenko et al., 2002). It has been noted in previous studies that an increase

in the molecular size of chemicals displays a positive correlation with increasing toxicity to fathead minnow (Protić and Sabljić, 1989) and that higher molecular weight and Z number OSPW naphthenic acids display a higher toxicity to zebrafish (Scarlett et al., 2013). These studies, in addition to the results presented herein, indicate that oil sands acids may exert different toxic mechanisms when comparing bacteria and fish.

The results of analysis of the hatch length endpoint (Fig. 3.6) indicate a trend common with mortality. Although the degree to which the reduction in acids affected hatch length varied, when compared to mortality, the overall trends were very similar. In both oxidant treatments OSPGW displayed a lower threshold effect concentration (greater reduction in hatch length at equivalent concentrations), and both OSPW and OSPGW displayed a reduction in toxic effect after 21 d. The threshold effect concentration for hatch length for unoxidized OSPW and OSPGW presented herein (12.3 mg $L^{-1}$ and 7.1 mg $L^{-1}$, respectively) is similar to those previously published for Japanese medaka (6.18 mg $L^{-1}$) exposed to Syncrude OSPW (Peters et al., 2007). Permanganate more effectively reduced the sub-lethal effects of OSPW than persulfate. The threshold effects concentrations for OSPGW from both oxidant treatments was very similar with both reducing toxicity to the same degree after 21 d. Because the reduction in toxicity to sublethal effects of oxidant treated OSPW mimic lethal effects, we propose that processes that govern mortality-associated toxicity also regulate hatch length. In general, it appears that higher Z-number acids have a greater propensity to reduce fathead minnow larval length at hatch.

### 3.4. Summary

Both permanganate and persulfate effectively oxidized most carboxylic acids present in OSPGW at 22 ˚C and rendered the OSPGW non-toxic, as judged by embryo-larval fathead minnow bioassays. Detoxification of OSPGW by permanganate mostly occurred by molecule structural transformations while persulfate oxidation mineralized most AEOs including carboxylic acids. Permanganate does oxidize C=C bonds readily (Siegrist, 2011) and the higher Z number carboxylic acids are more likely to have C=C double bonding (Ross et al., 2012; Frank et al., 2014). It appears that permanganate reaction with AEOs will be effective in remediating OSPGW, both in terms of reducing concentration and reducing or eliminating acute toxicity as measured here. Indirect evidence in the present study suggests that high Z number acids have the greatest toxicity in the OSPW and OSPGW carboxylic acid mixtures. Thus, because permanganate degrades higher Z number acids it quickly reduces toxicity without regard to the source of OSPW. Detoxification of OSPGW and OSPW, by persulfate, occurred when high Z number acids were removed; otherwise, no decrease in toxicity was observed (Fig. 3.4.B3). This finding provides more precise insight into toxicity of acid homologues. While Holowenko et al. (2002) suggested that smaller acid fraction including C ≤ 21 acids had higher level of toxicity to Microtox®, it was determined that C ≥ 22 were hydroxylated acids (Bataineh et al., 2006; Martin et al., 2008). Given the limitations of the GC/MS analysis (Martin et al., 2006) which was applied by Holowenko et al., ongoing research on toxicity of carboxylic acids should use sophisticated analytical techniques such as ultra-high resolution mass spectroscopy (Ross et al., 2012; Pereira et al., 2013; Frank et al., 2014) for more precise characterization of

carboxylic acids mixture. This study also indicates the importance of additional toxicological testing on various organisms as there may be differences in species sensitivity associated with AEO structural components.

This study indicates that in pond and in situ (groundwater) remediation targeting toxic AEOs, such as with ISCO, must be assessed not only by the reduction in carboxylic acid, NA, concentration, but also by some criterion for toxicity reduction. In a toxicity reduction remediation scenario, a sophisticated characterization method such as HPLC-Orbitrap−MS should be used periodically to confirm that the more toxic fractions of AEO are being removed, especially if mineralization is incomplete and DOC remains.

# Chapter 4:

# Potential for in situ chemical oxidation of the toxic fraction of oil sands process affected groundwater at the local aquifer temperature of 5 ˚C

## 4.1. Introduction

The processing of mined oil sands in NE Alberta, Canada has resulted in the generation of more than 1 x $10^9$ $m^3$ of oil sands process water (OSPW) which is retained in tailings ponds. While this OSPW is recycled in the extraction process, slow settlement of fine particles and the somewhat toxic nature of this process-affected (PA) water has resulted in the retention of increasing volume of OSPW. While increasing salinity of the pond water poses a long-term challenge (Allen, 2008), dissolved organic compounds have been recognized as the major toxicants to aquatic biota (MacKinnon and Retallack, 1981; Schramm et al., 2000).

Initially, the main contributors to acute aquatic toxicity of OSPW were considered to be saturated aliphatic and cyclic polar acids with two oxygen atoms, termed naphthenic acids (NAs) (Brient et al., 1995) with a general formula of $C_nH_{2n+z}O_2$ in which n represents number of carbon and z is a negative even integer that was first related to number of rings present in the acid structure (Brient et al., 1995). Further advances in ultra-high resolution mass spectroscopy of the acid extractable organic fraction (AEOs) identified compounds with more than two oxygen atoms ($O_x$), sulfur ($SO_x$, $S_2O_x$), and nitrogen ($NO_x$) (Grewer et al., 2010; Ross et al., 2012; Pereira et al., 2013). Aromatic

and un-saturated organics are also present in the AEO mixture (Ross et al., 2012). So, the Z integer is now considered equivalent to a combination of the number of rings and the carbon-carbon double bonds in the acid structure (Ross et al., 2012; Pereira et al., 2013). For example, an acid with Z = -4 has lost four hydrogen atoms due to the following possibilities: formation of two rings or one ring and one double bond, or only two double bonds in an acid with linear structure. Initially, NAs with C ≤ 21, which were considered lower molecular weight acids, were recognized as the group with higher toxicity (Holowenko et al., 2002) but later studies (Bataineh et al., 2006; Martin et al., 2008) found that acids formerly identified as NAs with C ≥ 22 were hydroxylated NAs (Bataineh et al., 2006). So now comparative toxicity of compounds with C ≤ 21 is targeted. Scarlett et al. (2013) examined the toxicity of fractionated acids and suggested that higher molecular weight aromatic compounds were somewhat more toxic than lower molecular weight NAs. Further, Sohrabi et al. (2014) suggested that high Z number NAs which likely include un-saturated, aromatic, and a fraction of the higher molecular weight acids (higher C) may be more toxicity than the low C, low Z NAs.

Since it appears that different fractions of AEOs present in OSPW have different levels of acute aquatic toxicity it seems unlikely that a direct relationship of toxicity to total carboxylic acid concentration or AEOs is an adequate indication or estimate for toxicity of OSPW.

While retention in settling ponds decreases the acute toxicity of OSPW (MacKinnon and Boerger, 1986), additional detoxification of the AEOs may be required for release to the environment. Progress has been made with treatment of tailings pond waters with biodegradation (Han et al., 2009), chemical oxidation (Scott et al., 2008; Drzewicz et al.,

2012), and adsorption (Janfada et al., 2006; Gamal El-Din et al., 2011). While treatment for pond water and water coming directly from the Clark hot-water extraction process can deal with the OSPW accumulating in tailings ponds, large volume of the OSPW exists within the pore spaces of the mature tailings and in the retaining sand dykes. OSPW can also infiltrate into associated sandy aquifers (Oiffer et al., 2009) and migrate towards surface water bodies (Ferguson et al., 2009; Frank et al., 2014). Control, for example with cut-off walls and traditional pump and treat systems (Vincent-Lambert et al., 2011), and, in some cases, active remediation of this PA groundwater, termed OSPGW, may become necessary. One attractive remediation approach is in situ chemical oxidation focused on the toxic AEOs in PA groundwater (Sohrabi et al., 2013). AEOs recalcitrance and the low local aquifer temperatures of 5 ˚C inhibit potential microbial bioremediation. While chemical oxidation by ozone and Fenton's reagents is effective in removing the toxicity of OSPW (Gamal El-Din et al., 2011; Afzal et al., 2012), these oxidants are not sufficiently persistent for remediation of AEOs dissolved in groundwater. Injection of water containing oxidant simply displaces impacted groundwater and the mixing required for oxidation only occurs via slow, weak dispersion (Payne et al., 2008). More persistent (week to months) oxidants, such as permanganate and persulfate, operating at ambient (5 ˚C) groundwater temperatures are therefore our focus for ISCO of groundwater AEOs in this chapter (Sohrabi et al., 2013 & 2014). Oxidation of OSPW, which was just discharged into a tailings pond, showed that both permanganate and un-activated persulfate successfully degraded AEOs and mitigated their toxicity at 22 ˚C. Similarly, degradation and detoxification of AEOs in potentially more recalcitrant OSPGW from a monitoring well in an abandoned tailings pond area

was also achieved at 22 ˚C (Sohrabi et al. 2014). While detoxification of OSPGW at 22 ˚C by permanganate occurred mostly by molecular structural change, persulfate tended to mineralize AEOs (Sohrabi et al., 2014). As a general observation, detoxification occurred when high z number acids, which tentatively consists of more aromatic and unsaturated acids (Ross et al., 2012; Pereira et al., 2013), were degraded (Sohrabi et al., 2014).

Although these studies at 22 ˚C were encouraging, the local aquifer temperature is about 5 ˚C. In this study, oxidation of AEOs in groundwater-derived OSPGW at 5 ˚C was investigated using permanganate and un-activated persulfate. Total carboxylic acid and dissolved organic carbon concentrations were measured to evaluate the extent of removal of AEOs and to indicate the extent of mineralization versus molecular structure transformation. Characterization of changes in the distribution of NA congeners and changes in the acute toxicity of the AEO fraction were also measured to assess any relationship between toxicity reduction and changes in the C and Z number acids, specifically to test our hypothesis that the greater contribution to NA toxicity is associated with high Z number acids.

## 4.2. Materials and methods

### 4.2.1. OSPGW

OSPGW was collected from a groundwater monitoring well in an abandoned tailings pond structure at Suncor Energy's property, 35 km Northeast of Fort McMurray, AB. Water samples were shipped, stored at 4 ˚C, and centrifuged at 10000 rpm for 30 min in order to reject fine particles prior to oxidation experiments. The un-oxidized OSPGW had 46.9±0.3 mg $L^{-1}$ total carboxylic acid concentration, including NAs, measured by

Fourier Transform Infrared (FTIR) analysis (Jivraj et al., 1995). Table 4.1 shows major ion chemistry of OSPGW sample.

Table 4.1. Major ion chemistry of OSPGW, as measured by ICP-MS

| **Parameter (mg $L^{-1}$)** | **OSPGW** |
|---|---|
| pH | 8-8.2 |
| Sodium | 280-292 |
| Calcium | 37-61 |
| Magnesium | 1-2 |
| Chloride | 18-19 |
| Bicarbonate | 1000-1040 |
| Sulphate | <0.5 |

### 4.2.2. Chemical reagents

Potassium permanganate ($KMnO_4$, purity 99+%, A.C.S. reagent) and sodium persulfate ($Na_2S_2O_8$, Sigma Ultra, purity 98+ %) were obtained from Sigma Aldrich and used as received. A saturated sodium bisulfite solution was prepared from analytical grade sodium bisulfite ($NaHSO_3$, Fisher Chemicals, S654-500) and used to stop the oxidation reaction during sampling episodes at different times (Forsey, 2004).

### 4.2.3. Oxidation experiments

Two volumetric flasks were filled with 12 L of centrifuged OSPGW and kept at 5 ˚C in a walk-in fridge one day before starting the experiment. In order to avoid dilution of AEOs by addition of oxidant solutions, each oxidant was weighted and spiked directly into its own 12 L volumetric flask with OSPGW and stirred until completely dissolved to provide initial concentrations of 5 and 10 g $L^{-1}$ for potassium permanganate and sodium persulfate in the OSPGW solutions. The 12 L flask of OSPGW and oxidant were immediately split into triplicate, 4-L amber jars or reactors for each oxidant. Another 4-L

container with centrifuged OSPGW, without oxidant, was retained as an un-oxidized control and sampled at each episode. Amber jars were stored in the fridge in the dark, at ~ 5 ˚C and sampled periodically over 120 d.

### 4.2.4. Sampling and analyses

Reactors were sampled for oxidant concentration, total carboxylic acid concentration, dissolved non-volatile organic carbon (DOC), AEO/NA characterization, and acute aquatic toxicity assessed. All samples except for DOC and oxidant concentration were first acidified to pH ~2-2.5, extracted with dichloromethane (DCM), and dried under a stream of nitrogen gas (Holowenko et al., 2002). This isolated the AEOs, including NAs, from residual oxidant. Further preparation was then performed for each analysis. Methods and equipments are described by Sohrabi et al. (2013) and in chapter 3 of this dissertation.

### 4.2.5. Toxicity bioassay

Toxicity testing of un-oxidized and oxidized OSPGW consisted of static-renewal, embryo-larval fathead minnow bioassays, as described in chapter 3, in accordance with Environment Canada toxicity testing protocols EPS 1/RM/22. Aquatox Testing & Consulting (ON, Canada) provided fathead minnow (*Pimephales promelas*) embryos for this testing. Both mortality ($LC_{50}$) and hatch length were assessed. In this chapter “toxicity” refers to this test.

