# Assessing the mobility of metals and dissolved organics in pit-lake models containing PASS-treated fluid tailings

by

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## Abstract

Oil sands surface mining produces considerable quantities of fine fluid tailings (FFT). Several reclamation strategies are being investigated to address the environmental concerns related to long-term FFT storage. One promising sustainable tailings management approach is End Pit Lake (EPL); however, concerns remain regarding the potential release of contaminants from FFT into the capping water. Preliminary tailings treatment with innovative Permanent Aquatic Structure Storage (PASS) technology is projected to enhance the dewatering and capping water quality in the EPL. Nevertheless, little is known about the geochemical stability of PASS-treated FFT, especially for the release of potentially toxic metals and organic compounds.

This dissertation thoroughly investigated the effects of PASS-treated FFT on EPL, starting with the FFT characterization, including the development of a novel method for analyzing naphthenic acids (NAs) in FFT. Subsequently, the study investigated the short- and long-term effects of PASS-treated FFT on contaminants of potential concerns (COPCs) mobility in a demonstrated EPL system. The dissertation concluded by examining COPCs desorption mechanisms from FFT to capping water.

A highly efficient extraction and cleanup process was developed to assess NAs in oil sands tailings. This method used several extraction solvents, mixing conditions, extraction times, and steps. Additionally, solid phase extraction (SPE) was fine-tuned using different elution conditions and reconstitution reagents. 0.5 M NaOH outperformed ten extraction solvents for NAs recovery effectively. The orbital shaking condition was 1.27 times more effective than the static condition. Mixing for over 40 minutes increased the recovery by 32% over 5 minutes. Two extraction steps yielded 26% more recovery than a single extraction step. Methanol/formic acid (43%), and methanol/water (82%), in SPE using Hydrophilic-Lipophilic Balance (HLB) cartridges, recovered the most NAs during cleanup. Using this developed procedure, NAs were measured in oil sands tailings at 56.10–112.25 mg/kg. The largest NAs level was detected in PASS-treated FFT tailings samples. The most abundant NA species in all tailings were classical, notably with carbon numbers 16 and 18. This finding provided fresh insight for analyzing NAs in tailings sediment, which is critical for evaluating treatment efficacy and monitoring NAs at FFT reclamation sites.

To investigate COPC fate in treated FFT storage, EPL models (columns of FFT/water ratio ½, 2.4 m deep, 75.4 L) were run for two years. During the first week, a high flux of contaminants from tailings deposits to capping water was quickly stabilized. Later on, the release of potentially toxic metals, ions, and dissolved organics was also decreased ($PO_4^{-3}$: 100%, $Ca^{2+}$: 33%, $Mg^{2+}$: 1%, $Fe^{3+}$: 100%, $Li^{+}$: 100%, $Cu^{+:}$ 100%, $Al^{+3}$:100%, and classical NAs: 10%). A short-term bench-scale column experiment was carried out to better understand the chemical release mechanism. It was determined that only advective mass transfer influenced the initial chemical flux, which was 0.002 $m^3m^{-2}d^{-1}$, 50% lower than the first commercial-scale EPL. Lake turnover did not affect advection flow. The high viscosity of FFT and diluted oil sands process water (OSPW) reduced chemical flux. PASS treatment efficiently immobilized COPCs, paving the way for self-sustaining mine closure at the EPL system, as exemplified by Lake Miwasin and its implementation of PASS-treated FFT.

Batch experiments examined the desorption of organics from treated FFT into capping water under varying dosages, contact duration, temperature, and ionic strength conditions. Higher FFT dosage and capping water organic matter increased dissolved organic carbon (DOC) desorption, whereas temperature and conductivity had minimal impact. Electrolytes controlled DOC equilibrium desorption capability, with cations ($K^+$ and $Ca^{2+}$) considerably affecting desorption from negatively charged FFT particles. Temkin isotherms displayed that desorption dynamics followed physically favorable patterns. The intraparticle diffusion kinetics model accurately predicted 0.65 mg/g of PASS-treated FFT DOC equilibrium desorption. A small percentage (5.82%) of the DOC and less than half of NAs species (39.1%) in PASS-treated FFT were potentially released. A high distribution coefficient value for DOC and NAs indicated that they were mainly stable in PASS-treated FFT deposition.

The study provided an effective approach for monitoring NAs across various oil sands tailings storage systems, facilitating the assessment of tailings treatment and reclamation practices. Research on the fate and impact of PASS-treated FFT in EPL reclamation landscapes helps explain COPCs flux from FFT to capping water. The chemical mass transfer and desorption investigation also shows that PASS treatment in this FFT management technique improves EPL system surface water quality over time.

## Preface

This thesis is an original work by Foroogh Mehravaran. The research was carried out under the supervision of Dr. Mohamed Gamal El-Din in the Department of Civil and Environmental Engineering at the University of Alberta. The majority of experiments, data analysis and composition of research papers have all been completed by Foroogh Mehravaran. The colleagues in Dr. Gamal El-Din's Research Group were also responsible for sample analysis, insightful discussion, as well as reviewing and revising the manuscript drafts. This thesis is written in paper format. All contents (except introduction, literature review, and conclusion chapters) are intended to be submitted to peer-reviewed journals. Contributions to each chapter are detailed as follows:

Chapter 3 is titled 'Method Development for Routine Determination of Naphthenic Acids in Oil Sands Tailings: Extractions, Cleanup and Characterization'. I prepared the tailings samples, performed the experiments discussed in Chapter 3, and analyzed the data. I conducted most of the characterization experiments of tailings. Dr. Mohamed Gamal El-Din contributed to the research, planning, final editing, and approval of the manuscript. Dr. Lingling Yang performed the analytical measurement of NAs in the samples. She also contributed to the research, planning, manuscript revision, and editing. Dr. Muhammad Arslan is also involved in the manuscript review and editing.

Chapter 4 is titled 'Mobility of Metals, Ions, and Naphthenic Acids from Tailings Deposits to Water Column: Demonstration Pit Lake'. The long-term monitoring column experiment was designed by Dr. Mohamed Gamal El-Din and received approval from Suncor Energy Inc., with the implication that it was not my original design. Apart from that, I was responsible for the experimental design of the bench-scale column experiment, the data collection and analysis as well as the manuscript composition. Dr. Mohamed Gamal El-Din contributed to the research, planning, final editing, and approval of the manuscript. Dr. Muhammad Arslan contributed to planning, manuscript revision and editing. Akeem Bello, and Dr. Jia Li, and Dr. Muhammad Arslan were involved in implementing and conducting long-term column monitoring. The analytical measurement of NAs in the samples was performed by Dr. Lingling Yang. X-ray diffractograms (XRD) were performed in the EAS X-Ray Diffraction Laboratory and Analytical and Instrumentation Laboratory of the University of Alberta. The elemental composition of trace metals and cations, and total organic content (TOC) content of the FFT samples were determined in the Natural Resources Analytical Laboratory of the University of Alberta.

Chapter 5 is titled ‘Desorption and Migration of Dissolved Organics from Oil Sands Tailings to Capped Water: Demonstration Pit Lake’. I was responsible for experimental design, laboratory experiments, data interpretation and analyses. Dr. Mohamed Gamal El-Din contributed to the research, planning, final editing, and approval of the manuscript. Dr. Muhammad Arslan was involved in planning, manuscript revision and editing. The analytical measurement of NAs in the samples was performed by Dr. Lingling Yang.

# Dedication

To my lovely family. Your unwavering love, boundless kindness, selflessness and tireless perseverance taught me to live and work in an upright manner. Your support has been my rock and my inspiration throughout this journey.

‘Life is a balance between holding on and letting go’

**Rumi**

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I want to express my heartfelt thanks to Dr. Muhammad Arslan and Dr. Lingling Yang for their transformative input, which has significantly enhanced my research by highlighting my strengths and addressing my weaknesses. I thank Dr. Lingling Yang and Dr. Zuo Tong How for their extensive NAs analyses in my projects. I am also grateful to my PhD colleagues and friends, especially Dr. Deborah Medeiros for her constructive feedback and Akeem Bello for helping monitor the pit lake project long-term. Finally, thanks to my reliable friend (Kako) Sina Neshati, who always helps me out.

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Last but not least, I would like to thank my family for their continuous support, which has fueled my ambition throughout my educational and personal journey. I also want to thank my partner, whose enduring love has been my constant source of strength throughout this journey.

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## List of Abbreviation

| | |
|---|---|
| AEF | Acid Extractable Fraction |
| AER | Alberta Energy Regulator |
| AM | Acrylamide |
| ANOVA | Analysis of Variance |
| APHA | American Public Health Association |
| BML | Base Mine Lake |
| BOD | Biochemical Oxygen Demand |
| CEMA | Cumulative Environmental Management Association |
| CHNS-O analyzer | Carbon, Hydrogen, Nitrogen, Sulfur, and Oxygen Elemental Analyzer |
| COD | Chemical Oxygen Demand |
| COPCs | Contaminants of Potential Concerns |
| CSS | Cyclic Steam Stimulation |
| DCM | Dichloromethane |
| DI | Deionized Water |

| | |
|---|---|
| DO | Dissolved Oxygen |
| DOC | Dissolved Organic Carbon |
| DPL | Demonstrated Pit Lake |
| D-R | Dubinin-Radushkevich |
| EPEA | Environmental Protection and Enhancement Act |
| EPLs | End Pit Lakes |
| FFT | Fluid Fine Tailings |
| FT-ICR-MS | Fourier Transform Ion Cyclotron Resonance Mass Spectrometry |
| FT-IR | Fourier Transform Infrared Spectroscopy |
| GC/MS | Gas Chromatography/Mass Spectrometry |
| HA | Humic Acids |
| HLB | Hydrophilic-Lipophilic Balance |
| HWP/CHWP | Clark Hot Water Process |
| ICP-MS | Inductively Coupled Plasma Mass Spectrometry |
| ICS | Ion Chromatography |
| IDP | Intraparticle Diffusion |

|  |  |
|---|---|
| $K_d$ | Distribution Coefficient |
| $K_{oc}$ | Organic Carbon Partition Coefficient |
| LC-MS | Liquid Chromatography-Mass Spectrometry |
| LW | Lake Water |
| MeOH | Methanol |
| MFT | Mature Fine Tailings |
| MS | Mass Spectrometry |
| MTBE | Methyl Tertiary-Butyl Ether |
| NaOH | Sodium Hydroxide |
| NAs | Naphthenic Acids |
| OM | Organic Matter |
| OSPW | Oil Sands Process Water |
| PAM | Polyacrylamide |
| PASS | Permanent Aquatic Storage Structure |
| PFO | Pseudo-First Order |
| $pH_{pzc}$ | Point of Zero Charge |

| | |
|---|---|
| pKa | Acid Dissociation Constant |
| PSO | Pseudo-Second Order |
| SAGD | Steam-Assisted Gravity Drainage |
| SRB | Sulfate-Reduction-Bacteria |
| SPE | Solid Phase Extraction |
| TDS | Total Dissolved Solids |
| TGA | Thermogravimetric Analysis |
| TKN | Total Kjeldahl Nitrogen |
| TMF | Tailings Management Framework |
| TOC | Total Organic Carbon |
| UPLC-QTOF-MS | Ultra-Performance Liquid Chromatography Quadrupole-Time-Of-Flight Mass Spectrometry |
| WCT | Water-Capped Tailings |
| XRD | X-Ray Diffraction |

# 1 Chapter 1: Introduction and Research Objectives

## 1.1 Background and Motivation

### 1.1.1 Oil sands FFT

Alberta is significant in Canada's economy, containing the third-largest oil reserves globally. According to the Alberta Energy Regulator (AER), oil production in the region has reached 3 million barrels per day, which is projected to be doubled within ten years (AER, 2020). A large portion of the reserves is in the form of bitumen mixed with sand. The bitumen is recovered from oil sands by either surface mining or in-situ extraction techniques. Although surface mining affords higher bitumen recovery than other extraction methods, it generates a large volume of bitumen extraction fluid wastes known as oil sands fine fluid tailings (FFT). Accordingly, the oil sands industry solely in Alberta, Canada, has generated more than 1.3 billion $m^3$ of FFT stored in FFT ponds that cover a total area of 100 $km^2$ (Kuznetsova et al., 2023). FFT behaves like a fluid with low shear strength due to a high level of water content (50-80%) (Dompierre et al., 2017). Further, pore water in FFT carries a large amount of dissolved inorganic chemical constituents and toxic organic compounds, e.g., naphthenic acids (NAs), petroleum hydrocarbons, and unrecovered bitumen (Allen, 2008; Dompierre et al., 2017; Kavanagh et al., 2011). Beyond government restrictions, proper characterization and management of FFT's toxic waste stream are crucial for environmental sustainability and responsible oil sands resource expansion. Oil sands operators in Alberta have implemented several FFT management and reclamation strategies. Earlier investigations have revealed that wet-based treatments offer inexpensive and eco-friendly solutions. The Cumulative Environmental Management Association (CEMA) has proposed the End Pit Lake (EPL) strategy, an engineered water body with a long-lasting wet reclamation stage.

EPL is formed by placing treated and untreated FFT in an open pit covered by mixed Oil Sands Process Water (OSPW) and freshwater, termed as capping water (Miller, 2012; Siddique et al., 2012; Yu, 2019). There are currently 23 EPLs planned for northern Alberta, with the intention that these will become permanent features in reclaimed mine closure landscapes (An et al., 2013). However, Alberta regulators have not approved this closure landscape for oil sands mining because very little is known about the geochemical stability of these artificial ecosystems (AER, 2020).

In 2013, Syncrude Canada Ltd. established the first full-scale demonstration pit lake known as Base Mine Lake (BML). BML comprised untreated FFT deposits which were covered by freshwater. FFT was dewatered naturally over time, and biological processes occurring in FFT and water interface increased consolidation and decreased the lake's toxicity rate (Clemente & Fedorak, 2005; COSIA, 2021a). Further, a significant release of contaminants of potential concerns (COPCs) from untreated FFT to capping water was observed (Clemente & Fedorak, 2005; Syncrude, 2019b; White, 2017). In 2016, as a step forward, Suncor deposited PASS (permanent aquatic storage structure) treated FTT in a pit lake known as Lake Miwasin. PASS treatment is expected to accelerate dewatering and improve the FFT consolidation (Suncor, 2019).

### 1.1.2 PASS treatment of FFT

The PASS treatment of oil sands FFT is a two-step process. To begin, FFT is treated with an alum coagulant to immobilize specific COPCs. Then, at the flocculation step, anionic polyacrylamide is added to chemically treated FFT to aid in the rapid release of water (COSIA, 2018b). The PASS-treated FFT is then delivered to a deposition site. Once deposited, the treated FFT behaves similarly to lake sediment, gradually settling over time. As the treated FFT settles, pore water (water surrounding the individual solid particles of the treated FFT) is continuously released from the treated FFT to the overlying capping water (COSIA, 2018b). The application of PASS-treated FFT initially is projected to increase dewatering, reduce turbidity, and reduce COPCs mobility into capping water (COSIA, 2021c). Subsequently, the treated FFT targets to accelerate the reclamation of permanent FFT storage landscapes, including EPLs, by meeting federal and provincial freshwater lake guidelines (COSIA, 2018a). Although PASS treatment has effectively improved FFT consolidation, limited research has explored the geochemical stability of this novel technology, involving both alum and PAM addition (Cossey et al., 2022). As it contains alum, PASS-treated FFT must be monitored for sulfur cycling after alum addition (Cossey et al., 2021). Meanwhile, the environmental fate of aluminum, which is toxic to aquatic organisms (Gensemer et al., 2018), in PASS-treated FFT should be investigated. Due to the presence of PAM, the long-term effects of adding polymers as well as the fate of the toxic impurity products of this treatment, including acrylamide (AM), have been rarely investigated (Li et al., 2023b). Another possible downside of PASS-treated FFT is that it might have higher hydraulic conductivities than untreated FFT, which could lead to large chemical fluxes in the short term (Cossey et al., 2021). The concern regarding the high chemical loading flux in treated FFT underscores the need for a comprehensive examination of the fate of metals, toxic ions, and organic compounds in FFT deposits. The characterization of water quality as well as the geochemical properties of the PASS-treated FFT would be critical for operators to better understand the spatial and temporal variations and trajectories over time. Eventually, the short- and long-term implications of PASS-treated FFT will provide valuable information for FFT management, including the reclamation of EPLs.

## 1.2 Research Scope and Objectives

Currently, oil sands companies are not allowed to discharge FFT into the environment.

Thus, the transformation of existing pit lakes into self-sustaining boreal aquatic ecosystems is encouraged. To this end, PASS treatment of FFT presumably can improve the stability of the FFT-water interface and increase the dewatering potential, thereby, higher volumes of FFT can be stored in pit lakes over a longer time period. Nevertheless, little is known about the geochemical stability of the PASS-treated FFT, specifically the fate of potentially toxic ions, metals, and organic compounds. This research aims to investigate both short- and long-term impacts of PASS-treated FFT on the mobility of COPCs in the conditions of Lake Miwasin. This dissertation adopted a holistic approach by starting with the characterization of the PASS-treated FFT, including method development for NAs quantification in FFT, which had not previously been reported. Then, chemical flux was studied between PASS-treated FTT to capping water to understand the potential migration of COPCs and chemical mass transfer. The last part of the dissertation evaluated the desorption and diffusion kinetics and mechanism of chemicals from the FFT to capping water. These aspects are explained in detail in the following sections:

### 1.2.1 NAs characterization within FFT particles

The main objective of this part of the study was optimizing and developing a method to quantify the actual concentration of NAs species in FFT. To this end, extraction, and cleanup conditions were optimized for quantification of the FFT, specifically the PASS-treated FFT. This addressed the effect of extraction solvents, mixing method, extraction time, and multiple extraction steps. The study then examined Solid Phase Extraction (SPE) elution and reconstitution reagents to find the optimum SPE cleanup conditions. Finally, the developed method was employed to analyze NAs in different FFT. The overview of the adopted methodology is depicted in Figure 1.1.

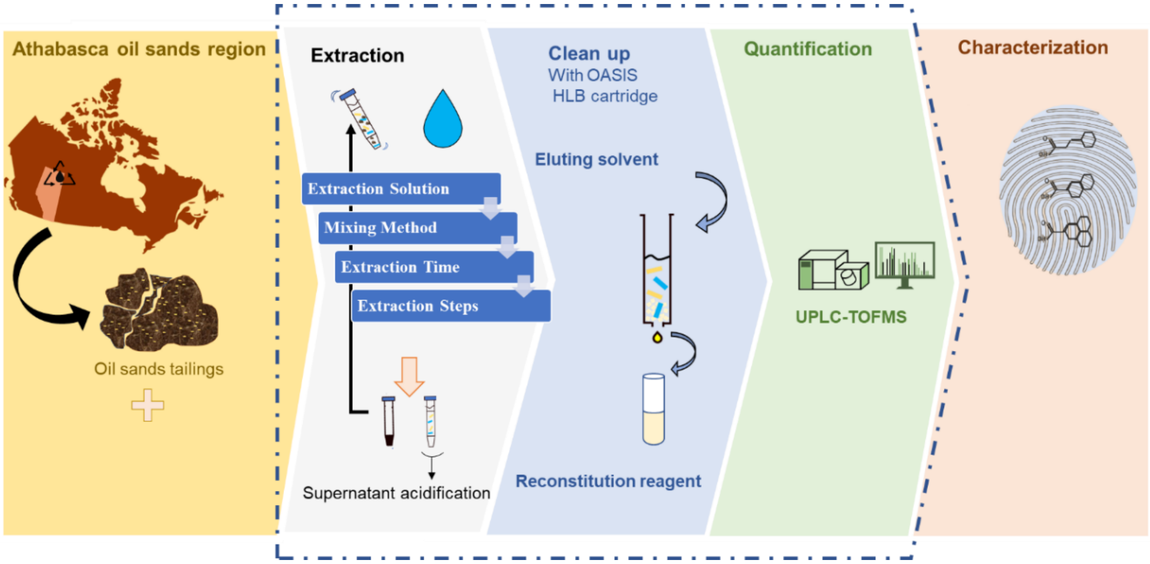

Fig. 1.1 Overview of optimizing NAs characterization in FFT: extraction, clean up and quantification condition.

1.2.2 Assess the mobility of metals, ions, and dissolved organics from FFT deposits to the water column in demonstration pit lake: studying the efficacy of PASS technology on the mass transfer mechanism.