## 4.3. Result and discussion

### 4.3.1. Total carboxylic acid concentration

Concentrations of total carboxylic acids, including NAs, measured by FTIR, in the un-oxidized control and oxidized samples were monitored over the 120 d experiment (Fig. 4.1). Over this period, total carboxylic acid concentrations in the un-oxidized control showed minimal decrease (12%), perhaps due to biodegradation. Interestingly, oxidation by persulfate did not decrease total carboxylic acid concentrations after initial decline (~ 20%) within 2 d. This suggests that there is a vulnerable fraction that reacted readily with persulfate. No change in total carboxylic acid concentration does not necessarily translate into no reaction. As discussed in chapters 2 and 3 acids may transform due to oxidation while retaining consist C=O moieties which are detected by FTIR. Characterization of samples by HPLC-Orbitrap-MS, which will be described in section 4.3.3 helped determine if further oxidation occurred. In contrast with persulfate, permanganate effectively degraded 75% of the total carboxylic acid in OSPGW at 5 ˚C, mostly within first 21 d. This suggests that the majority of the carboxylic acid fraction is susceptible to permanganate oxidation, even at 5 ˚C.

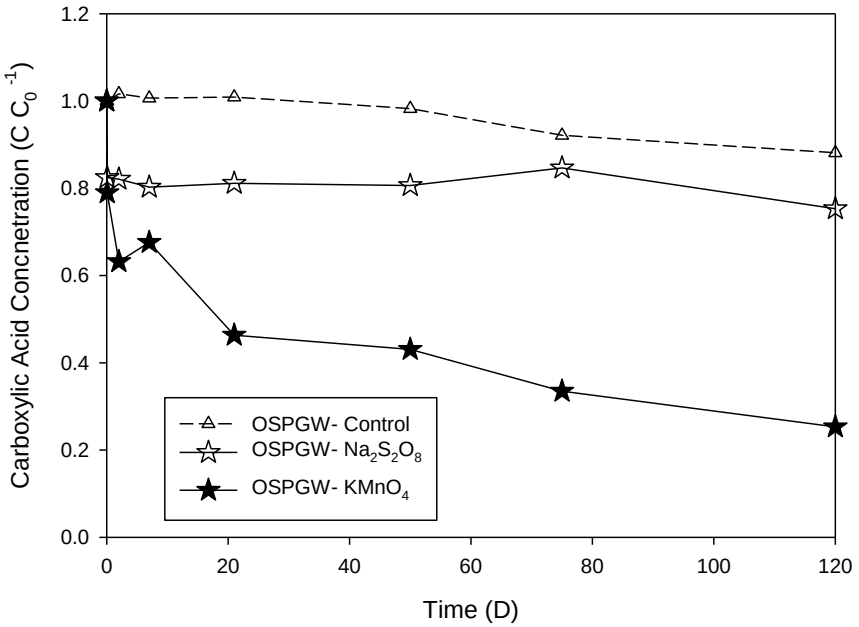


Fig. 4.1. Total carboxylic acid concentration changes at 5 ˚C. Each data point is average concentration ($C_t$) for three reactors shown relative to the initial un-oxidized control concentration ($C_0$ ~ 46.9±0.3 mg $L^{-1}$, measured by FTIR). Error bars derived from triplicate analyses are generally within the symbol.

### 4.3.2. DOC concentration

The non-volatile DOC content of un-oxidized controls and oxidized samples were measured to monitor mineralization of AEOs during oxidation (Fig. 4.2). No dramatic changes over the 120 d experiment were noted. After day 50, the DOC concentration in the control gradually declined to about 90% of the initial value. Persulfate oxidation appeared to cause about 10% reduction in DOC within 2 d, with little further reduction noted. Permanganate brought about a similar 10% DOC concentration decline, but within 7 d. This reduction was followed by a recovery in DOC concentrations. These inconsistent behaviors suggest that DOC declines due to oxidation may not have been analytically significant. Since neither oxidant decreased the DOC content of OSPGW at 5 ˚C, either no effective reaction between persulfate and AEOs occurred or molecular

transformation, without mineralization, occurred. In contrast, previous studies (Sohrabi et al., 2014, Sohrabi et al, 2013) found that persulfate effectively mineralized AEOs and DOC of OSPW and OSPGW at 22 ˚C. Also, permanganate oxidation of OSPW and OSPGW at 22 ˚C (Sohrabi et al., 2014, Sohrabi et al., 2013) involved at least partial mineralization as well as molecular transformation.

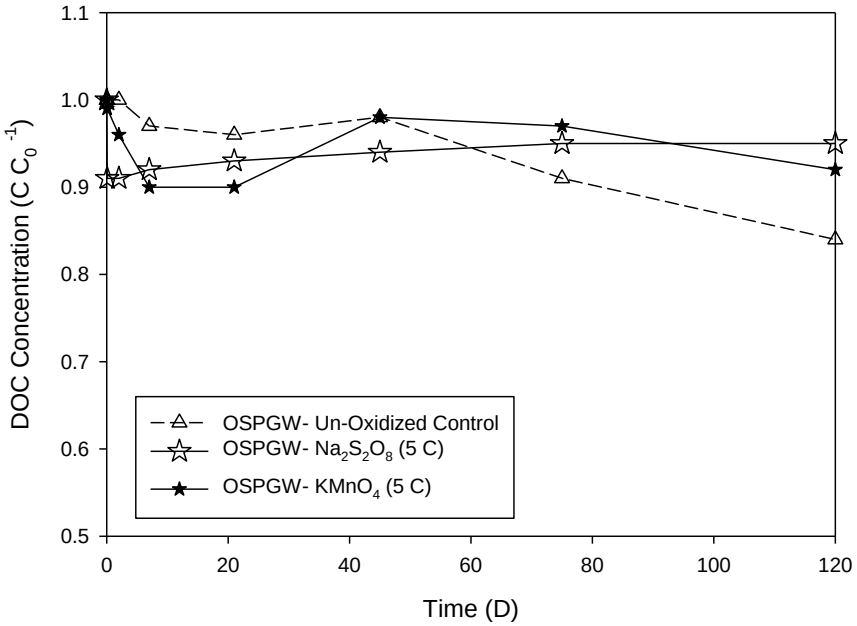


Fig. 4.2. DOC concentrations ($C_t$) relative to initial un-oxidized OSPGW DOC concentrations ($C_0$). Each value is the average DOC concentration for three reactors ($C_0$ ~ 49.4±0.7 mg $L^{-1}$, wet combustion analysis). Error bars derived from triplicate analyses are generally within the symbol.

### 4.3.3. Detailed characterization by HPLC-Orbitrap-MS

Since molecular transformations of AEOs without major mineralization could have occurred, un-oxidized controls and permanganate- and persulfate-oxidized samples of days 2 and 21 were characterized by HPLC-Orbitrap (Pereira et al., 2013). Here, we focused on characterization of $O_2$ species which traditionally are called NAs. Distributions of classical NAs were organized in 3D plots (Fig. 4.3) presenting the

relative abundance (bar height, Y axis) of each congener in terms of the number of carbon atoms (X axis) and Z number (Z axis). The Z number represents the cyclic rings and/or C=C double bonding. The changes in abundances of compounds with an oxygen atom, NAs, and hetro-atoms present in OSPGW are shown in Fig. 4.4.

Semi-qualitative comparisons of NA distributions in the un-oxidized control and oxidized samples (Fig. 4.3) demonstrate that both permanganate (Fig. 4.3.B1 & B2) and persulfate (Fig. 4.3.C1 & C2) reacted with NAs and decreased the concentration of all the NAs within 2 d. Like oxidation of OSPGW at 22 ˚C (Sohrabi et al., 2014), permanganate oxidation at 5 ˚C (Fig. 4.3.B1) showed significant degradation of high Z number acids while persulfate (Fig. 4.3.B2) did not show much reaction with this fraction within 2 d. No major additional change in NA distribution patterns was evident for both permanganate (Fig. 4.3.B2) and persulfate (Fig. 4.3.C2) by day 21.

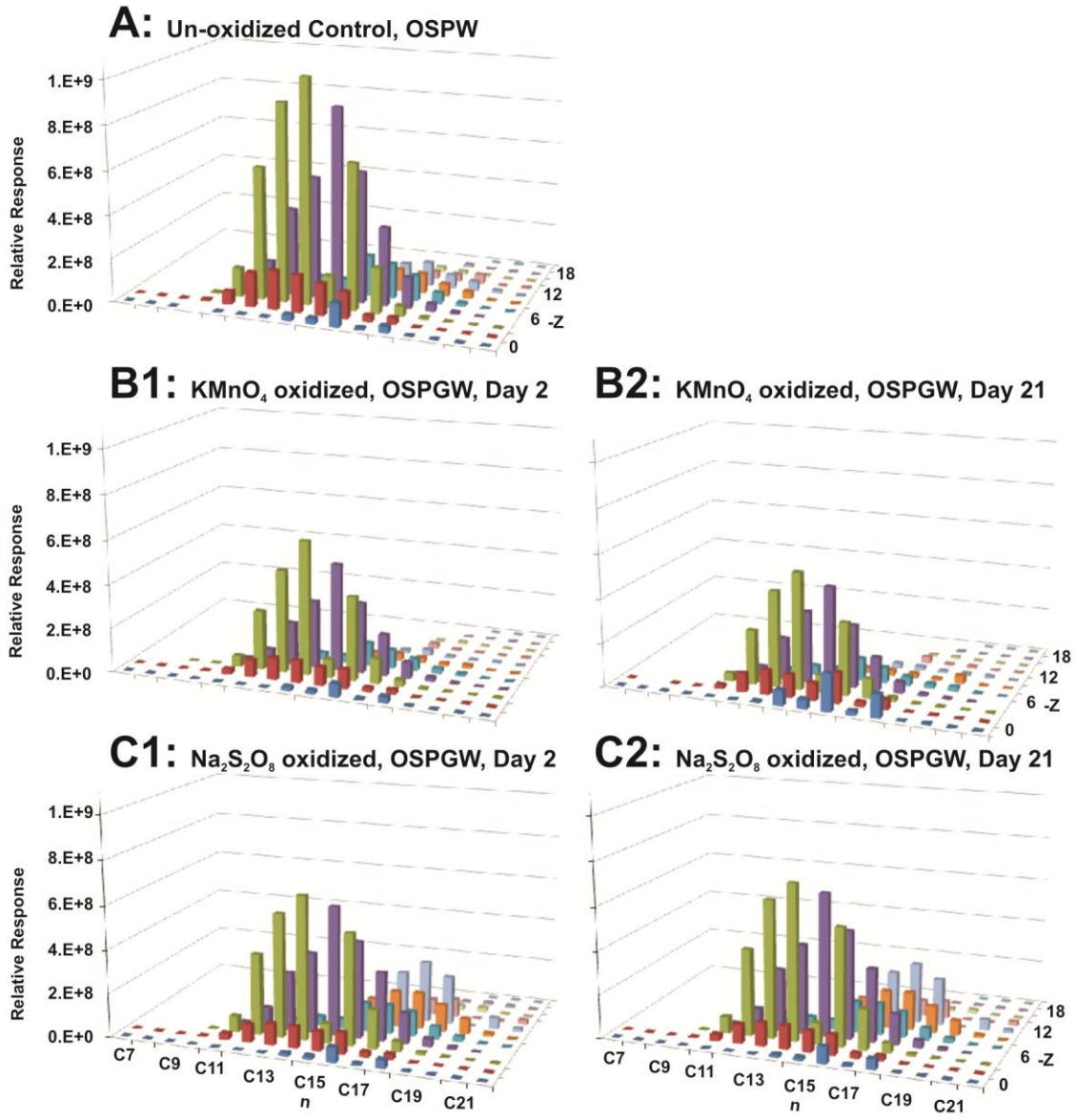


Fig. 4.3. Three dimensional distribution of Classical NAs in un-oxidized control and permanganate (5 g $L^{-1}$) and persulfate (10 g $L^{-1}$) oxidized OSPGW at 5 ˚C. A: un-oxidized control, B1: $KMnO_4$ oxidized day 2, B2: $KMnO_4$ oxidized day 21, C1: $Na_2S_2O_8$ oxidized day 2, C2: $Na_2S_2O_8$ oxidized day 21.

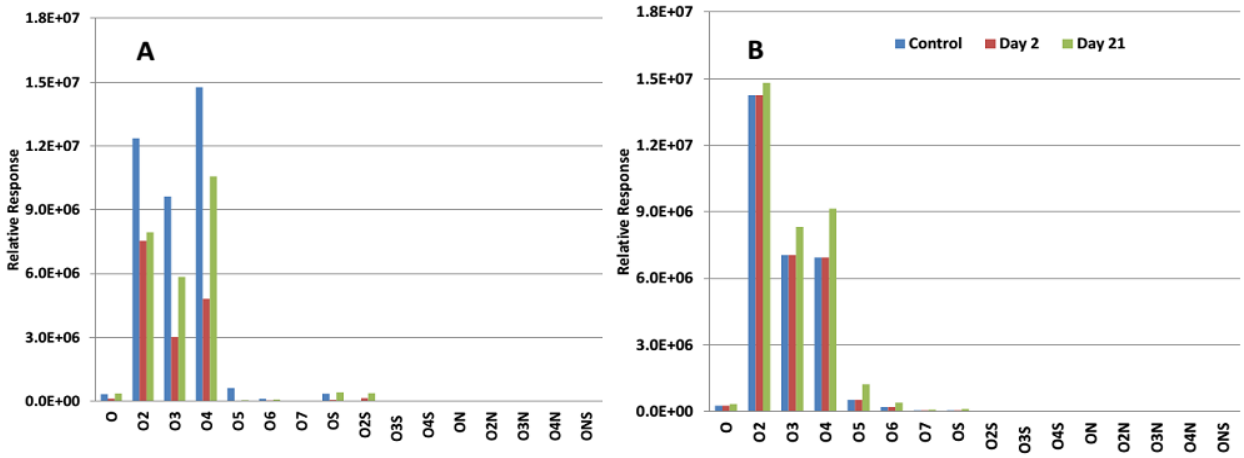


Fig. 4.4. Changes in abundance of hetro-atoms present in OSPGW detected by negative ion spectroscopy. A: permanganate oxidized samples, B: persulfate oxidized samples.

After Sohrabi et al. (2014) the ratio of each oxidized NA congener semi-quantitative concentration ($C_t$) was plotted relative to the concentration in the initial un-oxidized sample ($C_0$) (Fig. 4.5) to better display changes in NAs which were occurring during oxidation. If the ratio is greater than 1.1, the congener's abundance is considered to have increased (marked as red), the ratio of 0.9 to 1.1 indicates no significant change (marked as yellow), and a ratio less than 0.9 is considered as a decrease in the congener's abundance (marked as green). As depicted in Fig. 4.5.B1, permanganate oxidation of OSPGW at 5 ˚C reduced the relative abundances of all classical acids except a few congeners such as Z = 0 $C_{20}$ and $C_{21}$. Acids with higher Z numbers showed greater decreases. By day 21, further decrease in the relative abundance of some acids, but an increase in the relative abundances of Z = 0 and -2 acids, was observed which might be due to decomposition of higher Z number acids with two or more oxygen atoms.

Weak degradation of classical NAs by persulfate was delineated only at an early stage (Fig. 4.5.C1) with no further change in signature (Fig. 4.5.C2) after 21 d and no significant change in AEOs (Fig. 4.1) and DOC (Fig. 4.2) concentrations on day 21.

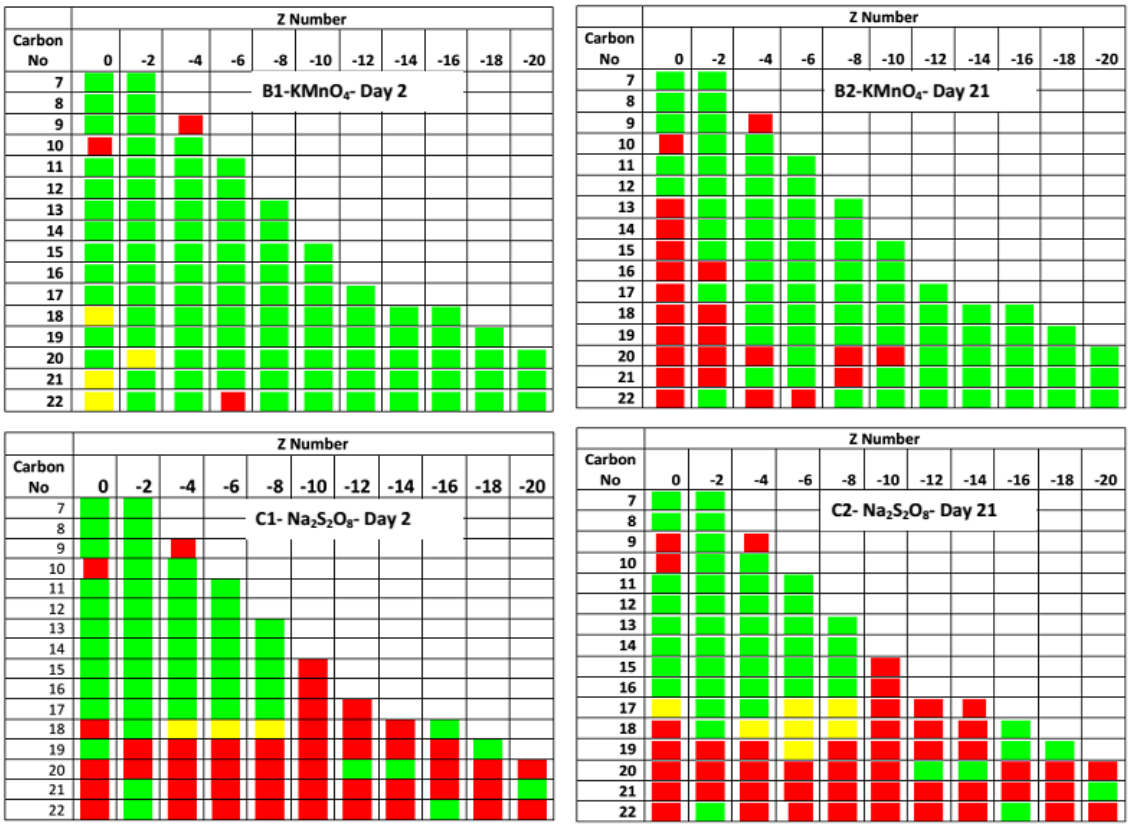


Fig. 4.5. Semi-quantitative comparisons of oxidized congeners relative to their initial abundances in un-oxidized OSPGW sample based on HPLC-Orbitrap-MS analyses. Ratios of time t abundance of each congener ($C_t$) to time zero abundance of the same congener ($C_0$) was calculated ($C_t/C_0$). Series B and C represent relative abundances of permanganate- and persulfate-oxidized congeners to the un-oxidized abundances at 5 ˚C.

### 4.3.4. Toxicity bioassay

*Pimephales promelas* (fathead minnow) is an indigenous specie to the Athabasca basin that has shown sensitivity to acute toxicity of OSPW (Peters et al., 2007; Kavanagh et al., 2011; He et al., 2012). Acid extractable organics, specifically NAs, were identified as

the main source of toxicity of OSPW (Dokholyan and Magomedov, 1983; MacKinnon and Boerger, 1986; Verbeek et al., 1993). As in the previous study by Sohrabi et al. (2014), the embryo-larval bioassay using *Pimephales promelas* (fathead minnow) was applied to the AEOs isolated from residual oxidant by extraction by DCM and redissolution in 5% M NaOH and the $LC_{50}$ was the criterion to evaluate toxicity mitigation/removal by oxidation. The $LC_{50}$ is the concentration of total carboxylic acid at which 50% of the fathead minnow eggs do not hatch.

The $LC_{50}$ values are shown in Fig. 4.6 along with the total carboxylic acid concentrations (as measured by FTIR). Permanganate oxidized samples showed toxicity mitigation with $LC_{50}$ of ~20 mg $L^{-1}$ at day 2 increasing to an $LC_{50}$ value of 48 mg $L^{-1}$ on day 21. The $LC_{50}$ value of day 21 (48 mg $L^{-1}$) was higher than the total carboxylic acid concentration (~ 22 mg $L^{-1}$) by FTIR. In contrast, the persulfate oxidized sample at day 2 still showed toxicity to fathead minnow larva, having an $LC_{50}$ of 10 mg $L^{-1}$, but a total carboxylic acid concentration (by FTIR) of about 37 mg $L^{-1}$. Little additional carboxylic acid concentration or toxicity reduction was found at day 21 for persulfate oxidized OSPGW with $LC_{50}$ of 12 mg $L^{-1}$ and total carboxylic acid concentration of 37 mg $L^{-1}$.

In the current study, mitigation in toxicity of permanganate samples oxidized at 5 ˚C appears to be due to preferred oxidation of high Z number NAs as suggested for 22 ˚C in chapter 3, while persulfate oxidation appears to form higher Z number acids, with a resulting increased level of toxicity.

The analysis of the hatch length endpoint (Fig. 4.6) indicates a trend common with mortality as seen in chapter 3. Although the degree to which the reduction in acids affected hatch length varied, when compared to mortality, the overall trends were very

similar. Permanganate microcosm displayed a reduction in toxic effect after 21 d. The threshold effect concentration for hatch length for unoxidized OSPGW presented herein (7.1 mg $L^{-1}$) is similar to those previously published for Japanese medaka (6.2 mg $L^{-1}$) exposed to Syncrude OSPW (Peters et al., 2007). Only permanganate reduced the sub-lethal effects of OSPGW at 5 ˚C. Similar to chapter 3, as the reduction in toxicity to sublethal effects of oxidant treated OSPGW mimic lethal effects, we propose that processes that govern mortality-associated toxicity also regulate hatch length. In general, it appears that higher Z-number acids have a greater propensity to reduce fathead minnow larval length at hatch.

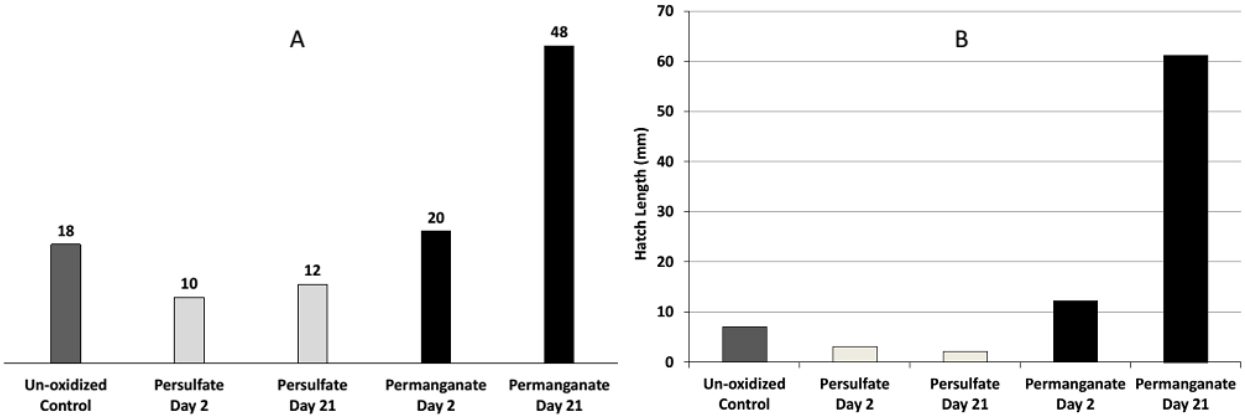


Fig. 4.6. A: $LC_{50}$ values (based on mg $L^{-1}$ total carboxylic acid concentration) of un-oxidized control and permanganate and persulfate oxidized AEOs for days 2 and 21, B: Hatch length threshold effects concentrations of the same samples from OSPGW oxidation experiment at 5 ˚C.

Relating the toxicity of persulfate oxidized samples with total carboxylic acid concentrations and sample characterizations with HPLC-Orbitrap-MS provides some insight into the likely NA fraction contributing most to toxicity and a rationale for the toxicity changes. Persulfate oxidized samples from days 2 and 21 showed higher level

of toxicity than the un-oxidized sample, likely due to formation and persistence of high Z number NAs. Given the total carboxylic acid concentrations of 47 mg $L^{-1}$ and $LC_{50}$ of 18 mg $L^{-1}$ for the un-oxidized control, 2 d of persulfate oxidation of OSPGW at 5 ˚C decreased the total carboxylic acid concentration to 37 mg $L^{-1}$ but level of toxicity increased ($LC_{50}$ = 10 mg $L^{-1}$). The FTIR concentration measurements and HPLC-Orbitrap-MS characterization suggested that after initial persulfate reaction with AEOs, only minor reaction might occur and so the level of toxicity on day 21 was not different from that on day 2. In contrast, permanganate oxidized samples of days 2 and 21 showed lower level of toxicities than the un-oxidized sample, likely due to preferential oxidation of high Z number NAs. Two d of permanganate oxidation of OSPGW at 5 ˚C increased the $LC_{50}$ to 20 mg $L^{-1}$ total carboxylic acids and 21 d permanganate oxidation elevated $LC_{50}$ value to 48 mg $L^{-1}$ while total carboxylic acid concentration in the microcosm was 22 mg $L^{-1}$. Similar to chapter 3, it appears that mitigation in toxicity of AEOs by permanganate was attributed to removal of higher Z number acids.

### 4.4. Summary

At the local in situ aquifer temperature, 5 ˚C, only permanganate oxidation mitigates acute toxicity of OSPGW as evaluated by embryo-larval bioassay using *Pimephales promelas* (fathead minnow). Persulfate was ineffective. Detoxification by permanganate at 5 ˚C mostly occurred by molecule structural transformations, not by mineralization. In contrast, at 22 ˚C, permanganate oxidized AEOs mainly via structural transformation with partial mineralization but persulfate tended mainly to mineralize AEOs (Sohrabi et al., in submission). This suggests that there are differences in AEO oxidation mechanisms with both oxidants at 5 ˚C and 22 ˚C. However, it appears that

permanganate retains its robust capacity for AEO detoxification even at 5 ˚C. Similar to oxidation at 22 ˚C, chapter 3, the combination of sample characterization with HPLC-Orbitrap-MS and toxicity testing using *Pimephales promelas* connects toxicity of OSPGW with high Z number acids. With regards to in situ remediation of AEO in OSPGW at the in situ aquifer temperature (5 ˚C), permanganate is the oxidant of choice. Further oxidation experiments in the presence of representative aquifer solids, as suggested by Sra et al. (2010), are presented in chapter 5 to confirm the potential application of this in situ technology for mitigation of the toxicity of OSPGW.