Regardless of potential high initial chemical release, PASS-treated FFT remains at the forefront of active research and innovation, with concerted efforts to refine the methodology and mitigate potential issues. The viability of this approach relies on several factors, including the natural characteristics of the FFT in question and the environmental milieu of their disposition. PASS-treated FFT deposits in DPL are expected to accelerate dewatering, keeping the water quality less disturbed. However, PASS-treated FFT has the potential to increase the initial hydraulic conductivity and chemical flux from FFT to the capping water (Cossey et al., 2021). This requires an in-depth understanding of the chemical flux between PASS-treated FFT and capping water in the pit lake to validate the superiority of using the PASS process for DPL. Here, two independent studies examined pit lake contaminant migration:

The first study focused on:

1) investigating the characteristics of PASS-treated FFT and how it affects the release of COPCs
2) quantifying the efflux of dissolved organics, ions, and trace elements from the FFT to the capping water over time.

The second study focused on:

1) Understanding the intricate mechanisms governing chemical mass transfer, focusing on chemical flux dynamics (encompassing advection-dispersion-decay) from treated FFT into the capping water in the initial phase.
2) Comparing chemical flux across diverse scenarios, accounting for with and without lake turnover conditions (evaluating lake water mixing effects), varying consolidation ratios, and contrasting water qualities (lake water vs. freshwater).

### 1.2.3 Understand the rate of desorption and diffusion mechanism of organic compounds from the solid content of the FFT.

In the case of Lake Miwasin, similar to other pit lake closure landforms, diffusion, and desorption are believed to be the primary mechanisms of chemical mass transfer as consolidation rate decreases (Samadi, 2019). However, the desorption rate and mechanism of toxic organic matter from FFT to the lake water remain poorly understood. Therefore, in this dissertation, observations were made to examine the desorption kinetics of dissolved organic carbon (DOC) and NAs from PASS-treated FFT to lake water, in order to evaluate the migration of organic contaminant and efficiency of PASS treatment. The objectives of the study were to:

1) investigate the desorption rate of NAs and DOC from FFT to lake water

2) evaluate desorption kinetics models to determine the controlling desorption process

3) examine the equilibrium data by using isotherm models to select the best-fitted model and

4) assess the effect of the lake water's salinity, DOC, hardness, chemical treatment by-product, and varying temperatures on DOC desorption capacity.

## 1.3 Hypotheses

A series of hypotheses are introduced throughout the dissertation to guide the research, including:

- Speculated impact of alum chemical treatment:
  - Alum chemical treatment of FFT, immobilizing highly concentrated negatively charged organic matter onto clay particles, may lead to elevated concentrations of TOC and NAs in the FFT.
- Hypotheses Influence of PAM in the treated FFT:
  - The presence of $NH_2$ functional groups within the FFT particles (because of PAM) is hypothesized to enhance the immobilization of carboxyl groups of NAs through hydrogen bonding on the treated FFT.
- Anticipation of NAs recovery:
  - Most NAs are expected to be dissociated (pKa = 4-6) in high alkaline conditions, potentially resulting in improved recovery from the solid FFT particles compared

to neutral conditions.

- Hypotheses on PASS Treatment Effects:
    - PASS treatment is hypothesized to enhance the settling of fine particles and reduce the mobility of selected multivalent and divalent cations ($Al^{+3}$, $Mg^{+2}$, $Ca^{+2}$, $Cu^{+2}$) by facilitating their immobilization onto FFT particles, possibly through anionic polyacrylamide compounds.
- Chemical Mass Flux Hypothesis:
    - The initial chemical mass flux from PASS-treated FFT to capping water is anticipated to be significantly higher than during the rest of the observation timeline due to the high consolidation rate, potentially enabling faster release of COPCs.
    - In EPL systems filled with PASS treatment, intermittent FFT disturbance caused by lake turnover is expected to result in low turbidity and is likely not to significantly increase the release of COPCs into capping water.
- Molecular Desorption Study Anticipation:
    - In the molecular desorption study, it is anticipated that under alkaline conditions, DOC will physically desorb from PASS-treated FFT. However, it can be expected that PASS treatment with alum and anionic PAM might reduce the mobility of negatively charged hydrocarbons, including NAs.

These hypotheses are intended to shed light on specific aspects of PASS-treated FFT behavior while also providing a structured framework for the study's objectives.

## 1.4 Thesis organization

The first chapter serves as an introduction, providing critical insights into FFT generation and management, with a focus on the EPL system's ability to facilitate self-sustaining FFT management. The potential use of PASS-treated FFT as an alternative method in the EPL system was discussed as a motivation for research. This was followed by a brief summary of research objectives and hypotheses. Finally, the thesis organization is provided for the reader.

The second chapter is a literature review. The initial focus of the chapter is on FFT generation from surface mining bitumen extraction. Following that, a literature review presents different FFT management approaches, particularly emphasizing the reclamation of self-sustaining EPL system. This chapter closes by highlighting a knowledge gap in understanding the geochemical stability of an EPL system.

The third chapter is dedicated to showcasing the result of PASS-treated FFT characterization and the development process of an optimal approach for characterizing NAs within FFT particles. Initially, the surface and geochemical characterization of PASS-treated FFT is identified. Subsequently, treated FFT is employed to optimize the method for NAs species characterization by optimizing extraction, cleanup, and quantification conditions. Eventually, the optimized method is used to measure NAs level in different tailings samples.

The fourth chapter demonstrates COPCs flux from PASS-treated FFT to capping water in controlled model EPL system for two years. In addition, the chapter describes the main mechanism of the system's chemical mass transfer. Following that, the effect of initial and intermittent seasonal variations in Lake Miwasin on chemical flux is presented.

The fifth chapter of the study results focused on the molecular desorption process of dissolved organic compounds from the FFT particles. In particular, this part presents the result of desorption kinetics and isotherms. The desorption distribution coefficients and the relationship between this parameter and the mobility of DOC and NAs on the FFT particles are discussed in parallel. Eventually, the result of impact of chemical and physical lake water quality on the mobility of organic compounds on the FFT particles is presented.

The sixth chapter of the study represents the thesis overview and summarizes the previous chapter's main findings. Additionally, the thesis would be finalized by highlighting the recommendations for further study.

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# 2 Chapter 2: Literature Review

## 2.1 Bitumen extraction

The majority of North America's oil reserves are bitumen mixed with sand, with extraction primarily conducted through surface mining or in-situ extraction techniques (AER, 2020) (Table 2.1). Surface mining (ex-situ recovery) is conventionally used for oil sands reserves under 75 m, while in-situ recovery is used for reserves located at greater depths (Li et al., 2023a; Li et al., 2021). In the northeastern Alberta region of Athabasca, oil sands ores are mainly extracted through surface mining, i.e., Clark Hot Water Process (HWP) (Chalaturnyk et al., 2002). HWP involves mixing crushed oil sands ore with hot water and caustic soda (sodium hydroxide, NaOH). This high-efficiency process allows bitumen to froth and float to the surface of separation vessels while solids settle at the bottom (Clark & Pasternack, 1932). The addition of NaOH increases the pH, making organic acids in bitumen water-soluble, reducing interfacial tensions, and promoting bitumen recovery (Chow et al., 2008). Although surface mining affords higher bitumen recovery than other extraction methods, it also generates a large volume of bitumen extraction fluid wastes known as oil sands FFT (Cossey et al., 2021).

## 2.2 Tailings generation and characterization

While bitumen froth is diluted to reduce viscosity and aid separation, separation vessels process the remaining slurry. This process results in three main tailings streams: coarse (55% solids), fine (6-10%), and froth treatment (Chalaturnyk et al., 2002). These streams have various amounts of sands, fines, OSPW, dissolved salts, NAs, petroleum hydrocarbons, and unrecovered bitumen. Most course tailings are sands (>44 µm) that sink and discharge from the bottom of the separating unit. Conversely, fine tailings have a lower than one Sand to Fines Ratio (SFR) and mainly contain fine particles (<44 µm) (Kasperski & Mikula, 2011). Froth treatment tailings separately produce and contain naphthenic acids or paraffinic solvents (Van Dongen et al., 2021). In the final stage, these tailings streams are temporarily stored in tailings ponds, either as a collective mixture or kept separated by operators (Cossey et al., 2021). The resulting deposition of tailings with more than 5 wt% solids in the pond is referred to as FFT (AER, 2020).

The composition of FFT samples can change depending on a number of factors, such as the location of the deposit, the operational processes that were used, the age of the FFT, and the potential treatment methods that were used (Jeeravipoolvarn et al., 2009; Siddique et al., 2014; Suncor, 2019; Syncrude, 2019a; Syncrude, 2019b). These factors result in variations of the FFT's composition, including bitumen content, water content, and solid compounds. A summary of typical FFT water content characteristics and the typical range of bitumen, solids, and fines content in oil sands FFT is provided in Tables 2.2 and 2.3 respectively (Syncrude, 2019a; Syncrude, 2019b; Van Dongen et al., 2021). The texture of the solid content of FFT mainly includes clay (2 µm), slit (2-50 µm), and sand (50-500 µm) (Cossey et al., 2021). The main FFT minerals are quartz, kaolinite, and illite-smectite, but they are not limited to these. The presence of calcium, aluminum, silicon, and titanium-bearing minerals in oil sands FFT solid content has a significant impact on the amount of toxicity that is released into the water (Cossey et al., 2021). For the dissolved organic compound, despite the fact that extensive research has been done on the characterization of NAs in oil sands process water (OSPW), the fate and behavior of NAs within FFT deposits are still areas that need additional investigations. Only few studies have been conducted for the quantification of oil contaminated soil and sediments (Table 2.4).

Table 2.1 Bitumen extraction methodology.

| **Bitumen Extraction technique** | **Classification** | **Process** | | **References** |
|---|---|---|---|---|
| | | **stimulator** | **Condition** | |
| Clark Hot Water Process (HWP) | Surface mining | Hot water and sodium hydroxide | Batch | (Clark & Pasternack, 1932) |
| Steam-Assisted Gravity Drainage (SAGD) | In-situ | Hot stream | Continuous | (Li et al., 2023a) |
| Cyclic Steam Stimulation In-situ (CSS) | | Hot stream | Batch | (Li et al., 2021) |
| Solvent-Based Processes | In-situ | Inorganic solvents (propane or butane) | Batch | (Li et al., 2021) |
| In-Situ Combustion | In situ | A steam ignition, Gas-air burner, Electric ignition Chemical ignition | Batch | (Li et al., 2021) |
| Catalytic | In situ | Hydrocracking, Hydrodesulfurization, Hydrodenitrogenation, Hydrodeoxygenation Hydrodemetallization, | Batch | (Li et al., 2021) |

Table 2.2 Bitumen, solids, and range in FFT.

| **Parameter** | **Value (wt %)** * |
|---|---|
| Bitumen | 0.7–5.6 |
| Fine Solid | 22-81 |
| fines content | 50-100 |

*Data resource: (Jeeravipoolvarn et al., 2009; Siddique et al., 2014; Suncor, 2019; Syncrude, 2019a; Syncrude, 2019b)

Table 2.3 FFT pore water characterization.

| **Property** | **Unit** | **Abundance**[*] |
|---|---|---|
| pH | | 8.5-8.8 |
| Conductivity | $\mu S\ cm^{-1}$ | 2600-3500 |
| Chemical Oxygen Demand (COD) | mg/L | 180-250 |
| Dissolved Organic Carbon (DOC) | mg/L | 40-50 |
| NAs | mg/L | 46-68 |
| $SO_4^{2-}$ | mg/L | 180-570 |
| $Na^+$ | mg/L | 570-745 |
| $K^+$ | mg/L | 19-30 |
| $Ca^{2+}$ | mg/L | 22-49 |
| $Mg^{2+}$ | mg/L | 15-26 |
| Sr | mg/L | 0.83-1.44 |
| B | mg/L | 2.2-3.8 |
| Cl | mg/L | 360-470 |
| As | mg/L | 1.75-10.2 |
| $CO_3^{2-}$ | mg/L | 12-46 |
| $HCO_3^-$ | mg/L | 720-990 |

*Data resource: (Syncrude, 2019b)

Table 2.4 NAs characterization in sediments.

| Solid environmental matric | Extraction method | | | | Clean Up method (Solid Phase Extraction) | | | Quantification method | References |
|---|---|---|---|---|---|---|---|---|---|
| | Solid dosage | solvent | Mixing apparatus | Mixing duration | SPE cartridg | Elution solvent | Reconstitution reagent | | |
| **Oil contaminated soil** | 1/10 (g/mL) | 0.1M NaOH, | N/A | N/A | Oasis MAX | FA/ methanol (1:50)<br>FA/ethyl acetate (EA) (1:50) | DCM | GC/MS | (Jie et al., 2015) |
| **Oil contaminated sediment** | 1/200 (g/mL) | Hexane (Hex), MTBE, EA, Hex/MTBE (1:1) | Oscillation mixer | 24 hrs. (3 times) | Oasis MAX | 2 M HCl/EA (1 :10) | 0.1 mL of methanol | UPLC-QTOF-MS | (Wan et al., 2014) |
| | | Hex/MTBE (1:1), Hex/MTBE (1:1), Formic acid (FA) (2 %) | Ultrasonic Bath | 24 hrs. (3 times) | | | | | |
| | | Hex/MTBE (1:1), Hex/MTBE/ ACN (1:1), Hex/MTBE/ MeOH (1:1) | Soxhlet | 24 hrs. | | | | | |
| **Sludge from wastewater treatment plant** | 1/200 (g/mL) | Hex/MTBE/ MeOH (1:1) | Soxhlet | 24 hrs. | Oasis MAX | 2 M HCl/EA (1 :10) | 0.1 mL of methanol | UPLC-ESI-QTOF-MS | (Wang et al., 2015) |
| **Oil contaminated sediment** | 3/5 (g/mL) | 0.1 M NaOH, DCM (v/v = 1:1), MTBE | shaker | 5 min (2-3 times) | - | - | - | GC–MS | (Zan et al., 2019) |

## 2.3 FFT management

Surface mining of oil sands ores have resulted in over a billion cubic meters of FTT, which are temporary stored in tailings ponds covering an area of 100 square kilometers in the oil sand Athabasca region. Therefore, an effective reclamation strategy is needed to reduce the environmental issues, enhance dewatering, and increase the bearing capacity/shear strength of the tailings brought on by FFT. The Directive 085: “Fluid Tailings Management for Oil Sands Mining Projects in 2017" issued by the AER, requires FFT to be treated and reclaimed throughout a project life span and all be ready for reclamations within 10 years of mine closure.

As of today, several wet and dry reclamation strategies have been applied by oil sands operators for FTT management (Samadi, 2019; Sobkowicz et al., 2013). Accordingly, several pretreatment methods have been also applied to improve the quality and consolidation of FFT, including physical/mechanical methods (filtration, centrifuge), natural processes (evaporation, freeze/thaw), and use of chemical additives (polymer, flocculant, and gypsum, coagulant) (Cossey et al., 2021). Methods for depositing FFT are diverse in oil sands industries; however, oil sands mining industries actively use four commercial-scale deposit types:

- Thin lifts deposits (freeze-thaw cycles after chemical and mechanical pretreatment).
- Deep in-pit disposal (self-weight consolidation after chemical and mechanical pretreatment)
- Sand deposal (self-weight consolidation)
- Water capping fines deposits (water-cap FFT, WCT) where FFT is placed at the bottom of an open pit of closed mine and covered with overlying freshwater (OSTC, 2012).

The first three disposal methods end up with terrestrial landforms; however, the WCT disposal method is anticipated to have an EPL landform (OSTC, 2012).

Conventional dry landscape reclamations are not economically efficient (Samadi, 2019). A massive volume of produced FFT escalates the risk of COPCs' seepage into the groundwater reservoirs, and a lower rate of remediation (Jordaan, 2012; Samadi, 2019; Wang et al., 2014). Based on the archived observations from several tailings' reclamation strategies in Northern Alberta, EPL has targeted to form self-sustaining aquatic ecosystems. Additionally, by using readily available and low-cost materials, FFT and OSPW in the EPL system could provide efficient FFT storage, gradual FFT consolidation without any pretreatment, and large water reservoirs (OSTC, 2012). Specifications of FFT storage systems among Northern Alberta oil sands companies are summarized in Table 2.5.

Table 2.5 Summary of several FFT storage strategies among Northern Alberta oil sands companies.

| Name of FFT Storage | Operator | Pretreatment Methods | Disposal Method | Landform | Reference |
|---|---|---|---|---|---|
| BML | Syncrude | Untreated | WCT | EPL | (Syncrude, 2019b) |
| Lake Miwasin | Suncor | Chemical Additive | WCT | EPL | (Suncor, 2019) |
| Imperial Kearl | Suncor | Chemical additives and mechanical thickener | Deep-in-pit disposal and thin lifts | Terrestrial deposit | ((Imperial). 2020) |
| Fort Hill | Suncor | Chemical additives and mechanical thickener | Deep-in-pit disposal and thin lifts | Terrestrial deposit | (Suncor, 2019) |
| Tailings Reduction Operation | Suncor | Chemical additive | Deep-in-pit disposal and thin lifts | Terrestrial deposit | (Imperial, 2020; Suncor, 2019) |
| Aroura North | Syncrude | Chemical additive | Deep-in-pit disposal and thin lifts | Terrestrial deposit | (Syncrude, 2019a) |
| Jackpine mine | Canadian Natural Upgrading Ltd. | Chemical additives and centrifuge | Deep-in-pit disposal and thin lifts | Terrestrial deposit | ((CNUL). 2020) |
| Muskeg River Mine | Canadian Natural Upgrading Ltd | Chemical additive | Sand disposal | Terrestrial deposit | ((CNUL). 2019) |
| Horizon | Canadian Natural Resources Limited. | Chemical additive | Sand disposal | Terrestrial deposit | ((CNRL). 2019) |

## 2.4 Pit lakes in the oil sands industry

EPLs are primarily used in the mining industry to reclaim waste streams in the form of closure mining pits (Mantero et al., 2020). In the oil sands industry, EPLs have the flexibility to be filled with either freshwater, a blend of OSPW and freshwater, and may include the presence or absence of FFT. Despite site-specific variations, general comparisons can be drawn between oil sands EPLs and pit lakes in global coal and metal mining sectors (COSIA, 2021a). While most EPL systems are deep (around 100 meters) with small surface areas (<1 sq. km), oil sands EPLs are shallow (5-40 meters) and expansive (2-26 sq. km) (Golder, 2017). The alternative design of this reclamation strategy in oil sands industries facilitates seasonal turnover and vertical mixing, promoting aerobic degradation of NAs and reducing the generation of methane and hydrogen sulfide gas (COSIA, 2021a). Additionally, in oil sands EPLs, bitumen extraction leads to alkaline waste streams, in contrast to the acidic waste streams in other EPLs (COSIA, 2021a). Unlike typical EPLs, the water chemistry of oil sands EPLs is different, containing organic constituents such as residual bitumen, NAs and polycyclic aromatic hydrocarbons with high levels of $Na^+$ and $Cl^-$ (Cossey et al., 2021).To date, Base Mine Lake (BML) and Lake Miwasin are the only two developed EPLs, as tailings reclamation technologies, by the oil sands industry in Alberta, Canada. Extensive studies have primarily concentrated on BML — established by Syncrude in 2013 — exploring its performance via biogeochemical characterization of untreated FFT and evaluating the water quality (Cossey et al., 2021). BML comprised 168 $Mm^3$ of untreated FFT deposits covered with 58 $Mm^3$ of freshwater (Dompierre & Barbour, 2016; Dompierre et al., 2017). In 2016, as a step forward, Suncor deposited PASS (permanent aquatic storage structure) treated FTT in a pit lake known as Lake Miwasin (18 ha). PASS treatment is expected to accelerate the FFT dewatering in the presence of a coagulant (alum) and flocculant (anionic polyacrylamide, via in-line flocculation) but there is little known about this alternative establishment and need further assessment (Cossey et al., 2021; Suncor, 2019). While moderately low costs and energy requirements make the EPL a promising long-term FFT management solution, its geochemical stability and environment fate are still concerns (Samadi, 2019). The EPL system relies heavily on surface water quality to achieve a self-sustaining aquatic ecosystem. As a result, research into the geochemical mechanisms that have the greatest impact on EPL lake water quality is required (Samadi, 2019).

## 2.5 Potential mechanisms of geochemical changes in pit lake

FFT storage in oil sands EPLs directly influence and change the capping water quality in pit lake system. In these reclamation strategies, geochemical changes are primarily driven by consolidation, biological processes, and the chemical mass loading introduced through pore water flux From the FFT (Cossey et al., 2021).