The findings of the current study re-emphasizes that decreases in AEO concentration measured by FTIR does not necessarily reflect reduction of toxicity of OSPW/OSPGW. In order to ensure that any treatment or remediation measure results in the required mitigation in toxicity of AEOs, application of advanced AEO characterization in support of sensitive toxicity testing with species such as Pimephales promelas is required.

# Chapter 5:

# Applicability of in situ chemical oxidation for remediation of oil sands process affected groundwater

## 5.1. Introduction

Oil production from the oil sands was 1.8 million b $d^{-1}$ in 2012 and is expected to grow to about 5.2 million b $d^{-1}$ by 2030 (CAPP, 2013). The modified Clark extraction process employs heat, water and caustic soda to separate bitumen from oil sands ore. Oil sands process affected water (OSPW) is transferred to tailings ponds. Currently tailings ponds cover 182 $km^2$ of land surface (CAPP, 2014) because fine solids have settled extremely slowly (Scott et al., 1985) and the oil sands industry has committed not to release somewhat toxic tailings water to the environment. Tailings water contains residual bitumen, increasing salinity, and organic compounds dissolved from bitumen (MacKinnon, 1993). Acid extractable organics (AEOs), including naphthenic acids (NAs), are considered as the main source of acute toxicity to aquatic organisms in OSPW (Herman et al., 1994). NAs are saturated aliphatic and cyclic acids with two oxygen atoms (Brient et al., 1995). Further studies have determined that compounds with more than two oxygen atoms, sulfur, and nitrogen as well as organic molecules with aromatic and unsaturated structures are also present in the AEO mixture (Grewer et al., 2010; Ross et al., 2012; Pereira et al., 2013). Although slow aerobic degradation/aging processes in the tailings ponds reduces the toxicity of OSPW (MacKinnon and Boerger, 1986; MacKinnon and Costerton, 1994), AEOs in the OSPW

infiltrating into the underlying sandy aquifers remain un-changed for decades (Scott et al., 2005) and some groundwater plumes are extending beyond tailings impoundments (Ferguson et al., 2009; Oiffer et al., 2009). Although several methods have been examined in laboratory studies including chemical oxidation by Fenton's reagent, a strong, activated, peroxide-based system (Lu *et al.*, 2010), ex situ remediation of OSPGW (oil sands process-affected groundwater) would require treatment facilities and groundwater extraction,. Unfortunately, the short life of peroxide makes it unsuitable for in situ aquifer remediation, due to the slow dispersive mixing of injected oxidant with OSPGW. In situ chemical oxidation (ISCO) treatment is attractive if detoxification of OSPGW can be accomplished within cost and time constraints, but persistent oxidants must be employed. ISCO is pursued in this research, employing the persistent oxidations: permanganate and un-activated persulfate.

ISCO requires direct contact of the oxidant with the target contaminants for treating aquifers impacted by mobile, dissolved toxicants, in this case AEOs. the oxidant must be dispersed in the aquifer to ensure maximum contact with dissolved AEOs. So, the select oxidant must be reactive with targeted compounds, but also must be persistent in the aquifer. This latter feature requires that oxidant consumption by non-target aquifer material be low. Previous laboratory studies have demonstrated that activated persulfate (Drzewicz et al., 2012), UV/$H_2O_2$ (Afzal et al., 2012), Fenton's reagent (Lu et al., 2010), and ozone (Scott et al., 2008) degraded AEOs/NAs and mitigated toxicity. However, these oxidants are short lived (Watts and Teel, 2006) and maintaining activation (typically with heat, extreme pH, metals, etc.) is difficult to implement in situ (Sra et al., 2010b), and so our studies have evaluated un-activated persulfate and

permanganate, both persistent, un-activated oxidants. Persistence in the aquifer not only relies on the oxidant's nature, but also on natural oxidant demand/interaction (NOD/NOI) by aquifer material. If NOD/NOI is low and dispersive mixing is high, ISCO may be an effective remediation approach for OSPGW.

The capacity of permanganate and persulfate to degrade AEOs/NAs from OSPGW was demonstrated (Sohrabi et al., 2014a, Sohrabi et al., 2013). Permanganate and un-activated persulfate are both able to degrade the toxic fraction of AEOs, from both tailings pond water (OSPW) and impacted groundwater (OSPGW), at 22 ˚C. So, both oxidants can be potentially considered for treating recent OSPW in active ponds with warm temperature or immediately upon discharge from extraction facility. When it comes to the local aquifer temperature of about 5 ˚C, only permanganate was effective in mitigating the acute toxicity of the AEOs from OSPGW (Sohrabi et al., 2014b). The acute toxicity removal/mitigation occurs quickly (< 21 d) but without the destruction of all AEOs.

The aim of the current study was to explore the feasibility of ISCO for mitigating the acute toxicity in the AEO fraction of OSPGW. A representative and as yet uncontaminated aquifer, the Wood Creek Sand Channel (WCSC), adjacent to the South Tailings Pond at Suncor's Millennium mine, 35 km north of Fort McMurray, AB, was selected. In this paper, stop-flow column tests were initially used to examine the capacity of permanganate and un-activated persulfate to degrade AEOs at 5 ˚C, the local aquifer temperature, in the presence of aquifer solids. Although, persulfate was shown ineffective for reducing the acute toxicity of OSPGW at 5 ˚C, it was possible that some AEO degradation and toxicity mitigation might be found due to natural persulfate

activation by aquifer minerals (Sra et al., 2012). Permanganate and persulfate consumption by aquifer material, termed natural oxidant demand/interaction (NOD/NOI), was also evaluated as a critical parameter influencing the longevity of oxidants in the aquifer. The minimum effective oxidant concentration was assessed to determine the degree of dispersive dilution at which the oxidant would no longer be effective. In this testing, a series of low concentrations of oxidants were applied to treat OSPGW collected from the subsurface adjacent to a former tailings pond. Hydrogeological data of the WCSC, as the representative aquifer, in association with results of the above experiments, were then used to simulate oxidant injection for in situ treatment purposes. This permitted at least an initial assessment of treatment costs.

## 5.2. Materials and methods

### 5.2.1. Aquifer material

Aquifer material was collected from shallow (12 to 18 mbgs) and deep sections (26 to 31 mbgs) of the WCSC southeast of the STP in September 2011 during sonic drilling of well STP-UW-MW11-08-SS. Core were kept at 4 ˚C before being divided into 10 cm sub-samples and dried at 80 ˚C. Grain size analysis on subsamples classified the core as fine to medium sand (Fig. 5.1). Falling head permeability testing of 10 cm intervals revealed a range of hydraulic conductivity (K) from $1.9 \times 10^{-6}$ to $3.7 \times 10^{-4}$ m $s^{-1}$ with a median K of $1.9 \times 10^{-4}$ m $s^{-1}$ (Fig. 5.2). Samples were stored in plastic bags until they were used for further testing described below.

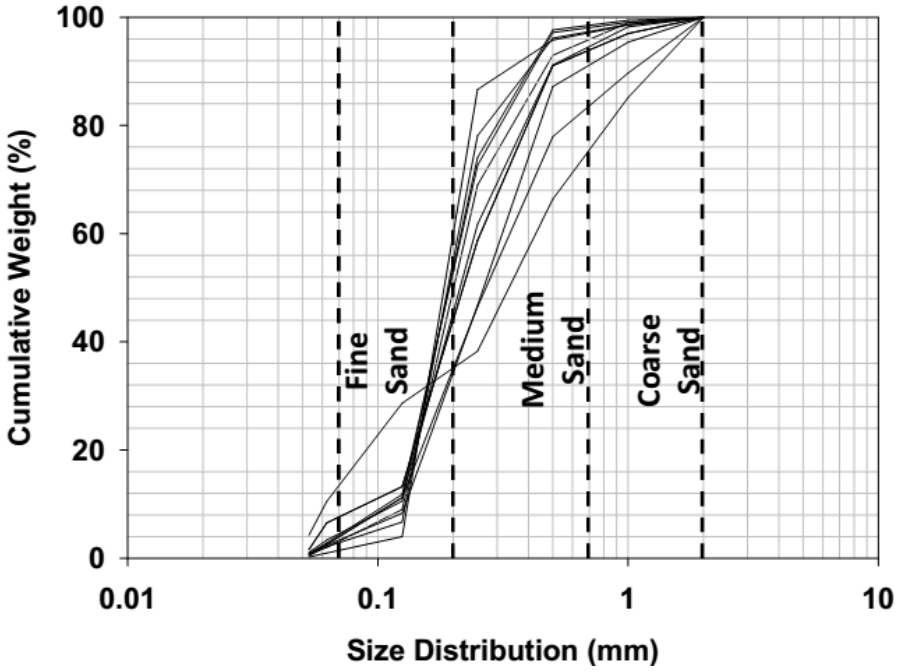


Fig. 5.1. Size distributions for select samples of shallow and deep horizon wells.

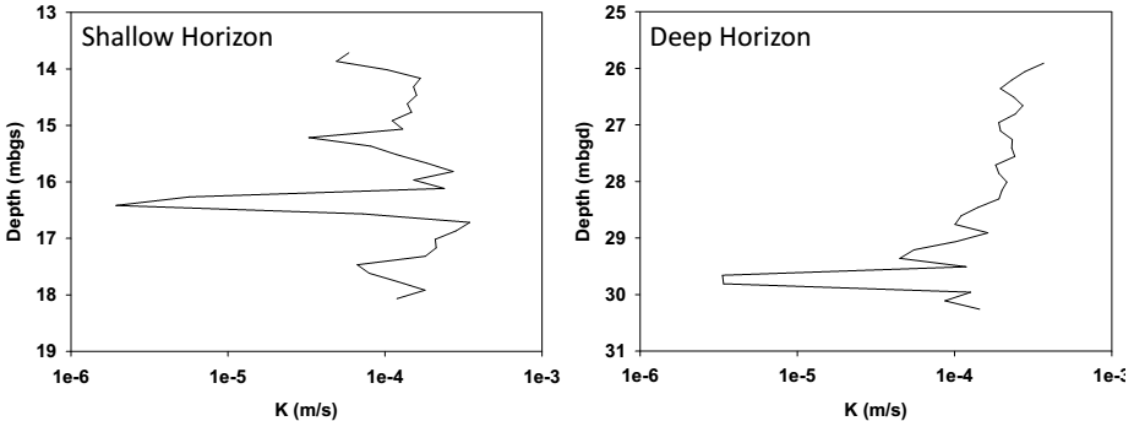


Fig. 5.2. Hydraulic conductivity (K, m $s^{-1}$) distribution in the WCSC core, measured by falling head permeameter.

### 5.2.2. OSPGW

The OSPGW was provided by Suncor Energy from an impacted surficial aquifer. This sample was groundwater typical of what may be considered for remediation in the future. The initial total carboxylic acid concentration, measured by FTIR, was ~ 56.5 mg $L^{-1}$. Table 5.1 shows major ion chemistry of OSPGW sample.

Table 5.1. Major ion chemistry of OSPGW, as measured by ICP-MS

| Parameter (mg $L^{-1}$) | OSPGW |
|---|---|
| pH | 8-8.2 |
| Sodium | 280-292 |
| Calcium | 37-61 |
| Magnesium | 1-2 |
| Chloride | 18-19 |
| Bicarbonate | 1000-1040 |
| Sulphate | <0.5 |

### 5.2.3. Testing and Analyses

Both permanganate and persulfate concentrations were measured as described by Sohrabi et al. (2013). NAs (more correctly total carboxylic acids) were quantified using a traditional Fourier Transform Infrared (FTIR) analysis of absorbance peak heights at 1743 and 1706 $cm^{-1}$ as per Jivraj et al. (1995) and Holowenko et al. (2001). These two absorbance peaks are related to the monomer and dimer C=O functional groups. Details are provided by Sohrabi et al. (2013). Fathead minnow embryo toxicity testing was conducted in accordance with Environment Canada toxicity testing protocols (EPS 1/RM/22) as described by Sohrabi et al. (2014a).

### 5.2.4. Natural oxidant demand/natural oxidant interaction (NOD/NOI)

Batch tests were conducted in triplicate to determine non-target permanganate and persulfate consumption by aquifer material. The NOD/NOI testing was conducted at 22 and 5 ˚C, the range of temperatures anticipated as OSPGW infiltrates and then migrates in the subsurface. Dried aquifer material (above) was mixed, screened (No. 10 U.S. standard mesh size sieve, 2.00 mm), and homogenized before starting the experiment. Reactors (150 mL amber glass bottles) containing 100 g of aquifer material were amended with 100 mL of 2, 5, and 10 g $L^{-1}$ of permanganate and 2, 10, 20 g $L^{-1}$ of

persulfate solutions prepared from analytical grade oxidants and milli-Q water. Control reactors, with no aquifer material, were prepared, stored and analyzed along with active reactors at 22 and 5 ˚C. Tests were run for 30 d with sampling at days 1, 4, 8, 15, and 30. Experiment containers were lightly flipped over every day in order to ensure appropriate contact between solids and oxidant. Water samples were filtered (0.2 µm) and then analyzed for permanganate and persulfate concentrations based on the procedure described by Sohrabi et al. (2013).

### 5.2.5. Stop-flow column tests

Our previous research demonstrated AEOs/NA oxidation by permanganate and, in some circumstances, by un-activated persulfate, but aquifer material was not present. So, in order to mimic in situ oxidation, stop-flow column tests (Thomson et al., 2009) were conducted including aquifer solids. Stop-flow column tests employed homogenously mixed oxidant and OSPGW filling pores of un-impacted WCSC aquifer material, at the aquifer temperature, 5 ˚C, as occurs under field conditions. Each column (58.25 cm long × 5 cm diameter) was packed close to field density. Nine columns were used; three for each of the un-oxidized control, permanganate and persulfate oxidant solutions. Columns had two inlets, one for oxidant and the other for OSPGW, coming together just before entering the sediment chamber. In order to determine breakthrough volume and to insure that complete mixing of oxidant and OSPGW occurs, tracer tests using a conservative tracer solution, 100 mg $L^{-1}$ sodium bromide (injected from one inlet), and milli-Q water (injected from the second inlet) were conducted at the operational flow rate of 1 mL $min^{-1}$ on all 9 columns. This was used to determine the

appropriate time for baseline solution sampling and for stopping flow for each reaction period.

Solutions of 25 and 100 g $L^{-1}$ permanganate ($KMnO_4$, purity 99+%, A.C.S. reagent) and persulfate ($Na_2S_2O_8$, Sigma Ultra, purity minimum 98%) were prepared in Milli-Q water at 22 ˚C a day before starting injection into the columns. The oxidant solutions were then stored for temperature equilibrium to 5 ˚C.

The desired oxidant concentrations were 5 and 10 g $L^{-1}$ permanganate and persulfate, respectively. For persulfate treated columns, the OSPGW injection rate was 0.9 mL $min^{-1}$ and the persulfate solution (100 g $L^{-1}$) injection rate was 0.1 mL $min^{-1}$ yielding 10 g $L^{-1}$ persulfate concentration after mixing at the column inflow. For permanganate treated columns, OSPGW and permanganate injection rates were set at 0.8 and 0.2 mL $min^{-1}$ to achieve the 5 g $L^{-1}$ permanganate concentration after mixing in the column inflow. Flow through un-oxidized control columns was fixed at 0.9 and 0.1 mL $min^{-1}$ respectively for OSPGW and Milli-Q water. Constant flow through columns was provided by peristaltic pumps with fixed flow rates.

Four episodes of column tests were conducted with injectate retention times in contact with aquifer material of 2, 2, 21, and finally 60 d. In order to evaluate and exclude any impact from the initial condition of the aquifer material on column test results, the first episode with a retention time of 2 d was repeated immediately.

Before each set of injections, columns were water-saturated, first by flushing with $CO_2$ gas for 1.5 h and then rinsing with Milli-Q water for three pore volumes (~24 h) using a fixed flow rate of ~1 mL $min^{-1}$ in the up-flow mode. Then OSPGW and Milli-Q water were injected for 24 h to establish the baseline conditions before each oxidant and

OSPGW injection. After injection of three pore volumes (based on breakthrough determined in the tracer test) was complete, an effluent sample from each column was collected for total carboxylic acid and oxidant concentration analyses as a baseline and then inlets and outlet were clamped for the reaction period. After the desired elapsed time, columns were sampled first by gravity drainage and then by adding nitrogen gas to the effluent end to provide sufficient volume (at least 200 mL) of effluent for analysis. Total carboxylic acid and oxidant concentrations were measured and toxicity testing was conducted on the collected effluent.

### 5.2.6. Minimum effective oxidant concentration (MEOC)

Batch tests were conducted to estimate the lowest concentration of oxidants that effectively reacts with AEOs/NAs present in OSPGW. Similar to the NOD/NOI evaluation, MEOC testing for permanganate was conducted at two temperatures: 5 and 22 ˚C; the higher temperature to include the temperature for OSPW recently exiting the extraction plant (~ 22 ˚C). Also, some active tailings ponds have temperatures around 15 ˚C and their detoxification is of interest. Due to the ineffectiveness of persulfate at 5 ˚C (Sohrabi et al., 2014), minimum effective persulfate concentration testing was conducted at 22 and 15 ˚C. The 5 ˚C testing for permanganate was conducted in a walk-in fridge; the 15 ˚C testing for persulfate in an incubator; and the 22 ˚C testing in a room-temperature cabinet. Four concentrations for each oxidant at each temperature were examined; 0.1, 0.3, 0.6, and 1 g $L^{-1}$. Analytical grade oxidant, permanganate or persulfate, was spiked into 2 L centrifuged, OSPGW and stirred until the oxidant was dissolved. The homogenous solutions were immediately transferred into 40 mL vials. Triplicate vials for each oxidant concentration at each temperature were sacrificed at

days zero, 2, 7, 21, 45, and 113 and analyzed for NA/total carboxylic acid and oxidant concentrations. The effectiveness of oxidants was then defined based on NA/total carboxylic acid and oxidant concentrations as well as outcomes of previous studies (Sohrabi et al. 2014a, Sohrabi et al. 2014b).

### 5.2.7. Simulation

The Visual Modflow Flex 2013.1 package (Schlumberger Water Services) was used to simulate scenarios treating a section of aquifer using permanganate. The properties of the aquifer were derived from the WCSC (Golder Associates, 2004, Klohn Crippen Berger Ltd., 2004) and, where possible, hydrogeological properties were measured at the In Situ Aquifer Test Facility (ISATF) at Suncor's STP (Table 5.2). The WCSC is a buried glaciofluvial channel aquifer. The geologic sequence at the STP includes 1-2 m of Holocene muskeg on the surface, 8-15 m Pleistocene glacial till, 10-50 m fine to medium sand of the WCSC, underlain by clay shale with thin interbedded carbonate cemented siltstone of the Cretaceous Clearwater formation. Here, the WCSC is fully-saturated and confined by the glacial till. Groundwater flow is essentially horizontal. A number of simulations were conducted using the USGS MODFLOW 2005 engine for physical groundwater processes coupled with MT3DMS V.5.1 for reactive transport. A 200 × 100 × 30 m block of the WCSC was selected so that there was no boundary effect during simulations. Glacial till and Clearwater formation was considered as no flow boundaries for the WCSC (Klohn Crippen Berger Ltd., 2004). A type one boundary condition, constant head, was applied at the east and west boundaries of the domain based on an average hydraulic gradient of 1/500 (variable, 1/700 to 1/300), for the WCSC (Golder Associates, 2004). A critical review of field scale dispersion in aquifers

by Gelhar et al. (1992) suggested that an appropriate longitudinal dispersivity could be an order of magnitude smaller than study site dimension along the water flow. So, for a 200 m length domain, longitudinal dispersivity of 10 m was selected. The diffusivity was incorporated into the simulations based on Jones et al. (2006).

Table 5.2. Hydrogeological characteristics of WCSC incorporated in ISCO simulations

| Parameter | Value | Source/Reference |
|---|---|---|
| Simulation Engines | Modflow 2005, MT3DMS V5.1 | Visual Modflow flex 2013.1 |
| Aquifer condition | Homogeneous | |
| Domain dimension | 200×100×30 m | |
| Hydraulic conductivity | $K_x=K_y=K_z= 4.98\times10^{-4}$ m $s^{-1}$ | Klohn Crippen Berger Ltd., 2004 |
| Specific storage | $6.67\times10^{-5}$ $m^{-1}$ | Klohn Crippen Berger Ltd., 2004 |
| Specific yield | 0.2 | Klohn Crippen-Berger Ltd., 2004 |
| Hydraulic gradient | 1/700 - 1/300 (average: 1/500) | Klohn Crippen Berger Ltd., 2004 |
| Longitudinal dispersivity | 10 m | Gelhar et al., 1992 |
| Transverse dispersivity | 1 m | Gelhar et al., 1992 |
| Vertical dispersivity | 0.1 m | Gelhar et al., 1992 |
| Diffusion coefficient | $1.03x10^{-4}$ $m^2$-$s^{-1}$ | Jones et al.,2006 |
| $K_{NOD}$ (5 ˚C) | $2.1\times10^{-2}$ $s^{-1}$ (2 g $L^{-1}$), $8.9\times10^{-3}$ $s^{-1}$ (5 g $L^{-1}$) | Experiments in this chapter |
| Injection rate | 300 $m^3$ $d^{-1}$ for 30 d | |

It was assumed that this block was fully saturated by OSPGW. Simulations were conducted for 120 d, about the time MEOC testing suggested permanganate would remain active. Two injection concentrations of permanganate, 5 and 2 g $L^{-1}$ were considered. It was assumed that permanganate would remain reactive at concentrations as low as 0.1 g/L, as demonstrated in MEOC testing results below. A fully penetrated injection well over the aquifer thickness was used to inject permanganate into the simulation block. In the initial simulations it was assumed that the oxidant solution was conservative and no reaction with aquifer material occurred. The maximum potential dispersed volume of injected permanganate exceeding 0.1 g $L^{-1}$, the concentration demonstrated to still be active with respect to NAs (see section 5.3.3 below) was calculated. For the second run for each permanganate concentration (5 or 2 g $L^{-1}$), the first order rate of reaction between permanganate and aquifer material at 5˚C was incorporated based on NOD/NOI batch testing (Table 5.3). No rate was assigned for reaction between total carboxylic acids, including NAs, and permanganate due to deficiency of FTIR analysis for differentiating reaction rates for each single acid in OSPGW mixture.

## 5.3. Results and discussion

### 5.3.1. NOD/NOI

Oxidant consumption by aquifer material limits the oxidant longevity in the aquifer. The more persistent the oxidant in the aquifer, the greater the dispersive mixing and thus greater the mass of contaminant that could be oxidized. The NOD/NOI values for the experiment period were calculated based on the following formula:

$$NOD_t = \sum_t \left[ m_{ox,t-1}^{test} - C_{ox,t}^{test} V_{ox,t-1}^{test} - \left( m_{ox,t-1}^{crtl} - C_{ox,t}^{crtl} V_{ox,t-1}^{crtl} \right) \left( V_{ox,t-1}^{test} / V_{ox,t-1}^{crtl} \right) \right] / m_{aq}$$

where $m_{ox}$: mass of permanganate, Cox: concentration of permanganate, $V_{ox}$: volume of permanganate solution in the reactor, $m_{aq}$: mass of dry aquifer material added to the test reactor, the superscripts test and crtl denote the test reactor and control reactor respectively, and the subscripts t and t-1 denote values at the current and previous sampling episodes respectively (Xu and Thomson, 2009).

Table 5.3 presents results of NOD/NOI testing for permanganate and persulfate over 30 d. The data are average of triplicate analyses for either permanganate or persulfate. Fig. 5.3 shows the oxidant concentration changes at both 22 and 5 ˚C. It should be mentioned that no NOD/NOI for persulfate was calculated due to its autocatalytic decomposition with no finite demand of persulfate by the aquifer material. The oxidant concentrations and accumulative 30 d calculated NOD/NOI for different concentrations (Table 5.3) reveal that the WCSC has low oxidant demand for both permanganate and persulfate when compared to NOD/NOI for other aquifers (Xu and Thomson, 2009; Sra et al., 2010b). This enhances longevity of both oxidants in the aquifer which results in better mixing with target AEOs via dispersion. It was also noted that the oxidant demand for both oxidants was lower at the actual aquifer temperature of 5 ˚C (Table 5.3).

Observed oxidant concentration declines (Fig. 5.3) were modest in the 30 d period. The oxidant decomposition rates were calculated from concentration changes over this period based on typical first order reaction for permanganate and persulfate (Xu and Thomson, 2009; Sra et al., 2010b). The rates were then applied in simulations to study

the distribution of the select oxidant, permanganate, in the block of aquifer with hydrogeological parameters of the WCSC.