### 2.5.1 Consolidation

FFT's consolidation rate depends on the treatment methods of the deposits. Untreated FFT has the lowest consolidation rate in the short term ($10^{-6}$ and $10^{-9}$ m/s) (Dompierre & Barbour, 2016). However, the chemical and mechanical treatment can increase the consolidation rate by a factor of five (Wilson et al., 2018). For EPL systems, it can be implied that treated FFT, with higher hydraulic conductivity, potentially will increase the pore water flux at the early stage of EPL establishment (Cossey et al., 2021).

### 2.5.2 Biogeochemical processes

Different redox conditions result in different microbial communities in pit lakes and prompt a wide array of biogeochemical processes (Boldt-Burisch et al., 2018; Foght et al., 2017). Theoretically, aerobic zones in EPL's capping water provide oxygen for the oxidation of hydrocarbons, while anaerobic zones in FFT deposits provide suitable habitat to anaerobes (fermenters/methanogens) to transform dissolved organics into carbon dioxide and methane (Samadi, 2019). The most studied processes are nitrate-reduction, sulfate-reduction, iron-reduction, and methanogenesis. These processes lead to contaminants degradation, minerals transformation, consolidation, and generation of greenhouse gas in a pit lake (Collins et al., 2016; Risacher et al., 2018; Stasik et al., 2014; Stasik & Wendt-Potthoff, 2014; Warren et al., 2016).

### 2.5.3 Chemical mass loading Flux

As FFT consolidates, the chemical flux via pore water is directly influenced by advection and diffusion mechanisms. Earlier investigation on BML elucidated that chemical mass loading into the capping water was primarily due to advection. However, diffusion and desorption of COPCs from the solid content of FFT would play a crucial role in chemical mass loading into the capping water when consolidation rates decrease over time (0.004 after one year -0.002 $m^3/m^2/d$ after 3 years) (Dompierre & Barbour, 2016; Dompierre et al., 2017). Apart from advection and diffusion-driven mass transfer regimes, temporal variation may influence mass loading flux from FFT to capping water in EPLs. Vertical mixing (lake turnover phenomena) within the lake due to seasonal thermal stratification of lakes and inflow freshwater flux can cause turbidity and add an extra chemical flux from FFT to capping water in EPLs (Charette, 2010; Tedford et al., 2019).

So far, it is observed that chemical treatment of FFT in EPLs (such as PASS-treated FFT in lake Miwasin) improved the dewatering and reduced turbidity issues, i.e., the highest value was 20 NTU (Suncor, 2019). However, it remains uncertain whether such treatment can mitigate additional chemical flux during vertical mixing within EPLs. Additionally, a potential drawback of FFT treatment is that treated FFT exhibits a higher initial chemical flux, primarily in the pit lakes, due to higher initial hydraulic conductivities (Cossey et al., 2021; Wilson et al., 2018). In the future, PASS-treated FFT by-products may elevate $SO_4^{2-}$, $K^+$, acrylamide (AM), and carboxylic acid in EPL capping water (Cossey et al., 2021). There is no data to understand chemical mass loading flux in EPL systems filled with PASS-treated FFT.

### 2.6 The potential of COPCs releases from FFT into capping water

Previously, Dompierre et al. used a mass balance by considering $Cl^-$ ion as a conservative element of BML water to estimate the advective vertical pore water flux in the pit lake system. However, the advection flux of several COPCs did not explain the chemical mass loading in BML due to the complexity of their biochemical reactions (Dompierre et al., 2017). So far, only comparative observations in BML before and after adding capping water are made to evaluate the possibility of COPCs migration rate over time. The summary of BML FFT and surface water quality is provided in Table 2.6 (Dompierre et al., 2016; Syncrude, 2019b; White, 2017).

Table 2.6 Summary of BML FFT and surface water quality.

| **Property** | **Characterization of** | | |
|---|---|---|---|
| | **FFT before adding fresh water** | **FFT 2019** | **surface water 2019** |
| pH | 7.4 ± 0.34 | 8.25 | 8.45 |
| Conductivity (μS/cm) | 4000 ± 400 | 3950 | 2600 |
| $Na^+$ (mg/L) | 880 ± 96 | 977 | 560 |
| Cl (mg/L) | 560 ± 95 | 550 | 390 |
| $Ca^{2+}$ (mg/L) | 19±4.1 | 27 | 25 |
| $Mg^{2+}$ (mg/L) | 11 ± 2.0 | 12.5 | 9.5 |
| $K^+$ (mg/L) | 16 ± 2.3 | 14 | 13 |
| $NH_4$-N (mg/L) | 9.9 ± 4.7 | 15 | 11 |
| $SO_4^{2-}$ (mg/L) | 92 ± 120 | 14 | 160 |
| NAs (mg/L) | 72 | 65 | 31 |
| B (mg/L) | N/A[1] | 3.41 | 1.77 |
| Si (mg/L) | N/A | 5.68 | 2.44 |
| Sr (mg/L) | N/A | 0.85 | 0.58 |

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[1] Not available

It was observed that 92% of salinity in BML surface water was due to $Na^+$ and $Cl^-$ ions, which were mainly released from untreated FFT in the BML project (Cossey et al., 2021; White, 2017). Concomitantly, a considerable fraction of toxic metals and acutely toxic organic constituents like residual bitumen, NAs (31 mg/L), and polycyclic aromatic hydrocarbons were also released from untreated FFT into the surface water of the BML. White et al. suggested that $Na^+$ and $Cl^-$ ions in the BML increased the bioavailability of NAs (White & Liber, 2018). On the other hand, the solubility of NAs was decreased with an increase in inorganic salts in oil-water systems (Peng et al., 2002). Therefore, it is likely that in a high salinity pit lake system like BML, salinity regulates the NAs' release from FFT but biologically increases the bio-uptake potential as well.

Advection study is not enough to understand the fate and mechanism of COPCs released from FFT particles and their interactive effects on each other. Thus, desorption of COPCs from the solid particle fraction of FFT is needed to understand the mobility of COPCs mechanism and rate under different conditions. Moreover, using the desorption study of COPCs from FFT can better explain the mobility of compounds that contribute to acute toxicity for long-term operation when the FFT consolidation rate decreases considerably.

## 2.7 Research gap on geochemical stability of EPL system in oil sands industries

According to the literature review done for this thesis, there is a significant lack of research on the following topics:

**Characterizing FFT particles concerning the presence of toxic organic matter, including NAs:** understanding the fate of COPCs released from FFT to capping water is essential to obtain the desired reclamation outcomes. NAs, the main cause of acute toxicity in OSPW, remains unquantified in oil sands FFT. While high-resolution instrumental methods enable precise NA quantification in aquatic environments, challenges arise in FFT due to limited sedimentary data, extraction inconsistencies, and complex FFT matrices.

- **Assessing the geochemical stability of End Pit Lakes (EPLs) in the context of chemical mass transfer within the oil sands industry:** EPLs are promising reclamation deposit to oil sands FFT management. However, several knowledge gaps in the long-term geochemical stability of EPLs as FFT reclamation technology are identified. This includes understanding salt fluxes, water quality, bioremediation, biogenic greenhouse gas emissions, and the possible consequences of FFT treatment methods intended to improve geotechnical properties of FFT, such as polyacrylamide and gypsum addition.

- **Examining the influence of lake water characteristics, temporal variations, and FFT characterization on chemical mass transfer processes:** Before installing EPL systems, understanding the interplay between lake water characteristics and FFT characterization on chemical mass transfer processes would be instrumental in potentially mitigating or controlling of COPCs from FFT to capping water. Particularly, the effects of adding fresh water or a mixture of OSPW and fresh water on lake ecosystem chemical movement and distribution are not well documented. Turbidity has been identified as a major factor contributing to excess chemical release in EPL systems filled with untreated FFT. Chemical treatments are observed to reduce seasonal turbidity. However, the effect of vertical mixing within lake water on chemical release from chemically treated FFT, including PASS-treated FFT, has not yet been investigated.

Addressing these fundamental research gaps collectively contributes to a more profound understanding of the environmental challenges and potential solutions associated with oil sands operations. This knowledge can facilitate a more ecological sustainability and responsible approach for FFT management.

## 2.8 References

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# 3 Chapter 3: Method Development for Routine Determination of Naphthenic Acids in Oil Sands Tailings: Extractions, Cleanup and Characterization

## 3.1 Introduction

In the northern region of Alberta, Canada, the extraction of bitumen from oil sands involves a caustic hot water process, yielding oil sands process water (OSPW) and tailings as by-products. Naphthenic acids (NAs), natural components in oil sands, are a combination of alicyclic and noncyclic alkyl-substituted carboxylic acids with a general chemical formula of $C_nH_{2n+z}O_x$, where ‘n’ denotes the carbon number, ‘z’ (zero or a negative even integer) indicates hydrogen deficiency due to ring or double bond formation, and ‘x’ represents the oxygen number. It is well known that NAs accumulate in OSPW and oil sands tailings during the process of bitumen extraction. NAs present in aqueous environments such as OSPW, have been extensively studied using high resolution mass spectrometry (MS) techniques, including time-of-flight mass spectrometry (TOF-MS) (Huang et al., 2018; Huang et al., 2019), Orbitrap mass spectrometry (Orbitrap-MS) (Ajaero et al., 2018; Pereira & Martin, 2015; Pereira et al., 2013), and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) (Ajaero et al., 2017; Ajaero et al., 2019; Hughes et al., 2017). However, there has been limited assessment of NAs accumulated in oil sand tailings, despite several studies investigating NAs in pore water or capping water of tailings (Ahad et al., 2013; Bowman et al., 2019; Bowman et al., 2020; Ross et al., 2012). Oil sands tailings are comprised of water, solids (e.g. sand, silt and clay), unrecovered bitumen, salt, trace metals, as well as organic compounds such as NAs. The chemical properties of tailings vary depending on the oil sands ore deposits and operators, which could result in distinct profiles and concentrations of NAs within tailings. The existence of NAs may influence the reclamation process of tailings due to the acute and chronic toxicity of NAs to living organisms and plants (White & Liber, 2018). Different treatment methods have been used to accelerate the dewatering and consolidation of tailings to restore the tailings ponds as sustainable wet and dry landscapes, preparing for the reclamation activities (Cossey et al., 2021; Degenhardt et al., 2023; MacKinnon et al., 2001; Omotoso et al., 2021). Thus, it is critical to comprehensively study the distribution, the behavior and fate of NAs in tailings before and after treatment, and then provide useful information for the improvement of tailings treatment and reclamation.

When considering the analysis of NAs in oil sand tailings, one of the primary challenges is to recover these compounds efficiently. This necessitates the implementation of a robust extraction process prior to conducting instrumental analysis. A few studies employed Soxhlet extraction, oscillation extraction, ultrasonic extraction, and agitation extraction (shaking) to extract NAs from solid samples. For example, Wan et al. compared the recovery efficiencies of model NAs from freeze-dried sediment using Soxhlet extraction, oscillation extraction, and ultrasonic extraction using ultrahigh pressure liquid chromatography coupled to a quadrupole time-of-flight mass spectrometer (UPLC-QTOF-MS) (Wan et al., 2014). The authors found that Soxhlet extraction with the mixture of hexane, MTBE, and methanol (1:1:1, v/v/v) for 24 h yielded the highest recoveries of all NAs model compounds including classical NAs ($O_2$-NAs) and oxidized NAs ($O_3$-$O_5$ NAs). Moreover, Soxhlet extraction was also utilized to extract NAs from oven-dried oil sludge to characterize molecular composition of NAs for investigating the formation of oil sludge deposition in China (Li et al., 2022). However, Soxhlet extraction, while effective, requires a long extraction time and consumes a large amount of harmful organic solvents (Wan et al., 2014). Therefore, other greener extraction methods, such as agitation extraction combined with aqueous solvents, have shown promise in simplifying the process for solid samples, particularly when handling a large number of samples. Zan et al. reported the efficient extraction of NAs from sediment samples in an oil-spilled area using a basic solution of NaOH and 5 min of shaking (Zan et al., 2019). Similarly, Jie et al. applied NaOH solution to recover NAs from oil contaminated soils for assessing the composition of NAs in the oil contaminated area (Jie et al., 2015). Additionally, a cleanup step using solid phase extraction (SPE) was typically employed after the above extractions of NAs from solid samples, which is vital for analyzing NAs by high resolution MS, enabling specific characterization and reducing matrix effects.

Oil sands tailings, being a complex matrix with water and various solids, require an efficient extraction process and a systematic cleanup procedure for complete NAs analysis. However, to our knowledge, there is no a specified standard protocol for extracting NAs from tailings samples and also no study reporting on fully accessing NAs species in oil sands tailings in terms of concertation, composition, and species abundance. Therefore, this study aims to present a routine method for extracting and cleaning NAs from oil sand tailings, followed by molecular characterization of NAs using UPLC-QTOF-MS. The NAs recovering from tailings was based on the simple extraction of orbital shaking with optimization of the main conditions including extraction solvent, mixing method, extraction time, and number of extractions. The SPE cleanup steps were also refined by determining most effective elution solvent and reconstitution reagent to enhance the NAs recovery and reduce the background interference of tailings matrix. This refined protocol was successfully applied for determining the NAs in different types of oil sands tailings. It is believed that this proposed method offers a promising tool for routine NAs measurement in tailings, enabling oil sands operations to monitor changes in NAs species before and after treatments. By providing valuable data and insights, this approach can help facilitate informed decision-making, ultimately leading to more effective reclamation efforts.

## 3.2 Materials and methods

### 3.2.1 Chemicals and materials

Dichloromethane (DCM), hexane, methyl tert-butyl ether (MTBE), methanol (MeOH), sodium chloride (NaCl), 2 N hydrochloric acid (HCL), sodium hydroxide (NaOH) and liquid chromatography (LC) grade formic acid (99.9%) were purchased from Fisher Scientific (Ontario, Canada). Potassium sulfate ($K_2SO_4$) was purchased from Sigma Aldrich. All reagents were at analytical grade and all solutions were prepared using ultra-pure water (Synergy UV, Millipore Sigma, USA). OASIS HLB (6 mL, 500 mg) cartridges were obtained from Waters Limited (Ontario, Canada).

Fluid fine tailings (FFT), mature fine tailings (MFT), and permanent aquatic storage structure (PASS) treated FFT (Suncor Energy, 2018), were provided by oil sands operators in Alberta and were stored in darkness at 4 ˚C until processed. The physicochemical properties of the three types of tailings were provided in Table 3.1. The PASS treated FFT was chosen for optimization of all conditions in extraction and SPE cleanup steps.

3.1 Physicochemical properties of three types of tailings.

| Parameter | PASS treated FFT | FFT | MFT |
|---|---|---|---|
| **Dean-stark (wt%)** | | | |
| Solid | 47.32 | 45.4 | 54.7 |
| Water | 52.21 | 53.12 | 42.4 |
| Bitumen | 0.47 | 1.2 | 2.8 |
| Total | 100 | 99.72 | 99.9 |
| **Texture (wt%)** | | | |
| Fine solids < 44 µm | 99.9 | 27.5 | 100 |
| Coarse solids > 44 µm | 0.1 | 72.5 | 0 |
| **Tailing pore water** | | | |
| pH | 8.4 | 7.5 | 8.3 |
| Conductivity (µS/cm) | 5124 | 6710 | 2326 |
| TDS (mg/L) | 3534 | 4628 | 1604 |
| Total NAs (mg/L) | 120.1 | 95.7 | 45.9 |

### **3.2.2** Tailings sample extraction and cleanup

PASS-treated FFT samples were freeze-dried for 8 hours, then ground using a mortar and pestle, and finally sieved through a stainless-steel mesh with a pore size of 0.2 mm. The homogenized dry tailings were stored at 4 ˚C before use.

For optimizing extraction conditions, initially, the solvents, including 0.5 M $K_2SO_4$, 0.5 M NaCl, 0.5 M NaOH, hexane, DCM, MTBE, DCM/hexane (1:1), hexane/MTBE (1:1), DCM/MTBE (1:1), hexane/MTBE/MeOH (1:1:1), and DCM/MTBE/MeOH (1:1:1), were used to extract NAs from dried PASS-treated FFT. The dried tailings (1 g) were initially mixed with 20 mL of an extraction solvent and shaken for 1 hour at a speed of 200 rpm at room temprature. Then the mixture was centrifuged at 9000 rpm for 10 min. The supernatant was collected in a clean tube and replaced with 20 mL of the same solvent for the successive second extraction. The supernatants from the successive extractions were combined for the following cleanup step. The extracts in aqueous solutions ($K_2SO_4$, NaCl, and NaOH) were acidified with HCl to pH of 2 and directly used in the SPE step. The extracts in organic solvents were air-dried in a fume hood to approximately 2 mL. Then, the residues were dissolved in 40 mL of acidified water (pH 2) and purified by the same SPE method for the aqueous samples.

For the cleanup of the extracts, the OASIS HLB SPE cartridge was employed because a previous study has shown that it had the best performance for recovering NAs from OSPW compared to other cartridges (Qin et al., 2019). Briefly, the HLB cartridges were firstly conditioned with 10 mL of methanol, followed by 20 mL of ultrapure water. Then, the extracts were loaded onto cartridges at a flow rate of 5 mL/min. The cartridges were further rinsed with 50 mL of acidified water (pH = 2) and then dried under a flow of nitrogen gas for 20 minutes. The cartridges were finally eluted by 20 mL of methanol followed by another 20 mL of acidified methanol (2 M HCl: methanol = 1:10, v/v). Two kinds of eluents for each sample were combined and dried under air at room temperature. The dry organics were reconstituted with 5 mL of $NaHCO_3$ (300 mg/L, pH = 8.7) for the primary analysis.

By using the aforementioned extraction and cleanup processes, the most effective extraction solvent yielding the highest recovery of overall NAs were determined. After identifying the optimal extraction solvent, the optimization journey continued in a stepwise manner in the order of examining mixing methods, extraction time, and extraction numbers. Under the best conditions of the extraction procedure, the elution solvent and the reconstitution reagents in SPE step were also tested to have the optimal conditions. The refined extraction and cleanup method were applied for NAs determination in other types of tailings samples.

### **3.2.3** NAs analysis using UPLC-QTOF-MS

The UPLC-QTOF-MS were applied for the molecular characterization of NAs in the tailings' extracts. The detailed methods for data acquisition and data processing have been reported in previous studies (Huang et al., 2018; Huang et al., 2021).

## **3.3 Results and discussion**

### 3.3.1 Optimization of NAs extraction and cleanup conditions from oil sands tailings

In this study, NAs extraction conditions (extraction solvent, mixing method, extraction temperature, extraction time, and number of extractions) and cleanup conditions (elution solvent and reconstitution reagent) were investigated and optimized in a stepwise manner. The NAs extracted from oil sands tailings were characterized using UPLC-QTOFMS.

#### 3.3.1.1 Selection of extraction solvents

In the extraction step, the primary parameter examined was the extraction solvent, which plays a pivotal role. During this investigation, the extractions were conducted using different extraction solvents with two successive extractions for 1 hour mixing each on an orbital shaker. As depicted in Fig. 3.1, three aqueous solvents, three organic solvents, and their mixtures were assessed for their ability to recover NAs from dried tailings. Aqueous solutions surpassed organic solvents by extracting higher concentrations of total NAs. Surprisingly, mixtures of organic solvents did not perform as anticipated, which obtained much lower concentrations of total NAs from the dried tailings. For the aqueous solvents, NaOH recovered the highest concentration of total NAs while $K_2SO_4$ and NaCl yielded moderate recovery of total NAs. This observation is consistent with previous studies where NaOH was identified as an effective extractor of NAs from various sediments (Jie et al., 2015; Zan et al., 2019). Compared to $K_2SO_4$ and NaCl with neutral pH, the basic solutions such as NaOH could likely enhance the desorption of NAs from the negatively charged particle ($pH_{pzc}$ =5.9) (Pourrezaei et al., 2014). As one of the most frequently referred properties, the polarity of the organic solvents is sometimes related to the extraction efficiency. However, in the present study, the correlation of the solvent polarity and the extraction efficiency of NAs was not observed. The polarity index of DCM, MTBE, and hexane are 3.1, 2.4, and 0.1, respectively, yet the concentrations of total NAs recovered by them were in the order of DCM > hexane > MTBE (Fig. 3.1). Moreover, mixtures of two organic solvents did not improve the extraction efficiency compared to the individual solvent (Fig. 3.1). When the more polar solvent methanol (polarity index 5.1) was combined with them, DCM/MTBE/MeOH (1:1:1) recovered slightly more total NAs compared to DCM/MTBE (1:1) by 3.1 mg NAs/kg tailings. However, methanol did not enhance the recovery of total NAs when combined with hexane and MTBE for tailings extraction. Regarding the pH of model tailings sample for the optimization part (pH of PASS treated-FFT = 8.4), the NAs consist of a combination of ions and molecules, and the specific ratio between them depends on the species-specific pKa values (Huang et al., 2016). Thus, since pH adjustment was not applied for samples before extraction, polarity property of organic solvent poorly could be used as proper scale to compare the extraction recovery of NAs in sediment. Non-polar solvents like hexane typically have low dielectric constants and they are less effective at solving electrolyte or polar species. Using a slightly polar organic solvent or mixing a more polar solvent with a non-polar solvent may enhance the extraction of NAs ions. However, it should not be expected that this modification will improve the overall NAs extraction, as it might not properly extract the NAs in a molecular form.

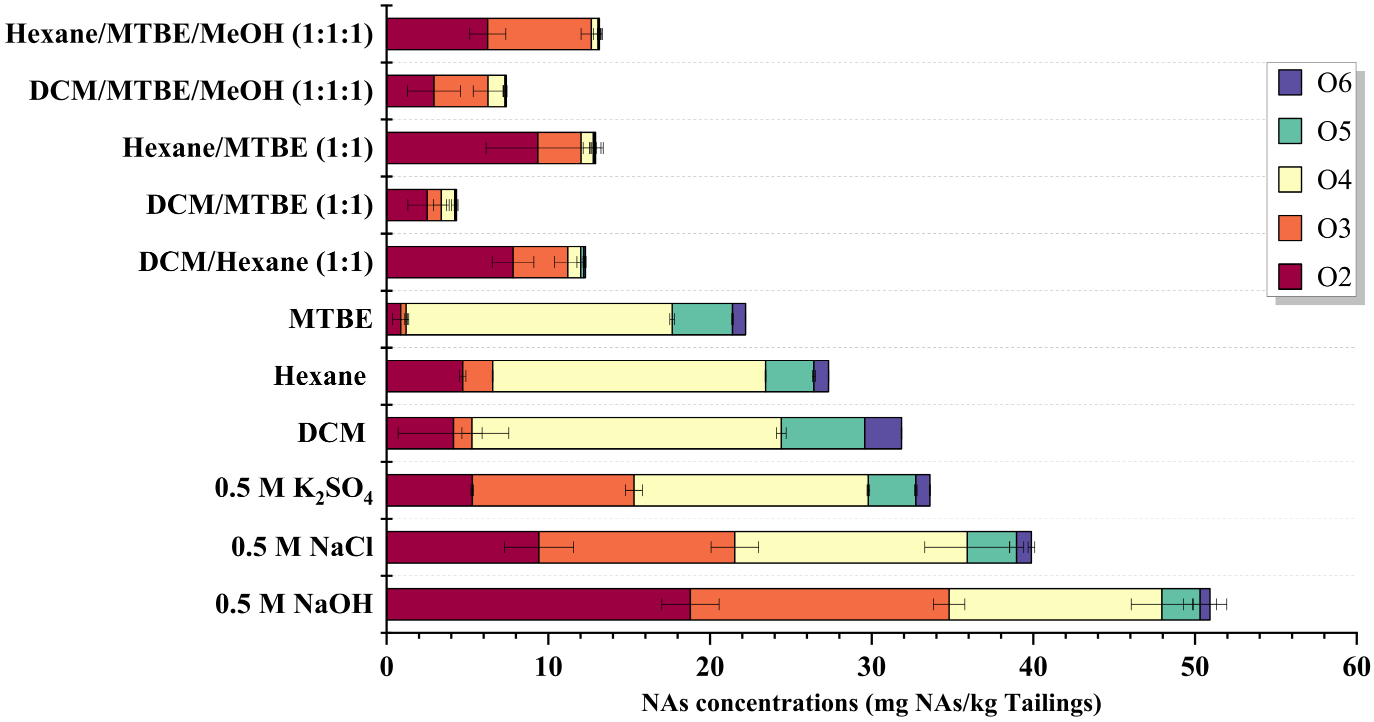


Fig. 3.1 The extracted concentrations of $O_2$-$O_6$ NAs and total NAs from dry tailings (PASS-treated FFT) using different extraction solvents.

In addition to the concentrations of NAs, the compositions of $O_2$-$O_6$ NA species in different tailings extracts are also distinct as shown in the Fig. 3.2. The extracts using NaOH had the highest total NAs and displayed a composition distribution in the order of $O_2$-NAs (37%) > $O_3$-NAs (31%) > $O_4$-NAs (26%) > $O_5$-NAs (5%) > $O_6$-NAs (1%), which is similar to the NAs profile in OSPW

(Huang et al., 2018; Huang et al., 2021). The $O_4$-NAs were the major species in $K_2SO_4$ and NaCl extracts, followed by the $O_3$-NAs, $O_2$-NAs, $O_5$-NAs, and $O_6$-NAs. Similar to $K_2SO_4$ and NaCl, the organic solvents DCM, hexane, and MTBE exhibited a higher preference for recovering $O_4$-NAs with relative abundances reaching 60%, 63% and 74%, respectively. However, the relative abundances of $O_3$-NAs were very low at 4% in DCM extracts, 7% in hexane extracts and 2% in MTBE extracts while the $O_5$-NAs accounted for a little higher than that in the three aqueous extracts. For the mixtures of two organic solvents, $O_2$-NAs obviously predominated at 64, 58% and 72% for the extracts in DCM/hexane (1:1), DCM/MTBE (1:1), and hexane/MTBE (1:1), respectively. They have similar percentages of $O_3$-NAs while DCM/MTBE (1:1) extracts possessed much more $O_4$-NAs (19%) than that (6%) in DCM/hexane (1:1) and hexane/MTBE (1:1). The mixture of three organic solvents DCM/MTBE/MeOH (1:1:1) extracted similar levels of $O_2$-NAs (40%) and $O_3$-NAs (45%) followed by $O_4$-NAs (14%), $O_6$-NAs (0.7%) and $O_5$-NAs (0.3%). The mixture of hexane/MTBE/MeOH (1:1:1) also retrieved similar levels of $O_2$-NAs (47%) and $O_3$-NAs (49%), but lower percentages of $O_4$-$O_6$ NAs. The results suggest that when a mixture of more than one organic solvent was used, the NAs recovery attenuated with increasing oxygen number. This observation aligned with findings from a previous study (Wan et al., 2014). Despite the use of an oscillating shaker (instead of an orbital shaker in the present study), Wan et al. reported that extracting NAs from sediment samples with hexane/MTBE rather than MTBE lowered the recovery efficiency of model oxidized NAs.

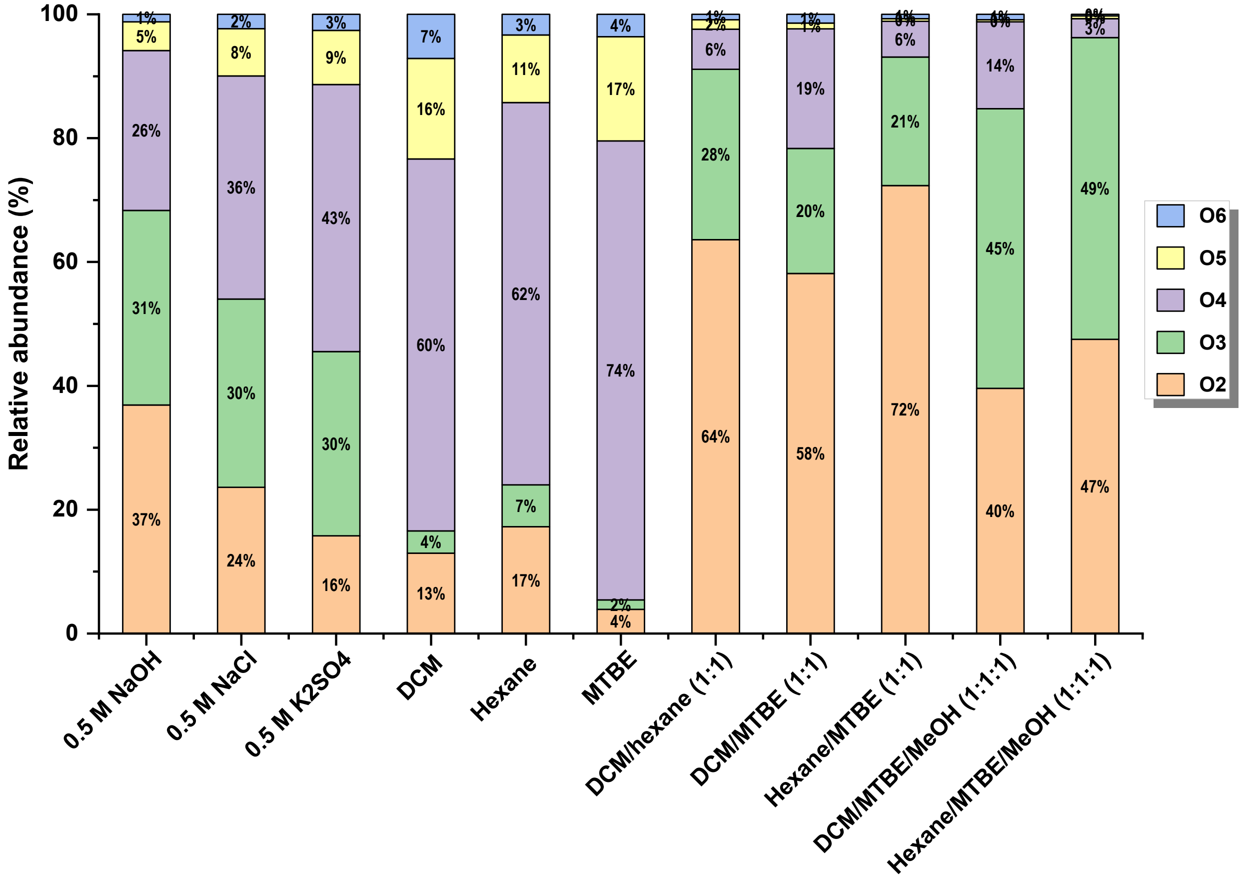


Fig. 3.2 Relative abundances of $O_2$-$O_6$ NAs species in total NAs from tailings (PASS-treated FFT) extracts in different extraction solvents.

As the classical NAs, $O_2$ species are reported as the dominant compounds in OSPW and they are strongly associated with the acute toxicity of OSPW (Huang et al., 2019). Since in this study the $O_2$-NAs also were determined to account for a large portion in tailings, the distribution of the extracted $O_2$-NAs species from tailings, regarding carbon number and -Z number, were generated to provide more information. Fig. 3.3 showed that the $O_2$-NA species in the extracts using NaOH, $K_2SO_4$ and NaCl had the same major carbon number at 14-15 and the same dominant -Z number at 4, 6 and 12. However, the $O_2$-NA species in the NaOH extracts possessed wider ranges of both carbon number and -Z number than that in $K_2SO_4$ and NaCl extracts. Moreover, the distribution profiles of the extracted $O_2$-NAs from the organic solvent extractions were evidently different from those in the aqueous extracts, as presented in Fig. 3.4. The $O_2$-NAs species with carbon number of 13 and 16 and -Z number of 0 and 4 favorably extracted by the individual organic solvents and the mixtures of two organic solvents. The mixtures of three organic solvents predominantly recovered the $O_2$-NAs species with carbon number of 13 and -Z number of 4.

These results revealed that aqueous solvents are more suitable for extracting NAs from dried tailings using orbital shaking compared to the organic solvents. In the extraction process, upon the introduction of solvents to the solid pellets, the molecules within or on the solid matrix endeavor to dissolve in the solvents and subsequently diffuse out of the solid matrix. The extraction efficiency could be notably influenced by the solubility of NAs in the solvents. As NAs are characterized as weak acidic compounds, their presence manifests in various forms across environments with varying pH levels, resulting in distinct solubility (Wu et al., 2019). In the alkaline NaOH solution, NAs in the dried tailings were likely converted to their ionic forms, rendering them highly soluble and thus facilitating their straightforward extraction in the solution. In $K_2SO_4$ and NaCl solutions with a neutral pH, some of NAs persisted in their conjugate base state, making recovery possible. However, the diffusivity and solubility of NAs in organic solvents differ from those in aqueous solvents, leading to distinct distribution behaviors during the extraction process. Organic solvents might be more appropriate for extraction processes, such as Soxhlet extraction, which demand prolonged extraction times to facilitate the transfer of solutes from the solid matrix into the organic solvent phase (Wan et al., 2014). Consequently, the basic solution of 0.5 M NaOH was chosen for recovering NAs from dried tailings using the orbital shaking method. Various factors, such as mixing methods, extraction duration, and extraction repetitions during the extraction step, and certain parameters related to SPE, play pivotal roles in influencing the extraction efficiency. Hence, to establish a standardized extraction and cleanup procedure for NAs determination in oil sands tailings, a comprehensive investigation and optimization of the aforementioned factors were undertaken.

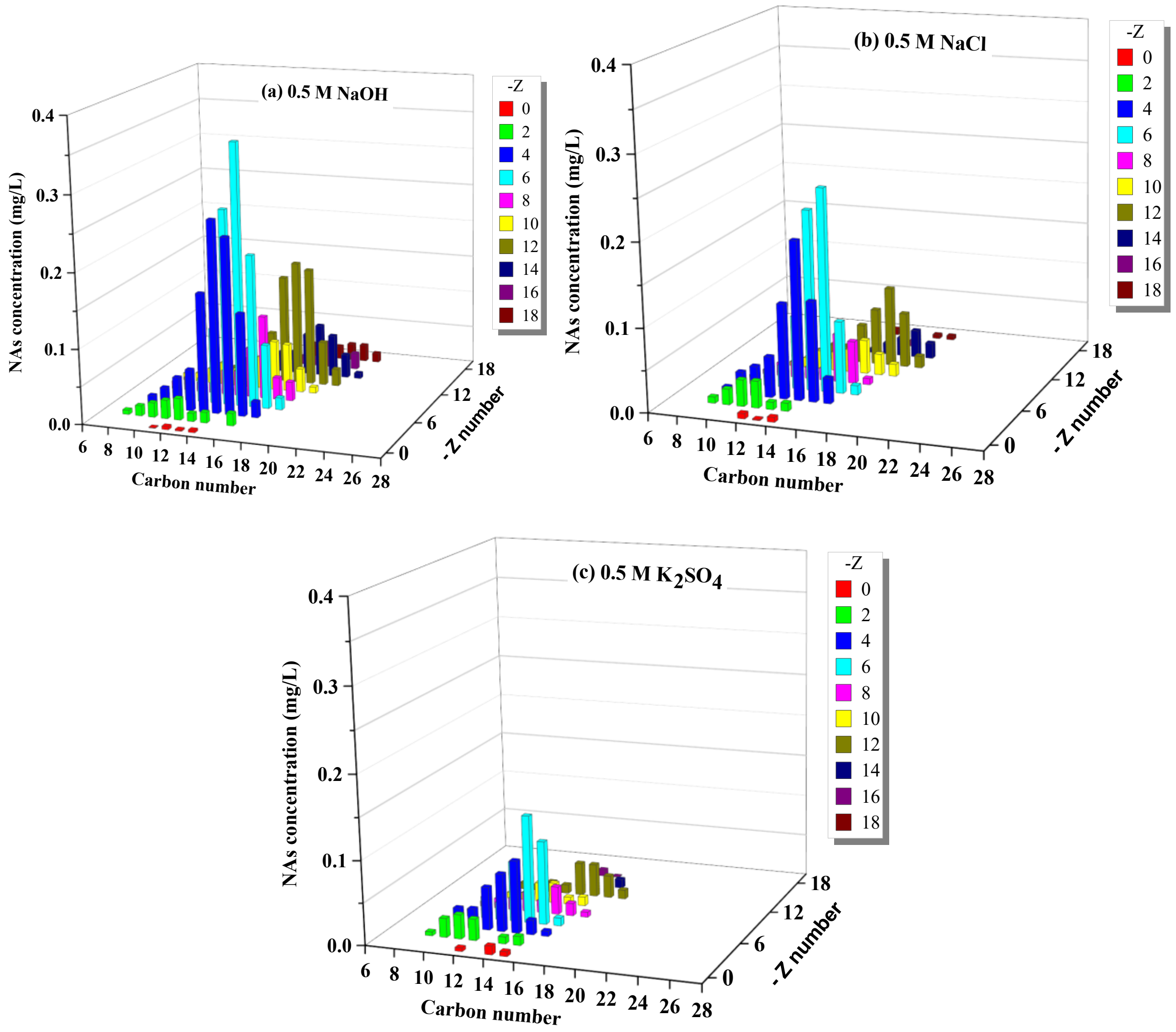
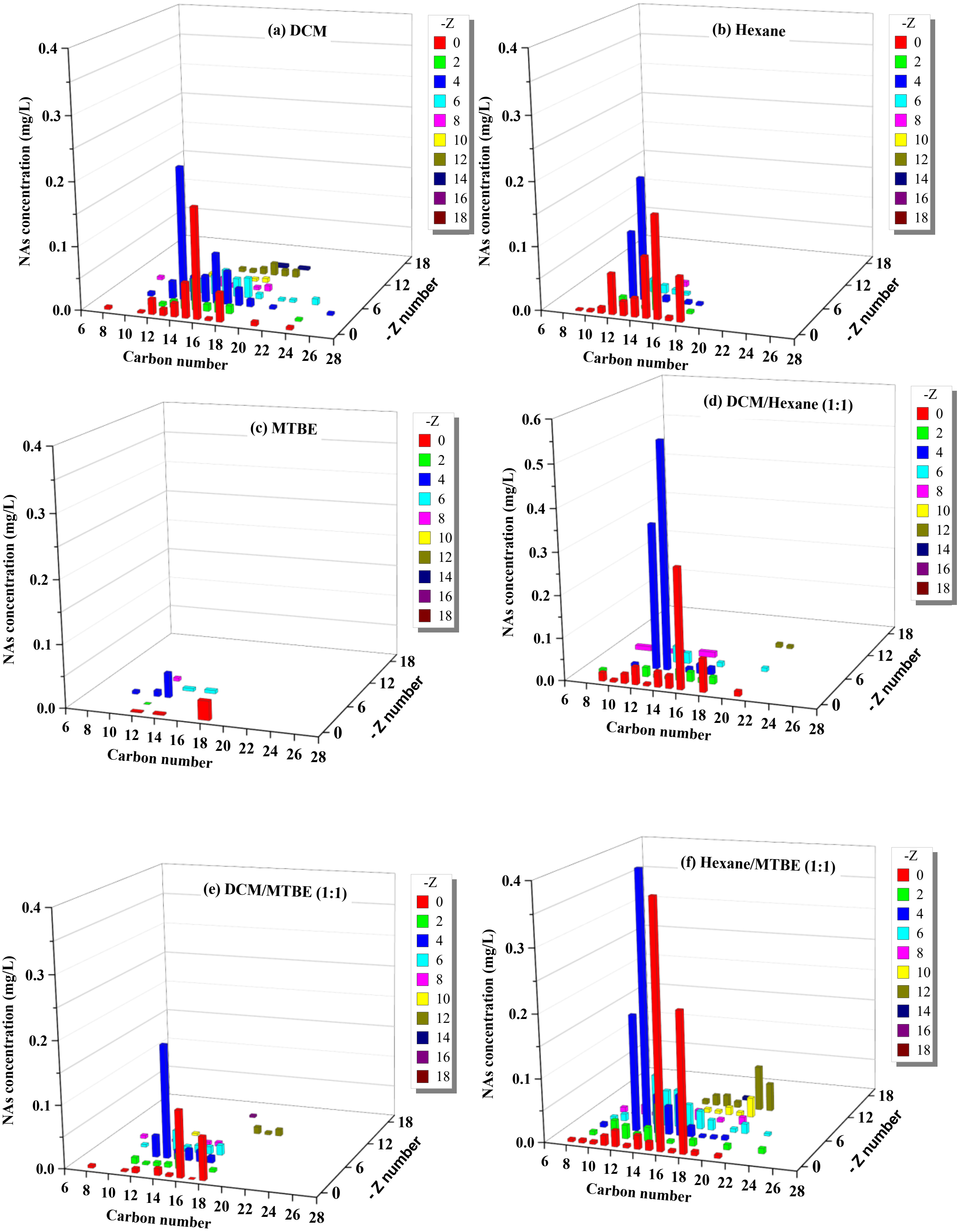


Fig. 3.3 The concentration distributions of the extracted $O_2$-NAs species in tailings (PASS-treated FFT), regarding carbon number and -Z number, extracted by (a) NaOH, (b) $K_2SO_4$ and (c) NaCl solutions.