Table 5.3. Results for 30 d NOD/NOI testing with sediment from the WCSC. The average and standard deviation of (3 replicate experiments) concentrations are provided.

| | Temperature (˚C) | Nominal Conc. (g $L^{-1}$) | Initial Conc. (g $L^{-1}$) | Final Conc. (g $L^{-1}$) | NOD Max g oxidant/Kg sediment | K ($s^{-1}$) |
|---|---|---|---|---|---|---|
| permanganate | 22 | 2 | 2.25±0.05 | 0.92±0.03 | 1.32±0.03 | $3.0e^{-2}$ |
| | 22 | 5 | 5.26±0.02 | 3.66±0.02 | 1.58±0.03 | $1.2e^{-2}$ |
| | 22 | 10 | 10.77±0.01 | 8.49±0.08 | 2.24±0.06 | $5.7e^{-3}$ |
| | 5 | 2 | 2.25±0.05 | 1.16±0.01 | 1.14±0.01 | $2.1e^{-2}$ |
| | 5 | 5 | 5.26±0.02 | 3.93±0.11 | 1.34±0.11 | $8.9e^{-3}$ |
| | 5 | 10 | 10.77±0.06 | 8.97±0.03 | 1.80±0.04 | $3.6e^{-3}$ |
| persulfate | 22 | 2 | 2.30±0.06 | 1.79±0.03 | Not applicable | $8.8e^{-3}$ |
| | 22 | 10 | 10.10±0.29 | 9.86±0.05 | Not applicable | $5.0e^{-4}$ |
| | 22 | 20 | 20.50±0.51 | 19.93±0.15 | Not applicable | $2.1e^{-3}$ |
| | 5 | 2 | 2.10±0.04 | 2.01±0.08 | Not applicable | $2.6e^{-3}$ |
| | 5 | 10 | 9.80±0.07 | 9.53±0.12 | Not applicable | $2.4e^{-3}$ |
| | 5 | 20 | 20.10±0.14 | 19.86±0.06 | Not applicable | $3.2e^{-3}$ |

### 5.3.2. Stop-flow column test

Stop-flow column tests (Thomson et al., 2009) were performed using both permanganate and persulfate at 5 ˚C to mimic in situ oxidation of AEOs in OSPGW with a realistic oxidant to aquifer mass ratio and at the aquifer temperature. Fig. 5.4 presents the effluent total carboxylic acid concentrations relative to initial total carboxylic acid concentrations injected into the columns. The carboxylic acid concentrations were corrected for dilution by dividing total volume of injected solution (oxidant + OSPGW) into volume of injected OSPGW. Un-oxidized control columns showed minimal carboxylic acid concentration changes over the 60 d experiment, consistent with the batch oxidation experiments. Permanganate columns showed about 50% carboxylic acid concentration decrease over the 60 d period. Interestingly, unlike batch oxidation experiment with no soil at 5 ˚C (Sohrabi et al., 2014), persulfate showed considerable reactivity with carboxylic acids (~ 70% total carboxylic acid degradation) with aquifer sediment present. However, as discussed earlier in chapters 3 and 4, total carboxylic acid concentration decrease does not necessarily result in mitigation in toxicity.

Fathead minnow toxicity testing on stop-flow column effluents provided interesting insight into the toxicity of AEOs oxidized by permanganate and persulfate. Table 5.4 presents $LC_{50}$ of un-oxidized control and permanganate and persulfate column effluents. Here, $LC_{50}$ is the concentration of total carboxylic acid at which 50% of fathead minnow eggs did not hatch after 7 d. The initial $LC_{50}$ for un-oxidized OSPGW was 24.7 mg $L^{-1}$. Permanganate mitigated the toxicity of OSPGW by increasing the effluent $LC_{50}$ to 35 mg $L^{-1}$ total carboxylic acid by day 21 and subsequently an average 28.1 mg $L^{-1}$ carboxylic acid concentration showed no acute toxicity to fathead minnow

larvae by day 60. Although the average total carboxylic acid concentration in persulfate columns decreased to 24.3 and 18.0 mg $L^{-1}$ by days 21 and 60, respectively, the effluent still showed toxicity to fathead minnow larva. The $LC_{50}$ values were 9.7 and 15.1 mg $L^{-1}$ total carboxylic acids. As noted in chapter 3, this suggests that even though persulfate degraded more carboxylic acids, permanganate preferentially degraded the more toxic fraction from OSPGW and rendered the OSPGW non-toxic. Therefore, permanganate appears to be the better oxidant in this case.

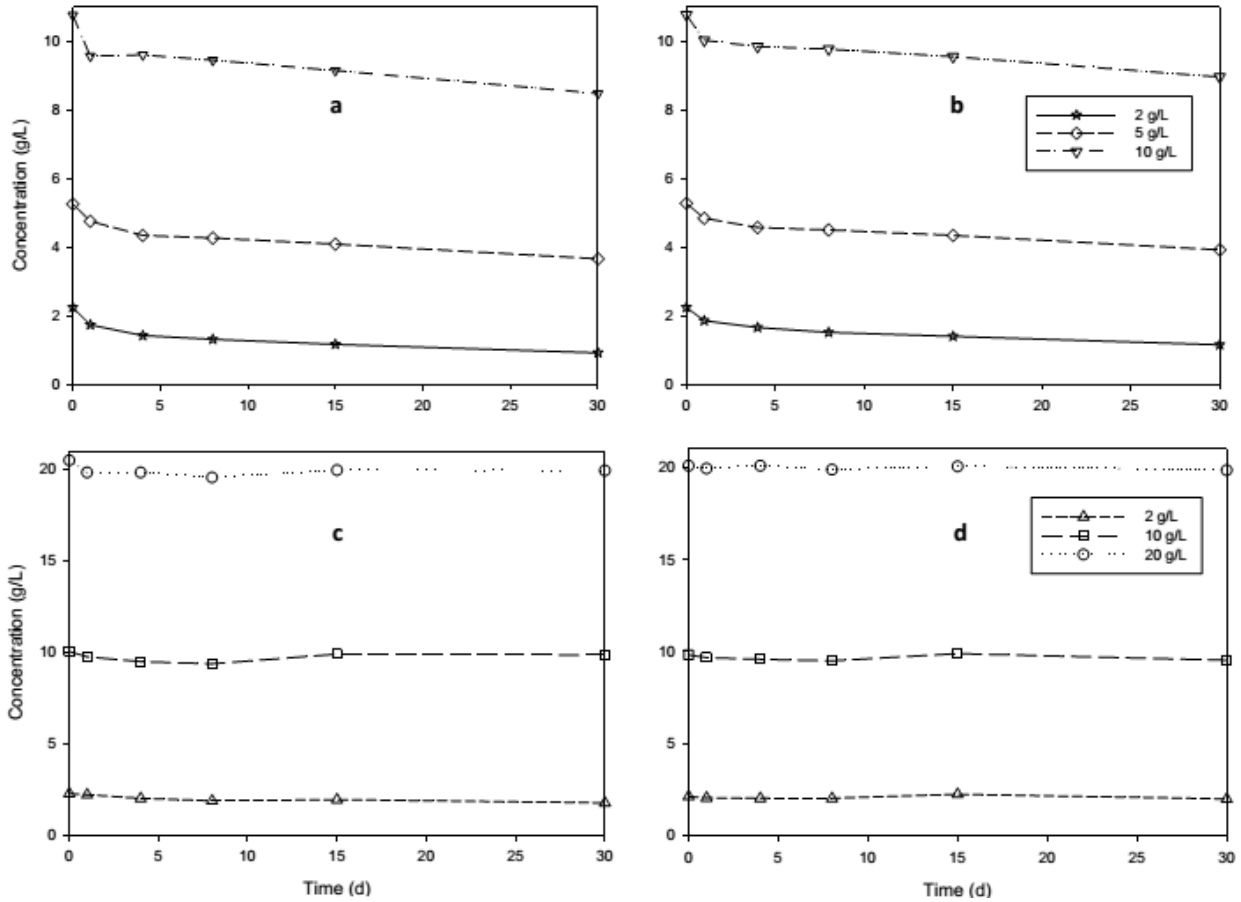


Fig. 5.3. Permanganate and persulfate concentration changes over the 30 d NOD/NOI experiment (average of triplicate experiments). Nominal initial concentrations were 2, 5, and 10 g $L^{-1}$ for permanganate and 2, 10, and 20 g $L^{-1}$ for persulfate) permanganate 22 ˚C, b) permanganate 5 ˚C, c) persulfate 22 ˚C, and d) persulfate 15 ˚C.

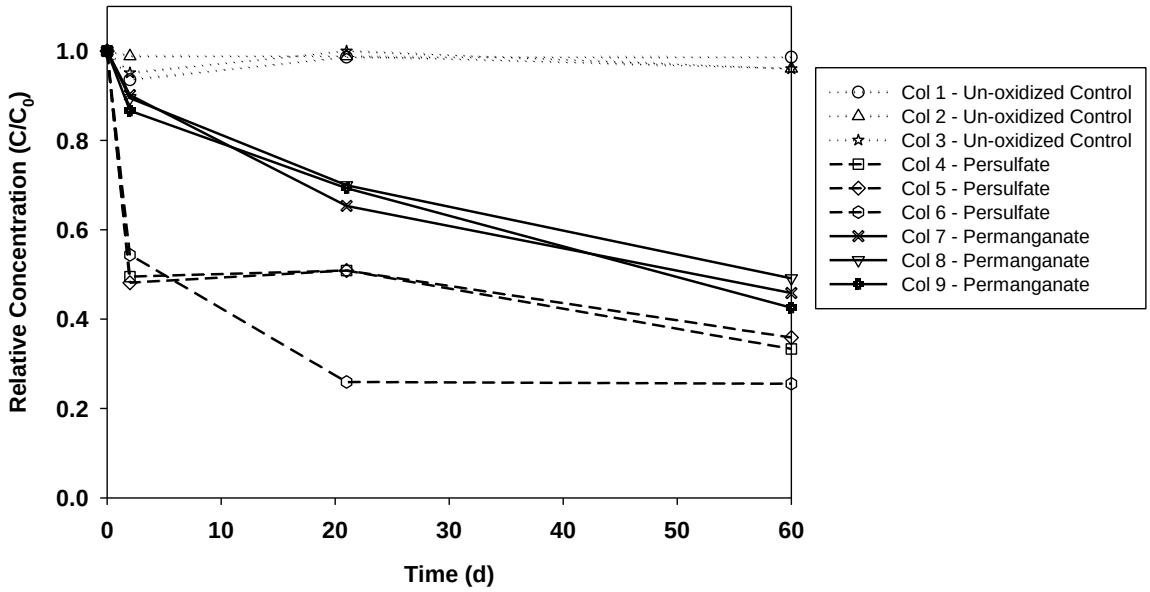


Fig. 5.4. The total carboxylic acid concentration ($C_t$) relative to the initial total carboxylic acid concentrations ($C_0$: 56.5 mg $L^{-1}$) over the 60 d stop-flow column test. Error bars derived from triplicate analyses are generally within the symbol.

Table 5.4. $LC_{50}$ values and total carboxylic acid concentrations of stop-flow column test effluents for days 21 and 60. **Bold** values indicate cases where the $LC_{50}$ is below the measured total carboxylic acid concentration after oxidation.

| | **OSPGW** | |
|---|---|---|
| **Water Sample** | **NA Conc. (mg $L^{-1}$)** | **$LC_{50}$ (mg $L^{-1}$)** |
| Un-Oxidized Control | 57 | 25 |
| Permanganate Day 21 | 39 | 35 |
| Persulfate Day 21 | 24 | 10 |
| **Permanganate Day 60** | 28 | **> 28** |
| Persulfate Day 60 | 18 | 15 |

### 5.3.3. Minimum effective oxidant concentration

Previous batch treatability and current column studies applied 5 and 10 g $L^{-1}$ permanganate and persulfate concentrations, respectively. When dispersed in the

aquifer, the oxidant will be diluted and as a result its effectiveness may be reduced. So, the lowest concentration at which oxidant still effectively degrades AEOs/carboxylic acids is of importance. This lowest oxidant concentration is termed the minimum effective oxidant concentration (MEOC). The lower the minimum effective concentration, the larger the treated zone of aquifer per injection and consequently the lower the mass of oxidant required, resulting in lower remediation cost. In order to determine the MEOC, a treatability test was conducted using OSPGW and four concentrations (0.1, 0.3, 0.6, and 1 g $L^{-1}$) of permanganate and persulfate.

Temperature may also play a role in effectiveness of oxidants. Aquifers are typically about 5 ˚C; some OSPGW impacted aquifers and inactive tailings pond have higher water temperatures, up to ~15 ˚C; and active ponds may reach temperatures of 22 ˚C and higher. Persulfate vials were incubated only at 15 and 22 ˚C as persulfate was not effective in previous treatability studies at 5 ˚C, (Sohrabi et al., 2014b). In contrast, permanganate showed effectiveness at both 5 and 22 ˚C and so MEOC for permanganate was investigated at both temperatures.

Fig. 5.5 presents the effectiveness of low concentrations of permanganate and persulfate to degrade carboxylic acids at 22, 15 and 5 ˚C. It appears that permanganate with a concentration as low as 0.1 g $L^{-1}$ still reacts with carboxylic acids present in OSPGW at both 22 and 5 ˚C. Carboxylic acid degradation in 0.1 g $L^{-1}$ permanganate at both 22 and 5 ˚C stopped after about 35% removal in 7 d (Fig. 5.5.a & b) due to depletion of oxidant. However, as depicted in chapter 4, permanganate preferentially degrades compounds with a higher level of toxicity and so 35% removal is likely sufficient to mitigate/reduce the acute toxicity. This suggests that at least partial

oxidation of the toxic AEO fraction occurs with as low as 0.1 g $L^{-1}$ permanganate concentration.