(a) DCM
(b) Hexane
(c) MTBE
(d) DCM/Hexane (1:1)
(e) DCM/MTBE (1:1)
(f) Hexane/MTBE (1:1)
NAs concentration (mg/L)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Carbon number
6
8
10
12
14
16
18
20
22
24
26
28
-Z number
0
6
12
18
-Z
0
2
4
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8
10
12
14
16
18

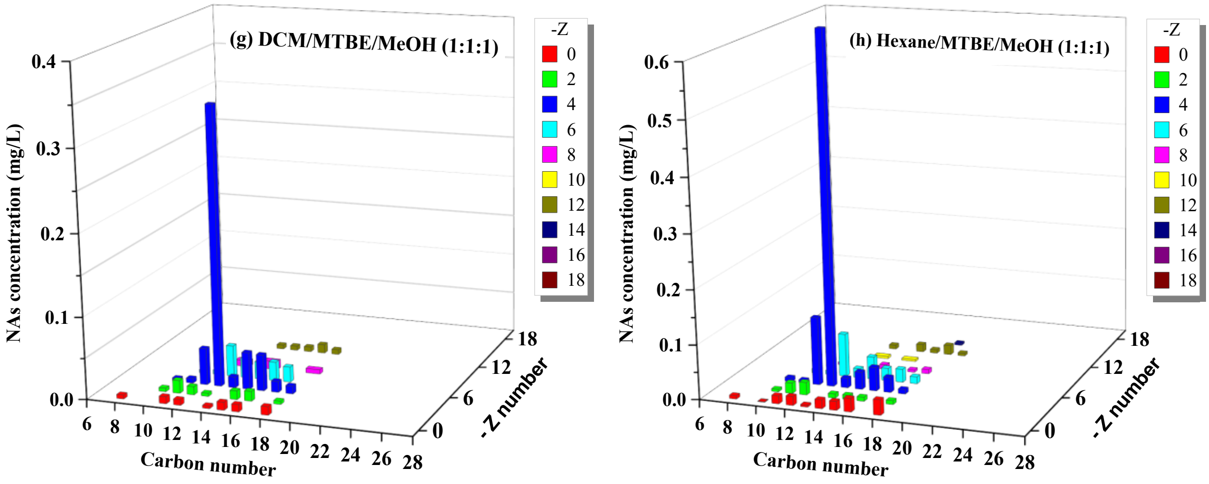

Fig. 3.4 The concentration distributions of the extracted $O_2$-NAs species in tailings (PASS-treated FFT), regarding carbon number and -Z number, extracted by (a) DCM, (b) hexane, (c) MTBE, (d) DCM/Hexane (1:1), (e) DCM/MTBE (1:1), (f) Hexane/MTBE (1:1), (g) DCM/MTBE/MeOH (1:1:1), (h) Hexane/MTBE/MeOH (1:1:1).

#### 3.3.1.2 Effect of mixing methods

In the extraction process, the recovery of NAs can be influenced by the choice of mixing technology, a crucial factor for facilitating the mass transfer of molecules from the tailings' pellets into the solvent. In the present study, the mixing techniques, including shaking and ultrasonication, were tested using 0.5 M NaOH as extraction solvent with a mixing duration of 1 hour. Additionally, a static extraction, involving the direct submersion of dried tailings in the solvent without any movement, was also conducted as a control condition. The initial condition was based on a prior study that reported a 1hour extraction time with 0.5 M of aqueous solution was sufficient to extract DOC from soil samples while minimizing the potential risk of microbial contamination or solute degradation (Jones & Willett, 2006). As presented in Fig. 3.5, the concentrations of the recovered total NAs were 31.25, 44.71 and 70.73 mg NAs/kg tailings for static, ultrasonic and orbital shaking extraction, respectively. As expected, static extraction exhibited the least efficiency, yielding a suboptimal extraction of all NA species due to the inadequate contact between the solid pellets and the solvent. It is noteworthy that ultrasonic mixing only marginally enhanced the recovery of NAs in comparison to static extraction. Ultrasonication is a powerful extraction process that is known for significantly reducing extraction time (Richter et al., 2006). However, the efficacy depends on a combination of analyte-matrix interactions and matrix composition (Tadeo et al., 2010). When analytes form strong bonds with the matrix, it is essential to ensure that enough cavitation power is provided. However, achieving this critical cavitation threshold with commercial ultrasonic baths can be challenging (Bendicho & Lavilla, 2000). In this study, PASS-treated FFT the matrix tailings model that used for optimization process was chemically treated by alum to immobilize NAs. This pre-treatment on tailings matrix likely resulted in the strong adherence of analytes, particularly NAs, to the solid content of tailings matrix, resulting in inadequate cavitation in the ultrasonic bath. The behavior might lead to inadequate contact between the solid pellets and the solvent during the ultrasonic extraction. This was evident as the tailing's pellets tended to congregate the bottom of the tube, failing to uniformly disperse in the solvent during ultrasonic extraction. Remarkably, the orbital shaking was determined to be the most effective mixing method using aqueous NaOH solution for NAs extraction from dried tailings. This efficacy can be attributed to the thorough mixing achieved through a continuous and circular pattern. Based on these insights, the orbital shaking was then employed in the subsequent optimization steps.

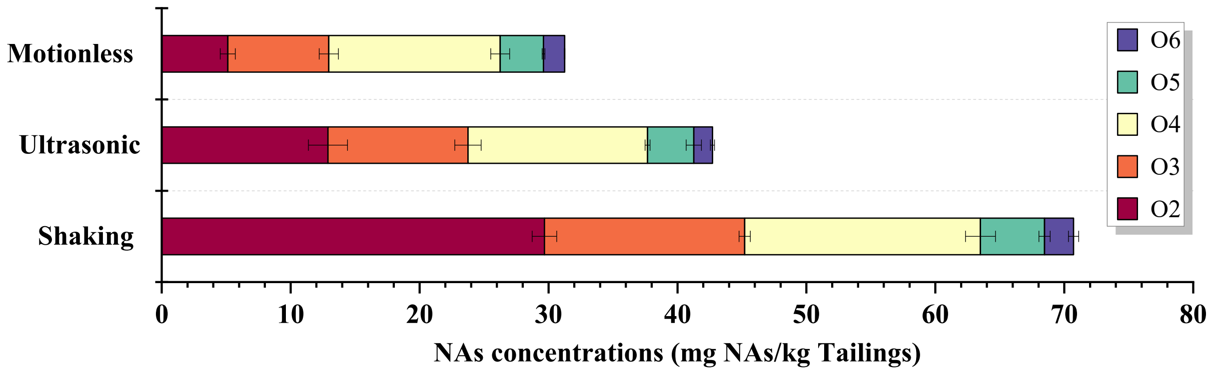

Fig. 3.5 The extracted concentrations of $O_2$-$O_6$ NAs and total NAs from dry tailings (PASS-treated FFT) using 0.5 M NaOH under different mixing conditions.

### 3.3.1.3 Effect of extraction duration

The impact of extraction duration, ranging from 5 to 60 minutes, on NAs recovery efficiency was investigated and is illustrated in Fig. 3.6. For $O_2$-NAs, the recovered concentrations exhibited a clear rise from 15.82 mg NAs/kg tailings with 5 min of shaking to 34.32 mg NAs/kg tailings with 60 min of mixing. Contrastingly, the oxidized NAs showed a different trend in the extraction efficiency with increasing mixing time. As the extraction time extended from 5 to 10 minutes, the recoveries were obviously enhanced for $O_3$-NAs (from 12.19 to 14.67 mg NAs/kg tailings), $O_4$-NAs (from 16.75 to 21.15 mg NAs/kg tailings), $O_5$-NAs (from 2.56 to 3.43 mg NAs/kg tailings), and $O_6$-NAs (from 0.78 to 1.08 mg NAs/kg tailings). However, beyond 10 minutes, further increases in extraction time up to 60 minutes resulted in trivial improvements in the recoveries of oxidized NAs. Moreover, the concentration of total NAs exhibited a noticeable increase followed by a plateau at 40 min, indicating an optimal extraction duration. Zan et al. used a 5 min shaking to extract NAs from sediment samples using 0.1 M NaOH for gas chromatography MS analysis (Zan et al., 2019). In this study, the results demonstrated that 5 min of mixing is insufficient for efficient extraction of all NA species, and 40 min of shaking was finally picked for subsequent optimization steps.

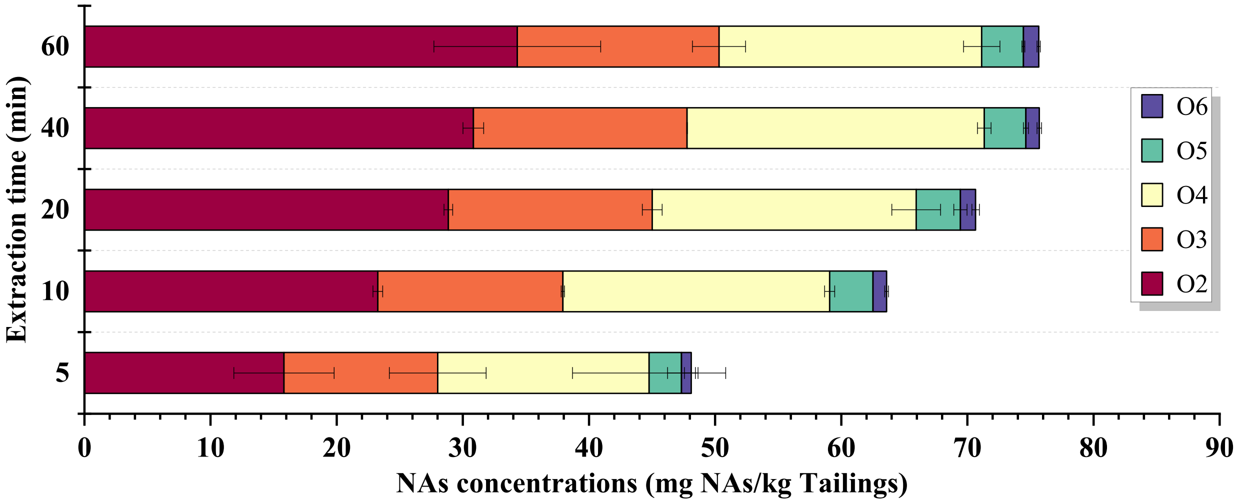

Fig. 3.6 The extracted concentrations of $O_2$-$O_6$ NAs and total NAs from dry tailings (PASS-treated FFT) using 0.5 M NaOH under different extraction time.

#### 3.3.1.4 Effect of number of extractions

The efficient extraction of NAs species from tailings could also be affected by the number of extraction steps. Therefore, multiple extractions were performed as illustrated in Fig. 3.7. When the extractions were conducted from one to two times, there was a notable increase in the amounts of recovered NAs, specifically, from 23.90 to 35.48 mg NAs/kg tailings for $O_2$-NAs, from 14.05 to 16.87 mg NAs/kg tailings for $O_3$-NAs, and from 15.5 to 16.85 mg NAs/kg tailings for $O_4$-NAs. However, the extracted amounts of $O_5$-NAs (from 4.37 to 4.01

mg NAs/kg tailings) and $O_6$-NAs (from 1.58 to 1.71 mg NAs/kg tailings) showed an insignificant increase. With a further increase in the number of extractions from two to six times, there was a slight decrease in the recovery of $O_2$-NAs while the amount of extracted oxidized NAs exhibited negligible changes. Simultaneously, it was observed that the total extracted NAs reached the maximum after two extraction cycles and maintained similar levels with subsequent increases in the extraction number. These results indicate that repeating the extraction process two times is sufficient for achieving efficient recovery of NAs from tailings. The results also suggest that two extraction steps increase NAs extraction from complex matrices of tailings by 26%. This was consistent with prior research, which found that a single-step extraction was not sufficient to extract petroleum hydrocarbon from soil samples by mechanical shaking (Ma et al., 2018; Schwab et al., 1999).

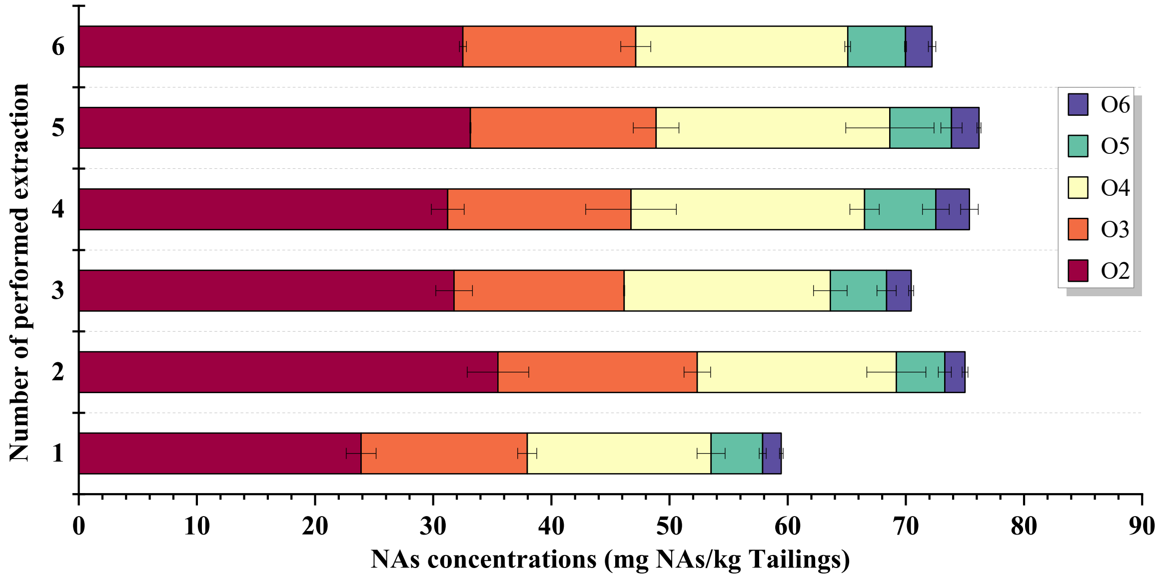

Fig. 3.7 The extracted concentrations of $O_2$-$O_6$ NAs and total NAs from dry tailings (PASS-treated FFT) using 0.5 M NaOH under one to six extractions.

### 3.3.1.5 Optimization of SPE cleanup step

During the SPE step, the initial conditions were employed following the procedure established in a previous study which demonstrated that Oasis HLB cartridge obtained the highest NAs recovery from OSPW as compared to other SPE cartridges (Qin et al., 2019). However, certain parameters, including elution solvents and reconstitution reagents for the dried SPE extracts, could be scrutinized to enhance the recovery of NAs in this cleanup step.

In SPE elution step, acids are often incorporated into elution solvents to enhance the desorption and elution of analytes from the solid phase within the SPE cartridge (Jie et al., 2015; Swenson et al., 2014). The inclusion of acids in the elution solvent is to disrupt the interaction between the analytes and the SPE sorbents, thereby facilitating their release into the elution solvent. Moreover, acids in the elution solvent might also contribute to stabilize certain analytes, particularly acidic compounds, throughout the elution process. Si et al. earlier observed that increasing the acidity of the eluent improves the carboxylic acid desorption rate from the SPE process due to π-π and other interactions participating in the SPE process (Si et al., 2019). In this study, the suitability of HCl (2M) and formic acid was compared for the acidification of methanol as the eluent in SPE elution step. As it was previously reported that the acid content in elution solvent had insignificant effect on the recovery of NAs from SPE cartridges (Jie et al., 2015), acidified methanol with a ratio of acid to methanol = 1:10 ( v: v) were utilized according to the previous research (Qin et al., 2019), and the result is presented in Fig. 3.8. It is obvious that formic acid acidified methanol achieved much higher recoveries for all NA species. As well as for the total NAs, the recovered concentration is much higher at 88.83 mg NAs/kg tailings using formic acid acidified methanol than that (61.37 mg NAs/kg tailings) using HCl acidified methanol. The findings suggested that formic acid in methanol is a superior choice for eluting carboxylic acid from SPE adsorbent cartridge. In alignment with these results, Heyen et al. established a robust methodology for extracting and quantifying organic acids from microbial samples through SPE (Heyen et al., 2020). The authors demonstrated that employing 5% formic acid in methanol as the elution solvent resulted in the highly successful recovery of 12 out of 15 aromatic and aliphatic acids, achieving outstanding recovery rates ranging from 100% to 111%. Moreover, Heyen et al. and Si et al. both concluded that increasing the formic acid concentration in methanol beyond 5% (higher acidity) did not result in improved elution of carboxylic acids from different SPE adsorbents (Heyen et al., 2020; Swenson et al., 2014). This finding implies that using 10% formic acid in methanol to elute NAs from HLB cartridge in this study was sufficient and appropriate choice. Formic acid, being an organic acid, also is the simplest carboxylic acid capable of accelerating the release of NAs from the SPE sorbents by competing for adsorption sites. Additionally, formic acid is commonly employed in SPE eluents due to its enhanced compatibility with subsequent HPLC or HPLC-MS analyses compared to the inorganic acid HCl (Swenson et al., 2014). Therefore, formic acid acidified methanol (v:v, 1:10) was ultimately selected for the following optimization steps.

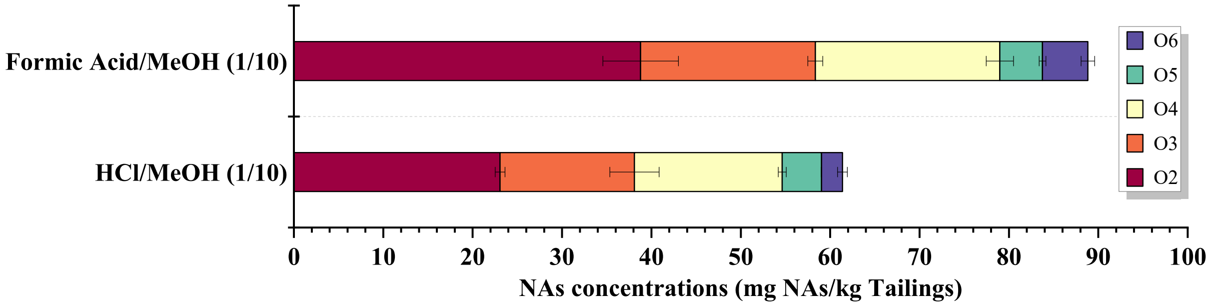

Fig. 3.8 The extracted concentrations of $O_2$-$O_6$ NAs and total NAs from dry tailings (PASS-treated FFT) using 0.5 M NaOH and using different elution solvents in SPE step.

After the SPE, the organic elution solvent is typically evaporated to dry the extracts, which are subsequently reconstituted in a smaller volume of a solvent for the enrichment of analytes before instrumental analysis. Hence, the reconstitution reagents for the dry SPE extracts assume a pivotal role in ensuring the proficient detection of analytes on analytical instruments. These reagents must not only facilitate the complete dissolution of analytes but also demonstrate compatibility with the chosen detection method, such as HPLC-MS. Various studies have utilized both aqueous and organic solvents for reconstituting the SPE extracts in NAs extraction process (Jie et al., 2015; Qin et al., 2019; Wan et al., 2014), yet there is a gap regarding an investigation into which solvent serves as the superior reconstitution reagent for NAs recovery. In present work, four reconstitution reagents, including 5mM $NaHCO_3$ buffer, water, methanol, and a mixture of methanol/water (v: v, 1:1), were explored as shown in Fig. 3.9. The recovered amounts of the total NAs from tailings were 60.11, 87.76, 94.23 and 109.43 mg NAs/kg tailings when using water, 5 mM $NaHCO_3$, methanol, and the mixture of methanol/water as reconstitution reagent, respectively. It should be pointed out that the choice of the reconstitution reagent significantly influenced the determination of $O_2$-NAs, which showed a substantial increase when using the methanol/water mixture. In contrast, the amounts of $O_3$-$O_6$ NAs exhibited negligible changes across the four types of reconstitution reagents. Initially, a 5 mM $NaHCO_3$ buffer was used for re-dissolve the SPE extracts because it has the same pH as OSPW, assuming to totally dissolve the extracted organics (Qin et al., 2019). However, methanol, an organic solvent, outperformed 5 mM $NaHCO_3$ and water, while the combination of methanol and water achieved the highest recovery of total NAs. Despite water being highly polar and methanol being a low-polarity solvent, they exhibit good miscibility, making it easy for them to form a homogeneous solution. This property enables effective dissolution of both polar and weak-polar NA species in their mixture, creating an improved condition for NAs measurement using UPLC-QTOF-MS.

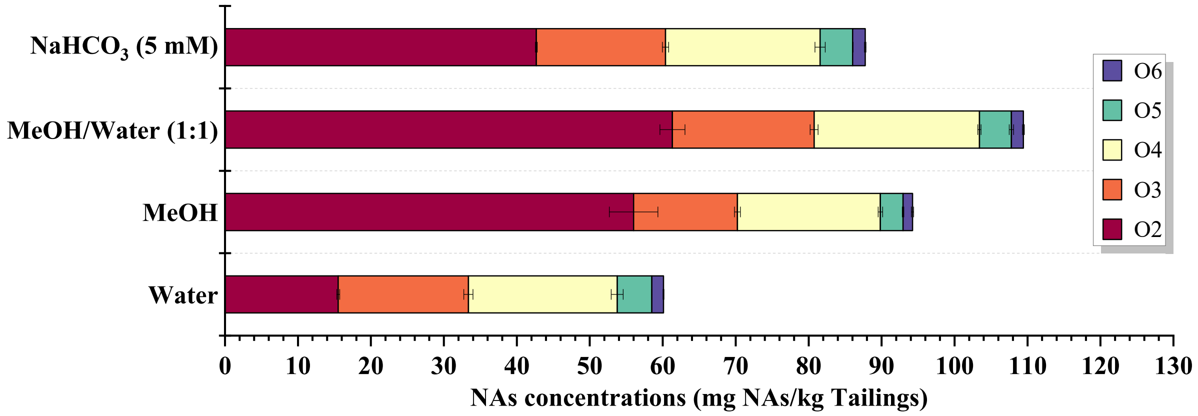

Fig. 3.9 The extracted concentrations of O2-O6 NAs and total NAs from dry tailings (PASS-treated FFT) using 0.5 M NaOH and using different reconstitution reagents in SPE step.

Collectively, this work marks a pioneering effort in optimizing extraction and cleanup procedures for the determination of NA species in oil sands tailings. The established protocol is clearly outlined, providing a robust foundation for future studies and practical implementations.

### **3.3.2** Characterization of NAs in different types of tailings

There are several terms that may be used to classify different types of oil sands tailings. FFTs are typically waste streams generated during oil sands processing, containing solid content more than 2 w% but lower than the liquid limit (the boundary between liquid and solid behavior) (OSTC, 2012). Over time, the solid components within the FFT gradually undergo sedimentation, resulting in the formation of a resilient, high-viscosity, gel-like suspension known as MFT with a solids content exceeding 30% (Cossey et al., 2021). Dewatering is integral to tailings management, which makes tailings more solid and easier to handle, thus facilitating the reclamation process. Simultaneously, it diminishes the environmental impact of oil sands operations by reducing the volume of tailings ponds. In the past few decades, the oil sands industry has explored the commercial applications of various dewatering technologies for oil sands tailings (Saborimanesh, 2021; Vajihinejad et al., 2021; Wang et al., 2023). One of the promising tailings treatment methods is the permanent aquatic storage structure (PASS) technology, which employs a coagulant (alum) and a polymer flocculant (polyacrylamide, PAM) to accelerate tailings dewatering and improve the quality of water release from dewatering immobilizing COPCs (Cossey et al., 2021; Omotoso et al., 2021) In this study, the PASS-treated FFT was used as a model for optimizing the extraction method of NAs and the subsequent SPE cleanup step. This section outlines the application of the proposed protocol to two additional types of tailings: FFT and MFT. It is important to emphasize that MFT, FFT and PASS-treated FFT utilized in this study, originated from three distinct oil sands operators (Fig. 3.10). The concentration of total NAs in MFT, FFT and PASS-treated FFT were 56.15, 57.64 and 112.25 mg NAs/kg tailings, respectively (Fig. 3.10). Specifically, the concentrations of $O_2$-to-$O_6$-NAs for PASS-treated FFT were 60.86, 22.09, 24.37, 3.66, and 1.26 mg NAs/kg tailings. The concentrations of $O_2$- to $O_4$-NAs in FFT and MFT were 47-49% and 51-53% lower than in PASS-treated FFT. For $O_5$-NAs and $O_6$-NAs, FFT exhibited 58% and 71% reduced concentrations relative to PASS-treated FFT. MFT's $O_5$-NAs concentration was similar to PASS-treated FFT, but $O_6$-NAs were 20% higher.

Additionally, the composition of $O_2$-$O_6$ NA species in different tailing extracts was analyzed (Fig. 3.11). Both PASS-treated FFT and FFT exhibited similar compositional distributions: $O_2$-NAs (54%), $O_3$-NAs (20%), $O_4$-NAs (22%), $O_5$-NAs (3%), and $O_6$-NAs (1%). The composition of MFT was slightly varied, with $O_2$-NAs (50%) being predominant, followed by $O_3$-NAs (19%) ~ $O_4$-NAs (21%) > $O_5$-NAs (6%) > $O_6$-NAs (3%). Generally, $O_2$-NAs dominated the composition in all tailings, decreasing as the oxygen number increased, which was consistent with OSPW profiles (Huang et al., 2018; Huang et al., 2021; Qin et al., 2019). High NAs concentrations in the treated FFT was expected because of the chemical immobilization process of PASS treatment technology (Omotoso et al., 2021). In this technology, an addition of high dosage of alum facilitates cation bridging between NAs and the solid content of the FFT (Omotoso et al., 2021). Additionally, the presence of the flocculant polymer of PAM (containing $NH_2$ functional groups) potentially contributed to hydrogen bonding interactions with polar organic compounds, especially between PAM and negatively charged NAs (Pourrezaei et al., 2014). These mechanisms could potentially result in increased NAs adsorption and higher NAs concentrations in the treated FFT. While storing MFT in a pond for an extended duration likely led to biodegradation and desorption processes, significantly reducing the NA species within the MFT (Vander Meulen et al., 2021).

The distribution of classical NAs, which were the NA species with higher concentrations in all tailings' samples, was also characterized based on carbon number and -Z number (Fig. 3.12). The classical NAs in the FFT, MFT and PASS-treated FFT profile were in the range of carbon number 8–25 and -Z number 0–18. In terms of carbon number, the majority of NAs across all tailing's samples were found within the range of 13–22 and with the major contributions at carbon number of 16 and 18. The most abundant NA species exhibited -Z values of 0, followed by 4, 6 and 12 in for all tailing samples. The relatively distinctive parameters such as age, type, source, and treatment of the tailings samples potentially lead to different characteristics and distribution of NA species in this study. In agreement with Cossey et al., these parameters contributed to varied tailings' chemical composition (Cossey et al., 2021).

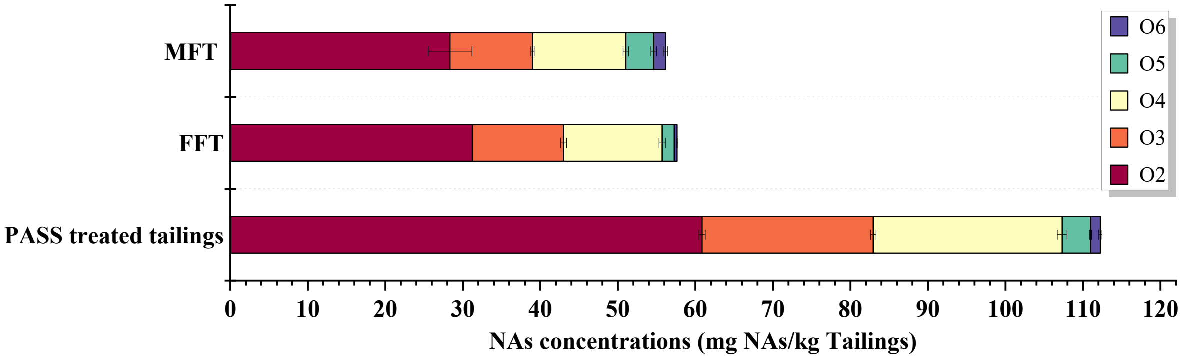

Fig. 3.10 Comparison of the extracted concentrations of $O_2$-$O_6$ NAs and total NAs from different types of dry tailings using the optical extraction and cleanup conditions.

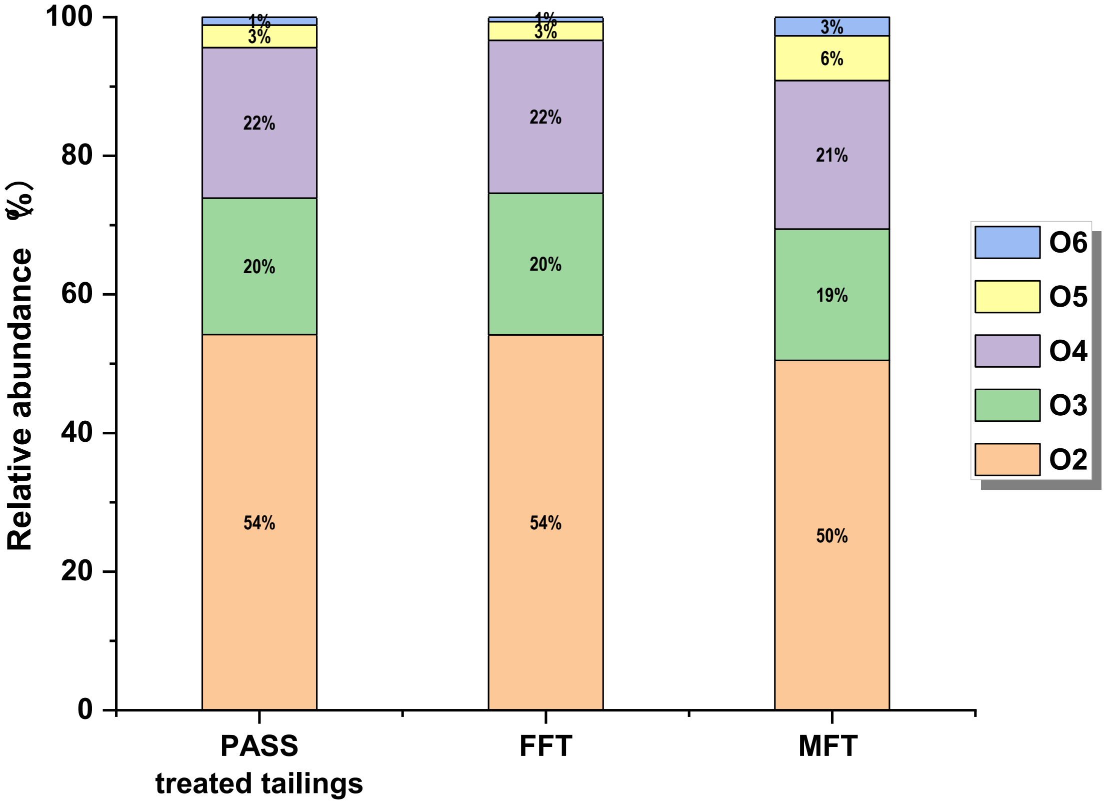

Fig. 3.11 Relative abundances of $O_2$-$O_6$ NA species in total NAs from different tailings using the optimal extraction and cleanup conditions.

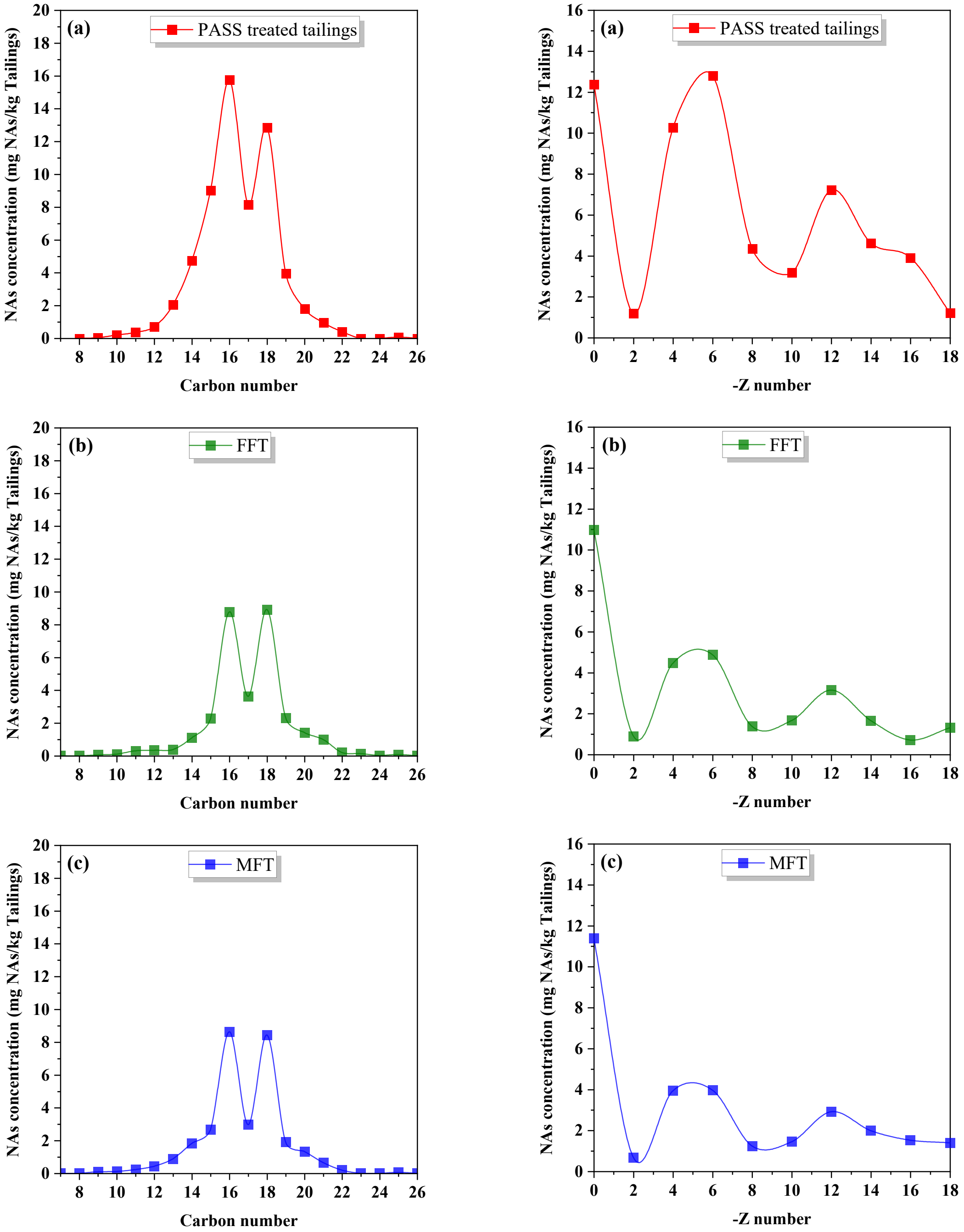

Fig. 3.12 Comparison of the extracted $O_2$-NAs from different types of tailings in terms of carbon number and -Z number.

### 3.3.3 The environmental implication

Developing methods for characterizing NAs in oil sands tailings carries significant environmental implications, as highlighted by the provided information:

**Enhancing environmental monitoring:** The growing interest in monitoring NAs, offers a more comprehensive evaluation of their ecological impact in the environment (Yang et al., 2019). This increase is driven by expanded environmental monitoring programs in Canada (Headley et al., 2016). It has been reported that NAs concentrations below 10 mg/L, extracted from OSPW, can cause congenital abnormalities and even death in living species (Kavanagh et al., 2012). However, the limited investigations into NAs concentrations in sediments, such as tailings, highlight the complexity of accurately comparing the ecological impacts. By characterizing NAs in tailings sediment, we gain the ability to accurately assess the fate of NAs and the potential impact on ecosystems. Additionally, determining varied NAs levels and profiles in sedimentary could provide a supplementary approach for monitoring biodegradation progress (Zan et al., 2019). Understanding the transformation and degradation of NAs in tailings sediment is crucial for evaluating the effectiveness of natural remediation processes and guiding strategies to enhance biodegradation, thereby reducing the environmental impacts.

**Improving tailings reclamation**: A profound understanding of the fate of NAs in tailings is crucial for effective tailings management. This knowledge enables oil sands operator to monitor NAs during reclamation, reducing the risk of NAs release in reclamation sites. More specifically, developing a method for characterizing NAs in tailings is essential for assessing the effectiveness of tailings treatment techniques and innovative reclamation practices. This involves assessing the effectiveness of treatment methods, such as PASS treatment of FFT, in dewatering and immobilizing NAs in tailings. This is particularly crucial for their potential use in long-term reclamation projects like end pit lakes. Furthermore, a novel reclamation practice had recently proposed the use of thickened tailings (TT, a chemically treated tailings) as reclamation material in wetland systems (Degenhardt et al., 2023). Their results found that plant survival was high on both uncapped TT and PMM capped TT, while plant growth was limited on uncapped TT. The chemical properties of the TT, marked by elevated concentrations of petroleum hydrocarbons and nutrient deficiencies, may challenge plant growth. Our study suggests that NAs in TT may also be a critical factor influencing plant growth, making it worthwhile to include this factor for a more comprehensive understanding. As another illustration, Chen et al. utilized different types of tailings as the sediments of aquatic mesocosms to examine how these tailings influenced the physical and chemical properties of the water column (Athabasca River water), which may affect the ecosystems for aquatic animals and plant communities (Chen & Melnichuk, 2021). Therefore, characterizing NAs in the tailings sample in this oil sands reclamation area is critical for monitoring changes in NAs composition, understanding their environmental impact, and adjusting reclamation strategies accordingly.

## 3.4 Conclusion

In present work, an exhaustive methodology for extraction and SPE cleanup of NAs in oil sands tailings, combined molecular characterization using UPLC-QTOF-MS, were introduced. For extraction, 0.5 M NaOH outperformed ten extraction solvents for NAs recovery effectively. The orbital shaking condition was 1.27 times more effective than static condition. Mixing for over 40 minutes was adequate and increased recovery by 32% over 5 minutes. Two extraction steps yielded 26% more recovery than a single extraction step. Subsequently for cleanup step, methanol/formic acid (43%), and methanol/water (82%), in SPE using Hydrophilic-Lipophilic Balance (HLB) cartridges, recovered the most NAs during cleanup. The optimized extraction and SPE conditions were successfully applied in determination of NA species in three different types of tailings. The largest NAs level was detected in PASS-treated FFT and relatively lower concentration of NAs were found in MFT (56.15), and FFT (57.64). The saturated $O_2$-NAs accounted for a large portion in the tailings among other NA species, particularly those with carbon numbers 16 and 18, which dominated across all tailing samples. The protocol outlined in this study provides a robust framework for NAs in various oil sands tailings storage systems, and gauging the efficacy of tailings treatments and innovative reclamation practice. By expanding the investigative parameters and adhering to this standardized approach, more conclusive data can be gathered, enabling a comprehensive comparison of NAs characterization across different forms of treated and untreated tailings concerning their chemical attributes.

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# 4 Chapter 4: Mobility of Metals, Ions, and Naphthenic Acids from Tailings Deposits to Water Column: Demonstration Pit Lake

## 4.1 Introduction

Surface mining of oil sands results in the production of considerable quantities of fine fluid tailings (FFTs). Accordingly, the oil sands industry solely in Alberta, Canada, has generated more than 1.3 billion m$^3$ of FFT, which is currently stored in FFT ponds covering a total area of 100 km$^2$ (Kuznetsova et al., 2023). FFTs are characterized by a mixture of water, sand, clay, residual bitumen, metals, ions, and, notably, toxic dissolved organics such as naphthenic acids (NAs) (Cossey et al., 2021; White, 2017). To address the environmental concerns stemming from the long-term storage of FFT and the associated release of contaminants, industry practitioners have embarked on an exploration of multiple reclamation strategies. Among these, the establishment of permanent aquatic closure systems, particularly end pit lakes (EPL), has gained tremendous interest. These systems are often exploited in other mining sectors, but their application for oil sands FFT deposition is relatively a nascent consideration (AER, 2020). The principal design intent behind EPL is the transformation of decommissioned mining pits into permanent closure system, which concurrently facilitate water release downstream (Charette, 2010; Dompierre et al., 2016). In this reclamation strategy, the treated or untreated FFT is stored in closed mine pits, subsequently overlaid with only freshwater or a composite of oil sands process water (OSPW) and freshwater, termed capping water (Miller, 2012; Siddique et al., 2012; Yu, 2019). Currently, plans are underway to establish 23 EPLs in northern Alberta, envisioned as permanent elements within the framework of the reclaimed mine closure landscape (COSIA, 2021b). However, regulatory approval in Alberta remains elusive, given the limited empirical understanding surrounding the geochemical stability of these engineered ecosystems (AER, 2020).