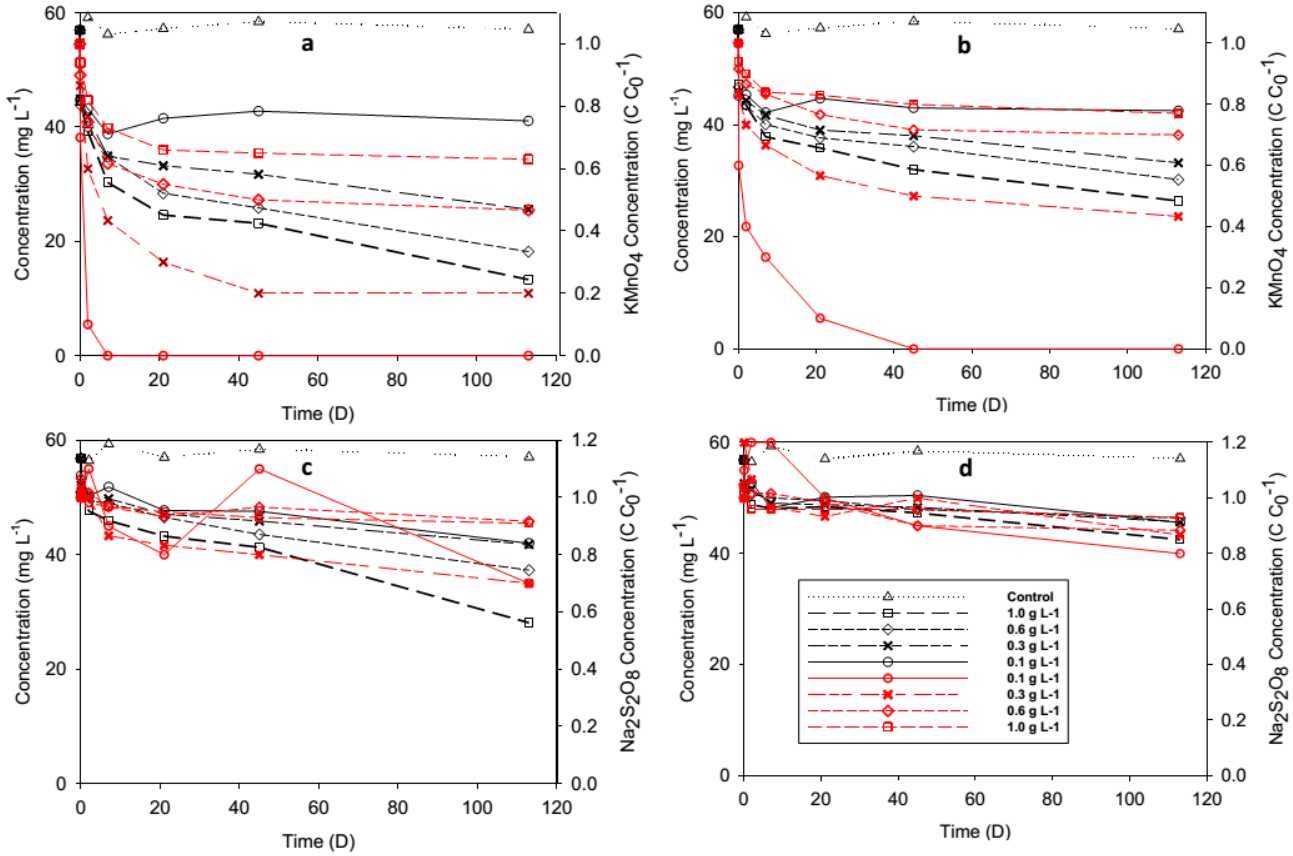


Fig. 5.5. MEOC experiment results: total carboxylic acid concentration changes over 113 d for 1, 0.6, 0.3, and 0.1 g $L^{-1}$ concentrations of permanganate and persulfate at different temperatures (black lines, left Y axis). The initial total carboxylic acid concentration was ~ 60 mg $L^{-1}$. (a) permanganate at 22 ˚C, (b) permanganate at 5 ˚C, (c) persulfate at 22 ˚C, and (d) persulfate at 15 ˚C. Red lines depict permanganate and persulfate concentration changes (right Y axis).

Persulfate showed 50% total carboxylic acid degradation with 1 g $L^{-1}$ whereas 0.1 g $L^{-1}$ persulfate produced only 25% total carboxylic acid degradation at 22 ˚C. Again, Chapter 3 and 4 showed that persulfate did not mitigate the acute toxicity of the AEO mixture in OSPGW unless most (> 80%) of the total carboxylic acids were removed (Sohrabi et al., 2014a). At 15 ˚C, persulfate initially removed about 20% of acids and then oxidation

ceased. This suggests that persulfate loses its effectiveness dramatically as temperature as well as oxidant concentration decrease. This phenomenon likely limits application of persulfate for remediating AEOs at in situ groundwater temperatures.

### 5.3.4. Simulation

Contact between oxidant and target compounds is critical for ISCO performance. In our study, the representative aquifer is impacted by mobile, dissolved compounds - AEOs. When injected into the aquifer, the permanganate solution merely displaces contaminated aquifer water due to limited dispersion and so initially minimal contact between oxidant and contaminant occurs. Advection and dispersion control oxidant delivery to the mobile, dissolved AEOs (Siegrist, 2011).

Mechanical dispersion and NOD/NOI are two main parameters influencing the mixing of the permanganate solution and OSPGW. In this study, longitudinal dispersivity of 10 m for a 200×100 m domain was selected based on the Gelhar et al. (1992) study which suggests that for plumes up to 250 m, a reliable longitudinal dispersivity could be about an order of magnitude smaller than the length of the field domain.

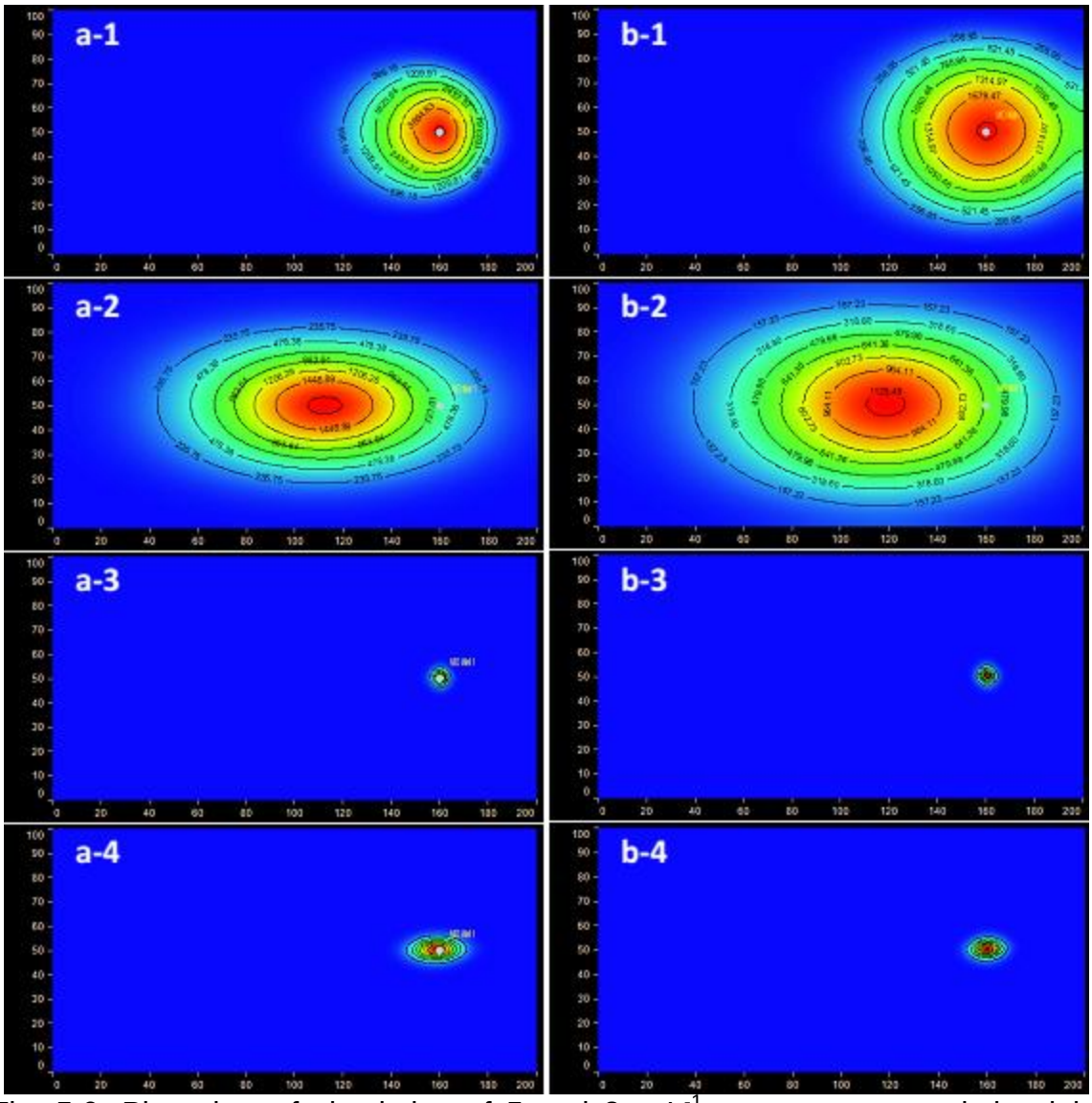


Fig. 5.6. Plan view of simulation of 5 and 2 g $L^{-1}$ permanganate solution injections. Injection of 300 $m^3$ $d^{-1}$ in a 30 m thick homogeneous block of WCSC for 30 d. See Table 5.2 for hydrogeological parameters. a-1: 5 g $L^{-1}$ non-reactive injectate after 30 d injection (outer contour: ~540 mg $L^{-1}$); a-2: 5 g $L^{-1}$ non-reactive injectate after 120 d (outer contour: ~230 mg $L^{-1}$); a-3: 5 g $L^{-1}$ reactive injectate plume after 30 d injection (outer contour: ~165 mg $L^{-1}$); a-4: 5 g $L^{-1}$ reactive injectate plume 90 d after injection (day 120) (outer contour: ≥ 1 mg $L^{-1}$); b-1: 2 g $L^{-1}$ non-reactive injectate after 30 (outer contour: ~260 mg $L^{-1}$) d injection; b-2: 2 g $L^{-1}$ non-reactive injectate after 120 d (outer contour: ~120 mg $L^{-1}$); b-3: 2 g $L^{-1}$ reactive injectate plume after 30 d of injection (outer contour: ≥ 1 mg $L^{-1}$); b-4: 5 g $L^{-1}$ reactive injectate plume after 120 d.

In order to evaluate the impact of dispersive dilution and oxidant reaction with aquifer material, two scenarios were simulated. The first assumed no NOD for permanganate in order to estimate the volume of the aquifer that might be impacted by still-reactive permanganate (greater than 0.1 g $L^{-1}$). The second attempted to include the NOD of permanganate in a very simplified manner. The objective was to estimate the volume of aquifer which could be remediated with a fixed injection of permanganate.

For each scenario, injection of a 5 g $L^{-1}$ and of a 2 g $L^{-1}$ permanganate solution was simulated. A zero reaction rate was assigned in the first scenario and so injected permanganate behaved as a conservative tracer in which mechanical dispersion was the driver for mixing. A 5 g $L^{-1}$ solution with 10 $m^3$ per every meter of saturated aquifer thickness (30 m), 300 $m^3$ $d^{-1}$, was injected for 30 d (Fig. 5.6.a-1), 9000 $m^3$ in total . Following the 30 d injection, dilution of injectate occurred via dispersion under horizontal flow ($8.6e^{-2}$ m $d^{-1}$ velocity). After 120 d, non reactive injectate was distributed over a large portion of the simulated block (Fig. 5.6.a-2). For the second scenario, a permanganate decomposition rate ($k=8.9\ e^{-3}\ d^{-1}$), based on NOD/NOI batch testing for the 5 g $L^{-1}$ permanganate solution (Table 5.3), was applied. The area of effective injectate (0.1 g $L^{-1}$ permanganate) dramatically decreased even during the 30-d injection itself (Fig. 5.7.a-3).

Application of lower permanganate concentration with higher injection flow rate has been suggested as more effective for delivery of oxidant (Heiderscheidt et al., 2008). Furthermore, the lower the concentration, the lower will be the maximum permanganate consumption by aquifer material (Xu and Thomson, 2009). In order to identify if application of a lower permanganate concentration will likely result in a larger effective

permanganate distribution, a 2 g $L^{-1}$ permanganate solution was applied in the next set of simulations. The mass of injected permanganate was kept the same as the previous simulations with a 5 g $L^{-1}$ permanganate solution. Here, the permanganate concentration was reduced by 2.5 times to 2 g $L^{-1}$ and flow rate was increased by 2.5 times to 750 $m^3$ $d^{-1}$. Simulations were run under similar initial and boundary hydrogeological conditions. As expected, this simulation showed a larger plume (Fig. 5.7.b-1). However, when the decomposition rate derived for the 2 g $L^{-1}$ permanganate solution ($k=2.1\ e^{-2}\ d^{-1}$) was applied, the extent of the generated plume with still-active permanganate concentrations (> 0.1 g $L^{-1}$) after 120 d again decreased dramatically. As mentioned, two extreme scenarios were simulated for both 5 and 2 g $L^{-1}$ permanganate solution injections; non-reactive and reactive based on NOD/NOI laboratory batch testing. The first scenario defined the maximum volume of the aquifer that can be influenced by the injected solution. The second scenario suggested a very limited distribution of reactive concentrations of permanganate would be generated. The latter simulation is considered unrealistic for the following reasons.