To date, Base Mine Lake (BML) and Lake Miwasin are the only two demonstrated EPL projects by the oil sands industry in Alberta, Canada. Extensive studies have primarily concentrated on BML — established by Syncrude in 2013 — exploring its performance via biogeochemical characterization of untreated FFT and evaluating the water quality (Cossey et al., 2021; White, 2017). Preliminary findings suggest a decline in lake water toxicity over time; however, a large proportion of contaminants of potential concerns (COPCs) are released from untreated FFT into the lake water (Table 2.6) (White & Liber, 2018). This release of COPCs from the pore water of FFT to the capping water appears to be orchestrated by both advection and diffusion processes (Dompierre et al., 2017). As FFT settling continues over time, diffusion becomes the predominant mechanism after advection (Dompierre et al., 2017). Lake dynamics — specifically turnover and internal waves prompted by seasonal shifts — not only affect the lake's oxygen profile and turbidity but also instigate additional chemical flux (Cossey et al., 2021; Dompierre et al., 2017).

At Lake Miwasin, Suncor has pioneered the implementation of chemically treated Permanent Aquatic Structure Storage (PASS) technology for FFT treatment. This preliminary PASS treatment, incorporating both alum (coagulant) and negatively charged polyacrylamide (PAM, flocculant), is devised to accelerate dewatering and, in turn, improve the consolidation of FFT (Suncor, 2019). The use of Alum, which facilitates chemical immobilization through inter-particle forces (Pourrezaei et al., 2011), and the use of PAM, which enhances it through hydrogen bonding (Pourrezaei et al., 2014), makes this treatment more effective. Ideally, this treatment could curtail the mobility of potentially toxic elements, ions, and dissolved organics (Suncor, 2018). However, this treatment is not devoid of challenges. Specifically, the plausible exudation of deleterious by-products, notably acrylamide (AM), and ions such as aluminum (Al) and sulfate ($SO_4^{2-}$), potentially result in capping water toxicity (Krupińska et al., 2019; Li et al., 2023b).

Further, an initial high hydraulic conductivity can lead to an increased chemical fluxes during the nascent phases of reclamation (Cossey et al., 2021). Despite potential challenges, PASS-treated FFT remains at the forefront of active research and innovation, with concerted efforts to refine the methodology and mitigate potential issues. The success of this treatment depends on a range of factors, which include the inherent properties of the FFT itself and the environmental context in which it is placed.

Here, we performed two independent studies to investigate the mobility of metals, ions and dissolved organics from the treated FFT deposits to the water column at Lake Miwasin. Specifically, the first study looked at the COPCs fate in water columns over an extended duration, particularly 1) The PASS-treated FFT impact on the release of COPCs to the water column, and 2) quantifying the efflux of dissolved organics, ions, and trace elements from the FFT to the capping water over two years. On the other hand, the second study focused on 3) the early stages of Lake Miwasin's mass transfer mechanisms, especially highlighting the complex dynamics of chemical mass transfer. This encompassed a thorough exploration of advection-dispersion-decay processes from treated FFT into the capping water. For a deeper understanding of this research, various scenarios were examined, including factors such as the presence or absence of lake turnover conditions to evaluate water mixing effects, different consolidation ratios, and a comparison of water qualities, specifically contrasting lake water with fresh water.

## 4.2 Material and method

### 4.2.1 Materials

PASS-treated FFT and lake water samples were collected in August 2020 from Lake Miwasin at Suncor Energy, Alberta, Canada. All samples were stored at 4 °C in a cold storage room prior to the establishment of pit lake models. The characterization of the lake water is detailed in Table 4.1. All chemicals used were of analytical grade and were used as received without further purification. All solutions were prepared using ultra-pure water ($R \geq 18.2$ MΩ) obtained from a Millipore Milli-Q system.

Table 4.1 Lake water characterization

| Parameter | Instrument/Method | Unit | Value | STD |
|---|---|---|---|---|
| Ammonia | APHA standard method (2005) | mg/L | < 0.1 | N/A |
| Phosphorus | APHA standard method (2005) | mg/L | <0.5 | N/A |
| TKN[2] | APHA standard method (2005) | mg/L | 2.785 | 0.417 |
| $NO_3$+$NO_2$ | APHA standard method (2005) | mg/L | 0.585 | 0.026 |
| pH | YSI Professional Plus handheld multi-parameter water quality meter | mg/L | 8.12 | 0.05 |
| DOC | TOC analyzer | mg/L | 38.305 | 0.219 |
| AEF [3] | FTIR Spectrometry (Thermo Scientific) | mg/L | 23.135 | 1.843 |
| BOD[4] | APHA standard method (2005) | mg/L | 16.54 | 0.22 |
| Conductivity | YSI Professional Plus handheld multi-parameter water quality meter | µS/cm | 1804 | 24 |
| AM [5] | HPLC | mg/L | 0.14 | 0.01 |
| Turbidity | T-100 handheld Oakton Tubi pH-meter | NTU | 1.435 | 0.035 |
| NAs | Time-of-flight mass spectrometry (TOF-MS) | mg/L | 2.71 | 0.04 |
| $Cl^-$ | Dionex ICS 5000 Ion Chromatography | mg/L | 227.81 | 0.07 |
| $SO_4^{2-}$ | Dionex ICS 5000 Ion Chromatography | mg/L | 114.04 | 0.08 |
| $Na^+$ | Inductively coupled plasma mass spectrometer (ICP-MS) | mg/L | 353.80 | 0.01 |
| $K^+$ | ICP-MS | mg/L | 7.76 | 0.08 |
| $Ca^{2+}$ | ICP-MS | mg/L | 39.430 | 0.004 |
| $Mg^{2+}$ | ICP-MS | mg/L | 16.000 | 0.005 |
| Sr | ICP-MS | mg/L | 0.494 | 0.001 |
| Si | ICP-MS | mg/L | 0.626 | 0.004 |
| B | ICP-MS | mg/L | 1.598 | 0.003 |

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[2] Total kjeldahl nitrogen

[3] Acid extractable fraction

[4] Biological oxygen demand

[5] Acrylamide

### 4.2.2 PASS-treated FFT characterization

The composition of FFT samples (bitumen, water, and solids) was determined using the Dean-Stark extraction process (Dean & Stark, 1920; Zhang, 2012). The mineral composition of FFT was identified through X-ray diffraction analysis utilizing a Rigaku Ultima IV powder X-ray diffractometer (XRD) available at the Department of Earth and Atmospheric Sciences, University of Alberta, Canada. The Rigaku Ultima IV XRD employed a Cobalt (Co) source operated at 38 kV and 38 mA. Mineral abundances were determined using Rietveld refinements (Bish & Howard, 1988; Hill & Howard, 1987; Rietveld, 1969) with XRD data using TOPAS 5 (Bruker).

The FFT samples were subjected to freeze drying for 8 hours to determine organic matter content. The resulting solid agglomerates were then pulverized using a mortar and pestle. Total organic matter in FFT was analyzed through thermogravimetry (TGA) using a thermal analyzer system (TGA/DSC 1, Mettler Toledo, Mississauga, ON, Canada). The dried particles underwent heating up to 600°C in the presence of nitrogen. TOC analysis for dried FFT samples was conducted using a Thermo Scientific FLASH 2000 CHNS-O Analyzer. 0.5 M $K_2SO_4$ (Sigma-Aldrich) extraction solution (FFT-to-solution ratio of 1:5 w/v) was used to determine DOC of PASS-treated particles (Jones & Willett, 2006).

The surface functional groups were determined between 400 and 4000 $cm^{-1}$ at 4 $cm^{-1}$ resolution using Fourier transform infrared (FT-IR) spectroscopy (Nicolet™ 8700 FT-IR Spectrometer, Thermo Scientific, USA). Prior to FT-IR analysis, samples were pressed into KBr pellets. The solid addition method was used to determine the adsorbent's pH point of zero charges

($pH_{PZC}$) (Bakatula et al., 2018). The summary of the initial characterization of PASS-treated FFT is provided in Tables 4.2 and 4.3 and Fig 4.1.

Table 4.2 Physicochemical property of PASS-treated FFT

| **Parameter** | **Value (wt%)** |
|---|---|
| Organic matter* | 12.66 ± 0.78 |
| TOC | 8.1 ± 0.4 |
| DOC | 1.15 ± 0.20 |
| NAs | 0.011 ± 0.004 |
| $pH_{pzc}$ | 5.91 ± 0.05 |
| Fine Solid | 47.32 ± 0.24 |
| Water | 52.21 ± 0.28 |
| Bitumen | 0.47 ± 0.16 |

* The organic matter in PASS-treated FFT comprised a mixture of hydrocarbons and polyacrylamide (PAM) (PAM dosage for the treatment was 1500 g/tonne clay).

Table 4.3 Mineral composition of FFT determined by XRD

| Phase | Amount (wt%) ±2.6 |
|---|---|
| Quartz | 47.7 |
| Kaolinite | 29.9 |
| Muscovite | 15.6 |
| Microcline ($KAlSi_3O_8$) | 5.7 |
| Rutile (natural mineral form of $TiO_2$) | 0.6 |
| Anatase (natural mineral form of $TiO_2$) | 0.6 |

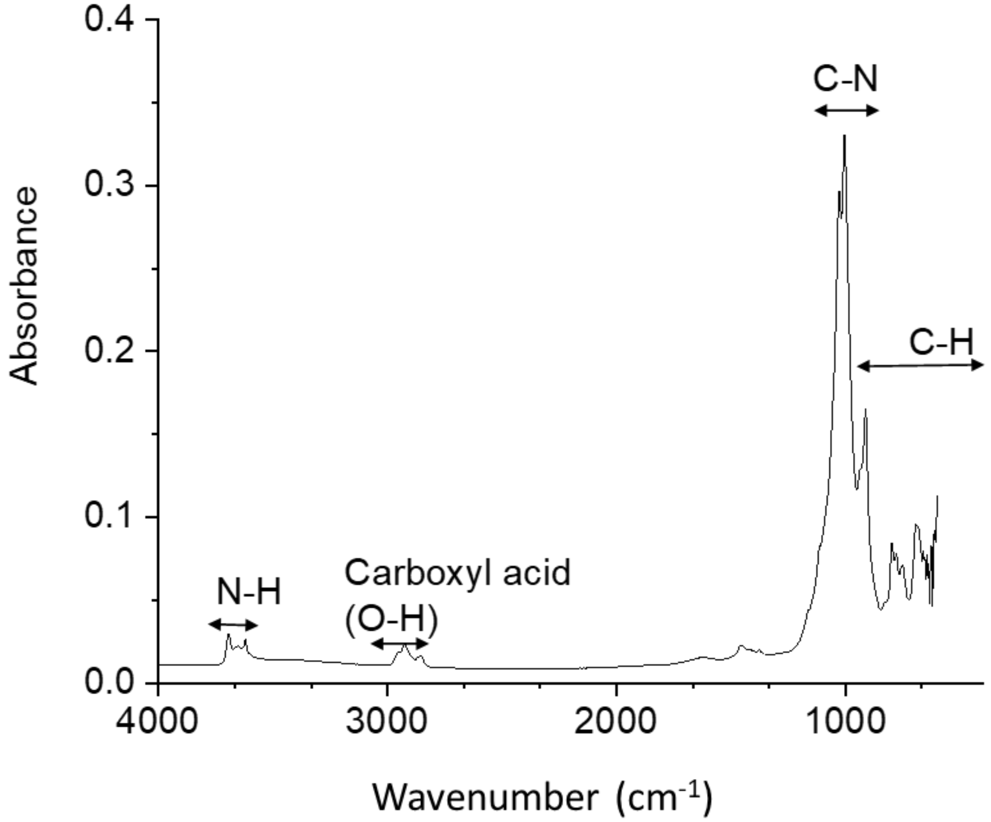

Fig. 4.1 FT-IR spectra of PASS-treated FFT

### 4.2.3 Study I

**Establishing and operating pit lake models:** Laboratory-based models simulating conditions of Lake Miwasin were operated for two years to investigate the long-term impacts of FFT attributes (Fig. 4.3a). Consequently, we set up eight vertical columns, each 2.4 m in height and 200 mm in diameter, with sample ports at 0.2 m intervals. These columns contained FFT deposits and were overlaid with lake water at a 1:2 ratio. This ratio was derived from the actual sediment to water ratio documented in Lake Miwasin a year after its establishment (COSIA, 2021b). The transition of the lake's dissolved oxygen (DO) profile from anoxic to oxic conditions (as depicted in Fig. 4.2) was challenging to replicate within the confines of a shallow 1.44 m pit lake model. This was primarily due to the reduced hydraulic pressures at the mudline in the models as compared to the natural conditions of lake (Kuznetsov et al., 2023). Thus, the oxic and anoxic profiles within the water column were established and analyzed in separate pit lake models. Of the models, six were operated under oxic conditions, while two were maintained under anoxic conditions (Fig. 4.3b). The documented DO profile from Lake Miwasin in 2019, along with the oxic and anoxic columns, can be seen in Fig. 4.2. The DO levels in each column were regularly adjusted every week by introducing pure oxygen gas ($O_2$) to the top and nitrogen gas ($N_2$) to the bottom of the capping water (Fig. 4.3b). The controlled conditions of this experiment facilitated intermittent sampling and monitoring of FFT, concurrently eliminating external variables that could influence chemical migration. The initial week, dedicated to system stabilization before sample collection, is referred to as the commissioning phase. To characterize the lake water quality, each time, 200 mL of lake water were taken from the sampling ports from the oxic and anoxic column at regular intervals (Fig 4.3c). The water sampling regime for the columns is specified in Table 4.4. To understand the geochemical properties of the FFT, 100 mL of the FFT were taken from the top, middle, and bottom of the FFT deposits in the columns, biannually.

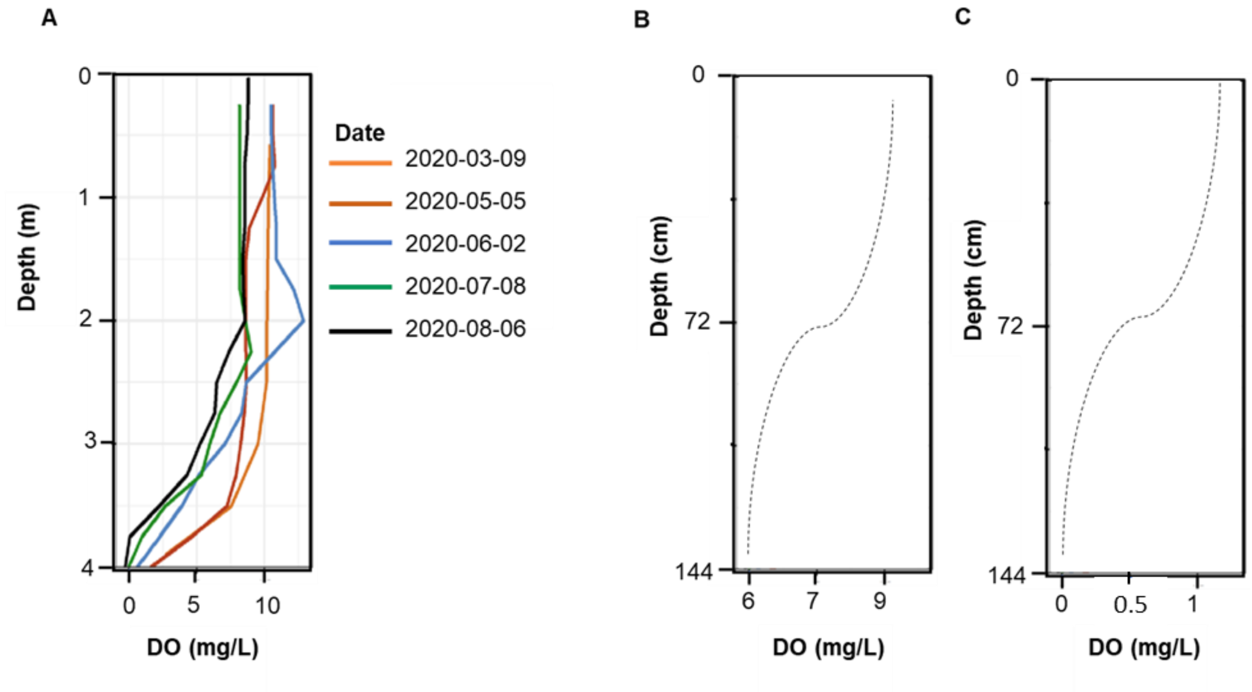

Fig. 4.2 The DO profile of a) Lake Miwasin 2019, b) oxic pit lake models, and c) anoxic pit lake models sampling.

Table 4.4 Sampling frequency specification for laboratory-based DPL columns.

| Time | Sampling frequency | The oxic columns |  | The anoxic columns |  |
|---|---|---|---|---|---|
|  |  | Column number | Sampling port | Column number | Sampling port |
| First month | Weekly | 1, 2 | 1, 2, 3 | 11, 12 | 2 |
| 2nd to 6th month | Monthly | 1, 2 | 1, 2, 3 | 11, 12 | 2 |
| 7th to 12th month | Monthly | 3, 4 | 1, 2, 3 | 11, 12 | 2 |
| Year 2 1st month to Year 2 12th month | Quarterly | 5, 6 | 1, 2, 3 | 11, 12 | 2 |

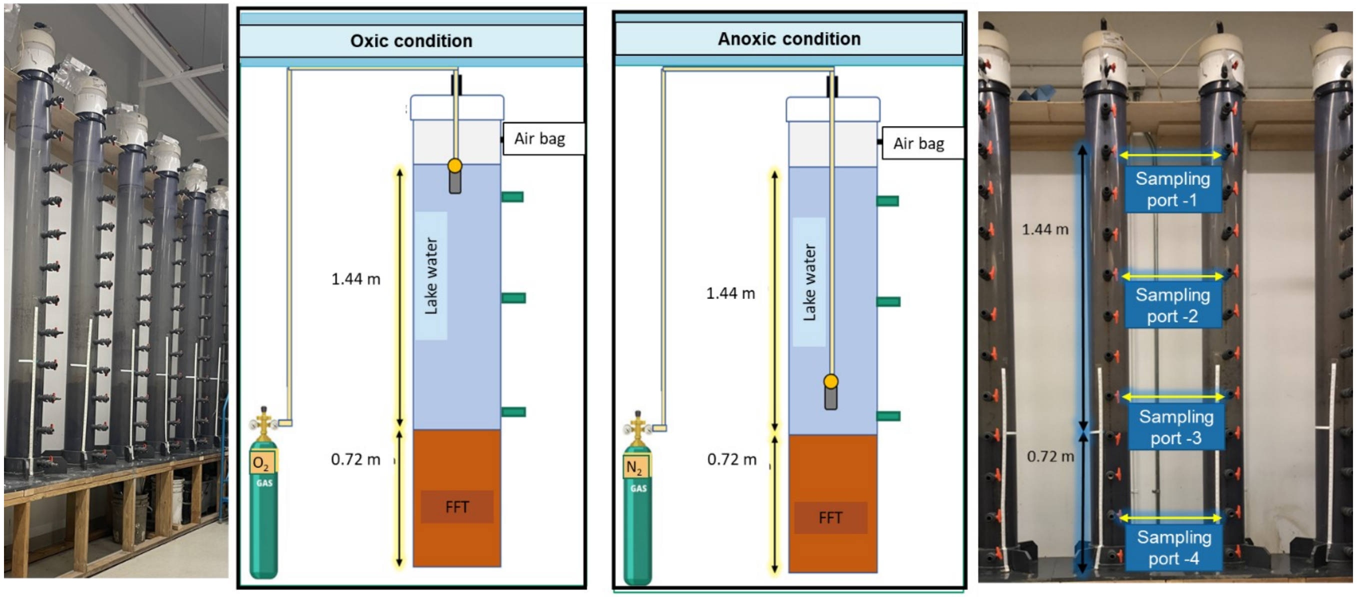

Fig. 4.3 Set up of laboratory-base model pit lake models at different DO profiles: a) configuration of DPL columns, b) monitoring DPL column specification under different DO profiles, and c) sampling.