1. Permanganate has been found to persist in other aquifers for months (Huling and Pivetz, 2006; Siegrist et al., 2011). Our simulations which incorporate a laboratory-based NOD reaction rate show very little persistence.

2. The unrealistically high apparent NOD for permanganate in these simulations likely reflects the limitations in the handling of the first order NOD reaction rates in MT3DMS. First of all, MT3D MS applies a single first order reaction rate continuously for the simulated period. However, Xu and Thomson (2009) suggest that there is a fast

reaction rate for early time followed by a lengthy slow reaction rate for most of the reaction period.

3. Laboratory batch tests overestimate the NOD/NOI for aquifers compared to actual performance during injection (Heiderscheidt et al., 2008; Xu and Thomson, 2009). In part, this is because when NOD/NOI of a section of aquifer (captured as a node in the simulation) is satisfied at an early time, subsequent permanganate is consumed at a slower rate in that section of the aquifer (Siegrist, 2011). The NOD has, in large part, already been satisfied. Our model could not account for this process.

4. The NOD/NOI tests demonstrated that the lower the permanganate concentration, the lower the NOD/NOI of the aquifer material. When injected into the aquifer, the permanganate concentration decreases by dispersive dilution as well as through NOD/NOI reactions. Therefore, adoption of a single, first-order rate based on the higher, injected concentration will overestimate the true NOD. Our model could not accommodate this phenomenon.

5. A pilot field injection trial was conducted in the WCSC with an initial 5 g $L^{-1}$ permanganate solution injected into uncontaminated aquifer. While the bulk of the injectate left the area of injection within 40 d, due to advection, 121 d later, permanganate had re-appeared in the injection well at a concentration of 0.1 g $L^{-1}$ (data not shown here). Clearly, some permanganate had persisted at the reactive concentration for 121 d. Such persistence of permanganate is not captured in the simulations.

For the above reasons, a very small NOD for permanganate seems most appropriate for the representative aquifer and so the simulation assuming no NOD seems a

reasonable first approximation. So, simulation of injection of 300 $m^3$ of a 5 g $L^{-1}$ conservative permanganate solution over a 30 m thickness of homogenous aquifer, repeated daily for 30 d, was conducted, with advection at 8.6 cm $d^{-1}$ and only mechanical dispersion. The simulation was carried out for 120 d so as to capture the maximum extent of the 0.1 g $L^{-1}$ potassium permanganate contour. So, for an injection of a total of 9000 $m^3$ of a 5 g $L^{-1}$ permanganate solution over 30 d the aquifer volume subjected to at least the effective concentration of 0.1 g $L^{-1}$ was 164 000 $m^3$. The porosity of the WCSC was assumed as 0.25, and so a volume of 40 600 $m^3$ of OSPGW was treated in this simulation. For comparison, using the unreasonably first order rate of NOD, for initial $KMnO_4$ concentration of 5 g $L^{-1}$, yielded treatment of 2350 $m^3$ of the WCSC aquifer and 600 $m^3$ of OSPGW.

This simulation provides a basis for an estimate of the cost of oxidant required. The simulated injection utilized 45 000 kg of potassium permanganate. The cost of this oxidant was estimated as $5.75 per kg (R. McGregor, personal communication, April, 2014). This represents $1.6 for each $m^3$ of aquifer treated or $6.4 for each $m^3$ of OSPGW whose AEOs are rendered non-toxic, as measured in our tests (Table 5.5). In a hypothetical example by Simpkin et al. (2011), the oxidant costs were about 15% of the total project costs. If current on site pumping and monitoring wells can be utilized and most monitoring, decommissioning, etc. costs are attributed to current operations, the cost of oxidant likely represents only 20 – 30% of the project costs. This cost estimate is certainly crude, but does point out the high cost of in situ chemical oxidation if required to remediate large volumes of OSPGW.

Conducting a field injection trial is clearly required to provide better insight into the response of this heterogeneous aquifer to ISCO. Possible clogging by $MnO_2$ precipitation is always of concern, although the slow oxidation anticipated over a large aquifer volume should minimize deterioration in hydraulic conductivity. While pH in our lab experiments remained in the 6.2 to 8.3 range and so metal mobilization is unlikely, field confirmation would be required. The impact of aquifer heterogeneitiy on the efficiency of ISCO is a key factor which would also be elucidated by a well-instrumented field trial.

Table 5.5. Summary of cost estimation based on permanganate price and simulation results

| **Parameter** | **Value** |
|---|---|
| Injected $KMnO_4$ solution concentration | 5 g $L^{-1}$ |
| Total volume of injected $KMnO_4$ solution | 9000 $m^3$ |
| Mass of injected $KMnO_4$ | 45000 kg |
| Cost of $KMnO_4$ per kg | $5.75 |
| Total cost of $KMnO_4$ | $258750 |
| Porosity of aquifer (n) | 0.25 |
| Threshold $KMnO_4$ solution concentration for effectiveness | 0.1 g $L^{-1}$ |
| Total volume of aquifer treated to threshold | 164000 $m^3$ |
| Total volume of treated OSPGW | 41000 $m^3$ |
| $KMnO_4$ cost of treatment for unit volume of aquifer ($m^3$) | $1.6 |
| $KMnO_4$ cost of treatment for unit volume of OSPGW ($m^3$) | $6.4 |

## 5.4. Summary and outlook

The WCSC has a low oxidant demand for both permanganate and persulfate. This suggests considerable dispersive dilution will provide active oxidant contact with large volumes of acutely toxic AEOs. Stop-flow column tests revealed the effectiveness of permanganate to degrade the toxic fraction of OSPGW when aquifer sediment was present at the local aquifer temperature of 5 ˚C. While persulfate had higher AEOs/NAs degradation, potentially due to activation by unknown source, in columns with aquifer sediment, persulfate did not mitigate the acute toxicity of OSPGW. Permanganate degraded the significant AEOs/NA fraction at concentrations at least as low as 0.1 g $L^{-1}$, even at 5 ˚C. This implies that contact between OSPGW and low concentrations of permanganate would still be effective after considerable dispersive dilution and consumption by interaction with aquifer materials. On the other hand, persulfate was not effective at 5 ˚C or at 15 ˚C even at concentrations as high as 10 g $L^{-1}$.

Although persulfate was not effective at 5 ˚C, there still might be potential for application of persulfate where high temperature OSPW discharges into the tailings ponds (Chapters 2 and 3). Addition of persulfate at an OSPW discharge point may result in detoxification and mineralization of most AEOs. However, at 15 and 5 ˚C, permanganate appears to be the preferred choice. If necessary, application of permanganate to abandoned tailings ponds at ~ 15 ˚C, looks capable of detoxifying the AEOs. Application of permanganate in impacted aquifers with 5 ˚C where the toxicity of OSPGW seepage is an issue might be beneficial, especially if this ISCO can be applied in narrow zones of high AEO concentration.

ISCO using permanganate to mitigate the acute aquatic toxicity of AEOs (or NAs) in OSPGW appears a promising technology. The representative aquifer, WCSC, had low NOD/NOI and permanganate appears to remove sufficient acute toxicity when only about less than 50% of acids are oxidized the cost of oxidant was estimated to be 6.40 $ per $m^3$ of aquifer treated or $1.6 per $m^3$ of OSPGW, although overall project costs are likely 4- or 5-fold higher.

It would now be useful to perform a pilot-scale permanganate injection into OSPGW to confirm its efficacy and to optimize operations. A more comprehensive evaluation of water quality issues (pH, TDS increase, metal mobilization, etc.) should also be a priority.

# Chapter 6:

# Closure

## 6.1. Conclusions and contributions

This research was the first study of the application of ISCO to OSPGW-impacted aquifers located in the area of oil sands mining. We applied two commercial persistent oxidants, permanganate and un-activated persulfate, in this research. The major contributions of this research are listed below.

- Laboratory batch oxidation experiments with OSPW at 22 ˚C revealed the effectiveness of permanganate and unactivated persulfate as in situ oxidation agents for remediation of AEOs in groundwater. Permanganate oxidation yielded some residual dissolved organic carbon (DOC) whereas persulfate mostly mineralized the AEO compounds with less residual DOC. Acid-extractable organics from oxidized OSPW had essentially no Microtox toxicity (Chapter 2 &3). Application of embryo-larval bioassay, *Pimephales promelas* (fathead minnows), indigenous to the Athabasca Basin, showed that both permanganate and persulfate mitigated the toxicity of AEOs extracted from oxidized OSPW (Chapter 3).
- Laboratory batch oxidation experiments on OSPGW demonstrated the effectiveness of permanganate and unactivated persulfate for degradation of AEOs. Again, permanganate oxidation mostly occurred by structural transformation of AEOs while persulfate mineralized most of the AEO

compounds. Application of embryo-larval bioassay, *Pimephales promelas* (fathead minnows) showed both permanganate and persulfate mitigated toxicity of AEOs in OSPGW. Interpretation of toxicity bioassay results in association with mass spectrometry characterization suggested a direct connection between abundances of high Z number acids with the level of toxicity of AEOs. So, the higher the abundances of high Z number species, the higher the level of toxicity of the AEO mixture (Chapter 3).

- At the local in situ aquifer temperature, 5 ˚C, permanganate oxidation mitigated toxicity of OSPGW while persulfate was ineffective. Little AEO mineralization occurred with either permanganate or persulfate and so detoxification of AEOs by permanganate occurred by molecule structural transformation. The oxidation of OSPGW at 5 ˚C confirmed that toxicity mitigation was connected to degradation of high Z number acids by permanganate. These findings re-emphasizes that decreases in AEO concentration measured by FTIR does not necessarily reflect reduction of toxicity of OSPGW (Chapter 4).
- The WCSC, considered a representative aquifer un-impacted by OSPW, has a low oxidant demand for both permanganate and persulfate and so is a favorable aquifer in which to apply ISCO. This suggests considerable dispersive dilution will provide active oxidant contact with large volumes of acutely toxic AEOs under reasonable injection scenarios (Chapter 5).
- Persulfate was not effective at 5 ˚C or at 15 ˚C. Also, persulfate effectiveness in degrading the toxic fraction of OSPGW dramatically decreases with concentration and temperature and so its performance is limited (Chapter 5).

- Stop-flow column test revealed the effectiveness of permanganate to degrade the toxic fraction of OSPGW when representative aquifer sediment was present at 5 ˚C. While aquifer material appears to activate persulfate, persulfate did not mitigate the acute toxicity of OSPGW. This again re-emphasizes that decrease in total carboxylic acid concentration does not necessarily translate into toxicity mitigation (Chapter 5).
- Minimum effective oxidant concentration testing revealed that permanganate degraded the AEOs/NA fraction at concentrations at least as low as 0.1 g $L^{-1}$, even at 5 ˚C. This implies that contact between OSPGW and low concentrations of permanganate would still be effective after considerable dispersive dilution and consumption by interaction with aquifer materials (Chapter 5).

### 6.2. Recommendations

Some specific issues for ISCO of dissolved phase target compounds, AEOs, were elucidated in this research. However, there are many unanswered and additional questions remaining.

- Although general pathways for oxidation mechanisms of AEOs by permanganate and persulfate were suggested in Chapter 3, the nature of AEO oxidation by these two oxidants is still unknown. So, further study of the oxidation of model compounds present in OSPW is suggested.
- It is recommended that for any treatment or remediation measure to mitigate toxicity of AEOs, application of advanced AEO characterization should support toxicity testing.

- The hydrogeology of the aquifer controls, to a large extent, the delivery of the ISCO technology. For example, aquifers such as the WCSC with mainly fine to medium sand, in fact, are composed of sequences of clay, silt, and fine to coarse sand. This heterogeneity may impair mixing of injected oxidant and OSPGW. Detail hydrogeological studies including frequent hydraulic conductivity measurements, tracer tests and pilot-scale ISCO tests monitored by multi-level monitoring well nests, is recommended in order to understand the initial OSPGW distribution and to design efficient oxidant injection into the aquifer.
- The cost of oxidant per unit volume of aquifer treatment was estimated based on recent permanganate cost. It is recommended that a more comprehensive cost evaluation and feasibility study for permanganate ISCO consider cost and technical issues, and that a comparison of costs of ISCO with extraction and ex situ oxidation be conducted.
- In order to achieve a better perspective of permanganate persistence in the aquifer, a pilot scale permanganate injection is recommended. The site characterized by Oiffer et al. (2009) may be more practical that the site in the WCSC.
- If ISCO remains a viable option for remediation of OSPGW, performing a pilot-scale permanganate injection into OSPGW to confirm its efficacy and to optimize operations would be essential. A more comprehensive evaluation of water quality issues (pH changes, TDS increase, metal mobilization, etc.) should also be a priority. Conducting a pilot scale injection trial with follow-up coring and groundwater sampling, will also provide better insight into the alteration of aquifer

properties, both physical and geochemical, that may occur during permanganate injection.

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