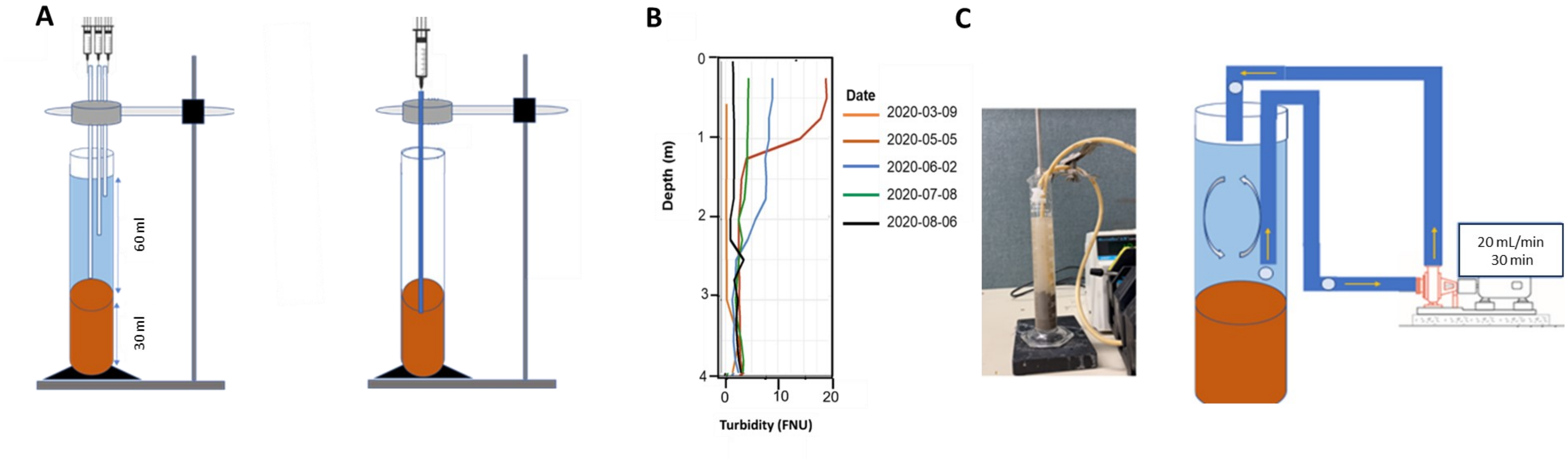

Fig. 4.4 a) Sampling regime for bench column study, b) lake Miwasin turbidity profile for the year 2019, c) setup and design to simulate lake turnover conditions of lake Miwasin for the bench-scale column study.

### 4.2.4 Study II

**Impact of PASS-treatment on early-stage chemical transport:** Here, the main aim was to investigate the pore water flux under different conditions from the FFT to the overlying capping water over one week in the early stage of EPL establishment. Precisely**,** this study evaluated the effect of the water quality, consolidation ratio, and the effect of lake turnover on pore water advective flux in the early stages of operation. For this purpose, a total of 40 bench-scale small glass-wear columns (capacity 100 mL, Cole-Parmer) were filled with the FFT deposits, which were covered with capping water in 1:2 ratio. Systems were operated at specific intervals in duplicates, i.e., 1, 12, 24, 96, and 168 h. The details of the sampling and experimental design specifications of the bench columns study are provided (Table 4.5, Fig 4.4). To recreate the turnover mixing conditions of the Lake Miwasin in our models, the capping water was circulated at the rate of 20 mL/min for 30 min, which is the highest turbidity of the lake water during turnover as per the annual Lake Miwasin report for 2019 (Fig 4.4b, c).

The chemical pore water flux was measured using chloride ion ($Cl^-$). $Cl^-$ is water-soluble and is not affected by the biogeochemical processes (biological, chemical weathering, or adsorption/desorption) in a solution (Feth, 1981). Therefore, it can serve as a reliable conservative tracer to assess chemical mass flux in model pit lakes (Dompierre et al., 2017).

Table 4.5 Experiment design specifications for bench column experiment

| NO. | Item | Note |
|---|---|---|
| 1 | Column size | 100 mL glassware column |
| 2 | Sampling duration | 1 week |
| 3 | Frequently of sampling | (1 hr, 12 hr, 24 hr, 96 hr, 168 hr) |
| 4 | Number of columns for each situation | 2 (duplicated for accuracy) |
| 5 | Effect of turnover conditions | **1-before turnover** (CW*= lake water (60 mL), FT = PASS-treated FFT (30 mL)<br>**2-after turnover** (CW= lake water (60 mL), FT = PASS-treated FFT (30 mL) |
| 6 | Effect of consolidation ratio | **1-low consolidation ratio** (CW= lake water (60 mL), FT = diluted PASS-treated FFT with FT pore water (20% dilution) (30 mL)<br>**2-high consolidation ratio** (CW= lake water (60 mL), FT = PASS-treated FFT (30 mL) |
| 7 | Effect of capping water quality | **1-DI water** (CW= DI water (60 mL), FT = PASS-treated FFT (30 mL)<br>**2-lake water** (CW= lake water (60 mL), FT = PASS-treated FFT (30 mL) |

* CW=Capping water

**Mass balance calculation theory:** In a real full-scale EPL system such as BML, $Cl^-$ mass balance was evaluated within the capping water to understand the pore water advective flux from FFT (Dompierre et al., 2017). In this study, chemical mass balance included an initial assessment of the water balance within the water cover, and a field sampling campaign was carried out to characterize the $Cl^-$ concentrations of BML and all inflow and outflow waters (Fig. 4.5). The change of $Cl^-$ concentration in capping water over time was calculated by using **Eq. 4.1.**

$$dM = I_M - O_M = M_{Pin} + M_{prec} + M_{ro} + M_{pw} - M_{Pout} \qquad \textbf{(4.1)}$$

where dM represents the change in $Cl^-$ concentration in the lake water (mg/m$^2$/d), $I_M$, is the total input mass of $Cl^-$ (FFT pore water, $M_{pw}$, pump-in water, $M_{Pin}$; precipitation, $M_{prec,}$ and runoff, $M_{ro}$). Further, the total output mass of $Cl^-$ from lake water, $O_{M,}$ was the $Cl^-$ mass discharged from BML with the pump-out water ($M_{Pout}$). The volume of capping water [V (m$^3$)] and $Cl^-$ concentration, [C (mg/L)] of each input or output of the lake water (except for the FFT pore water) were used to determine its associated chemical mass. The pore water released by FFT was not directly measured and remained unknown in the above equation. In the BML, the change in $Cl^-$ concentration in the lake (dM) was calculated based on Eq. **4.2**.

$$dM = \frac{(C2 - C1) * V}{A * t} \qquad (\mathbf{4.2})$$

Where C2 was an average lake water $Cl^-$ concentration at the end (mg/L), C1 was an average lake water $Cl^-$ concentration at the beginning (mg/L), V was the capping water volume (m$^3$), A was the surface area of column (m$^2$) and t (day) was the time of the experiment. In an EPL system and in wet landform where FFT is covered with capping water, vertical one-dimensional advection-dispersion mass transfer regime is expected to be the dominant mass transport process due to FFT dewatering and shifting concentrations in the water cover over time (Cilia, 2018; Dompierre et al., 2017). Thus, $M_{pw}$ (mg/m$^2$/d) was evaluated by a combination of Darcy and Fick's laws (**Eq. 4.3**).

$$\mathrm{dM} = \mathrm{J}_\alpha + \mathrm{J}_\mathrm{d} = \mathrm{C} * \mathrm{q} + \mathrm{n} * \mathrm{D}_\mathrm{h} * \mathrm{dc/dz} \qquad \mathbf{(4.3)}$$

Where $J_\alpha$ (mg m$^{-2}$ d$^{-1}$) and $J_d$ (mg m$^{-2}$ d$^{-1}$) represented advective and diffusive solute mass flux, respectively. The q[6] (Darcy flux, m$^3$/m$^2$/day) and C (average concentration of $Cl^-$ at the water-FFT interface, mg/L) were used to determine $J_\alpha$. Similarly, n (FFT porosity due to water content in FT), $D_h$ (hydrodynamic dispersion coefficient for FFT. m$^2$/day), and dc/dz ($Cl^-$ concentration gradient in FFT, mg m$^{-2}$), were used to determine $J_d$. Accordingly, pore water advective flux in BML was indicated by q and was evaluated by a combination of **Eq. 4.2** and **Eq. 4.3** during the second year of operation (Dompierre et al., 2017).

The same strategy was adopted to study the pore water advective flux from PASS-treated FFT to capping water for a short time. Here, dM only represents FFT pore water ($dM = M_{Pw}$). $M_{pw}$ was directly calculated by the change in $Cl^-$ stored in capping water over time (**Eq. 4.4**).

$$\mathrm{M}_{\mathrm{pw}} = \frac{(\mathrm{C2}-\mathrm{C1})*\mathrm{V}}{\mathrm{A}*\mathrm{t}} \qquad \mathbf{(4.4)}$$

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[6] Darcy flux or apparent velocity that It represents the volume of water that flows through a unit cross sectional area of porous media per unit time

Since the chemical advective flux was only determined for a short period, the effect of $J_d$ was considered insignificant for dM. Thus, based on **Eq. 4.3,** $J_\alpha$ (mg $m^{-2}$ $d^{-1}$) is equal to dM and $M_{pw}$**.** Accordingly, chemical advective flux, q, was evaluated by **Eq. 4.5**.

$$\frac{(C2-C1)*V}{A*t} = C*q \qquad \textbf{(4.5)}$$

The mass advective flux of NAs was also studied to compare with the mass advective flux estimated by $Cl^-$.

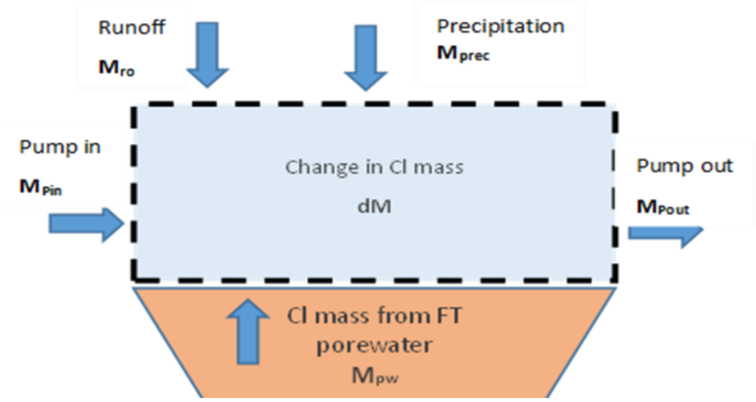

Fig. 4.5 Mass balance over capping water in BML (Dompierre et al., 2017)

### 4.2.5 Data analysis

Prior to analysis, all lake water and pore water samples were centrifuged and filtered using 0.45 µm syringe filters (Basix™ Nylon Syringe Filters, Fisher Scientific, USA). The concentration of TOC was determined using a high temperature combustion TOC analyzer (TOC-L analyzers, Shimadzu), according to the Standard Method 5310-B (APHA, 2017). $Cl^-$ and $SO_4^{2-}$ were quantified by Dionex ICS Ion Chromatography. Dissolved oxygen (DO) concentration and conductivity were monitored by using a YSI Professional Plus handheld multi-parameter water quality meter (Yellow Springs Instrument Company, USA). pH was determined by using Accumet Research AR20 pH/conductivity meter (Fisher-Scientific). Total phosphate, ammonium, total Kjeldahl nitrogen (TKN), nitrite ($NO_2^-$), and nitrate ($NO_3^-$) were determined using a Spectrophotometer (DR 3900, HACH, Germany) with Hach TNTplus Vial Test kit 844, 832,880 and 839, respectively.

For quantification of NAs concentration, 500 µL of sample supernatant (passed through 0.2 µm nylon filter) was transferred to LC-MS vials and analyzed using UPLC-TOF-MS. The chromatographic separation was conducted using a UPLC (Waters, ON) coupled with a high-resolution TOF-MS (Synapt G2, Waters, ON) operating in negative electrospray ionization (ESI) mode. The MS system was equipped with a Phenyl BEH column, and myristic acid-1-$^{13}C$ served as the internal standard. The analysis method and data acquisition techniques using this UPLC-TOF-MS have been previously described (Huang et al., 2018). The concentrations of metal and cations were quantified by inductively coupled plasma mass spectrometry (ICP-MS, Elan 6000 ICP mass spectrometer, PerkinElmer, Waltham, MA, USA). The concentration of acid extractable fraction (AEF) was determined using Fourier transform infrared (FT-IR) spectroscopy (Spectrum 100, PerkinElmer Ltd, Bucks, UK) following a previously established method (Abdalrhman et al., 2019). The extraction of AEF was performed twice in separation funnels using dichloromethane (DCM) after acidifying the samples to pH 2.0 using $H_2SO_4$. The extract was then evaporated to dryness and dissolved in a known amount of DCM. The DCM samples were then analyzed for monomeric and dimeric carboxylic- containing organics using FT-IR at absorbance 1743 and 1706 $cm^{-1}$, respectively (Xue et al., 2018). The concentrations of AM and model PAM used in PASS treatment were determined using HPLC with UV multiple wavelength detector (Agilent 1100). The procedure was adapted from methods reported previously (Li et al., 2023b). The entire analytical procedure was conducted in duplicate.

## 4.3 Result and Discussion

In the first study, pit lake models were operated to study the migration of contaminants during two years under oxic and anoxic columns. The rate of chemical release from the FFT was tracked by measuring concentrations in the column's headspace and the capping water. The results were further verified in the second study, a parallel study conducted to assess the early stages of pit lake mass transfer mechanisms, focusing on chemical mass migration from treated FFT into capping water through advection-dispersion-decay processes.

### 4.3.1 Study I

#### 4.3.1.1 The fate of trace metals in pit lake models

Trace elements can be released into the tailings landforms in oil sands mining primarily through weathering of parental rock mining and leaching (Kochkodan et al., 2015). For Lake Miwasin, water samples revealed higher levels of B (1.598 ± 0.003 mg/L), Si (0.626 ± 0.004 mg/L), and Sr (0.494 ± 0.001 mg/L). B concentration increased significantly over time in the capping water for both oxic and anoxic columns ($P < 0.05$) (Fig.4.6). Specifically, for oxic columns, the concentration of B was increased by 33% during the first ten months and then was stable in the remaining period. A majority of this release (up to 40%) occurred during the first week of operation (Fig 4.6). For anoxic columns, B concentration was increased to 36% in the first two months and then did not show a continuous significant trend ($P < 0.05$) (Fig. 4.6). As such, the release of B was nearly 76% during the first week. The observed discrepancies are unlikely to be associated with the DO profile. However, the variances in the FFTs' origins, despite coming from same source, may have been the primary contributing factor. Particularly, lower solid content (36%) of the FFT in the anoxic columns was observed as compared to the oxic columns (47%) (see section 4.3.2.3). B in aquatic environments is only affected by adsorption and desorption with sediments and soil (Butterwick et al., 1989). Being water soluble (solubility: ~216 mg/L), it is difficult to remove B from the water via biological processes (Bolan et al., 2023). The form of dissolved B in aquatic environments is primarily determined by B levels and water solution pH (Lin et al., 2021). Soluble B is likely found as mononuclear species such as $B(OH)_3$ and $B(OH)_4^-$ (Hilal et al., 2011). Also, an increasing pH trend can result into a high accumulation of monovalent borate anion $B(OH)_4^-$ over uncharged boric acid molecules in capping water (Lin et al., 2021) (Fig. 4.7).

The concentration of Si increased continuously (~50%) until the end of the study for both oxic and anoxic columns (Fig. 4.6). With respect to the silica-based minerals of the FFT (Table 4.3) and the increasing pH trend, the findings support the hypothesis of self-acceleration and hydroxide-driven silica dissolution (Fig. 4.7) (Schaefer et al., 2018). For Sr, the concentration change was minimal over time, indicating <7% increase for both oxic and anoxic columns. The column commissioning did not result in an increase in concentration for Sr, differing from other trace elements' behavior (Fig. 4.6). The concentration changes of other trace metal element (Ba) were minor (Table 4.1). Earlier studies reported that the consolidation of FFT and the presence of anaerobic microbial communities in tailing deposits may enhance migration of some elements (e.g. Ba and Sr) from untreated FFT to the capping water (Arkell et al., 2015; Kuznetsov et al., 2023). However, outcomes of the present study did not indicate such a release of Ba and Sr, which is likely due to PASS treatment of the FFTs. Apparently, negatively charged particles of FFT at Lake Miwasin, characterized by a pH of 8.12 and a point of zero charge ($pH_{PZC}$) at 5.9, might have impeded the migration of weakly soluble cations such as Ba and Sr. Similarly, at high pH, negative particle charge has the potential to bond the Sr via adsorption and precipitation on particle surfaces (Hasan et al., 2019; Pourrezaei et al., 2014) (Fig. 4.7).

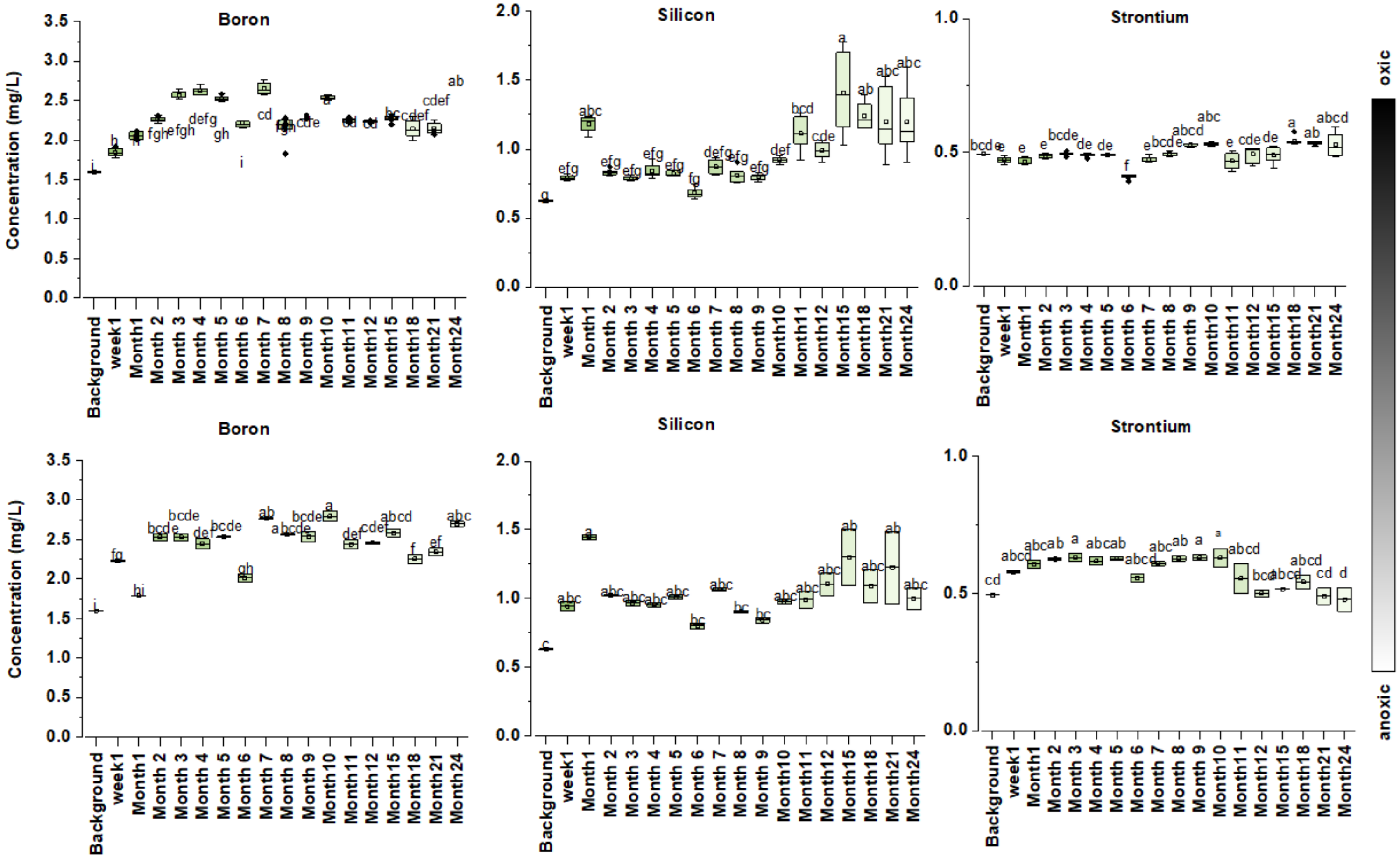

Fig.4.6 The concentration of main trace metals in capping water in oxic and anoxic columns over time.

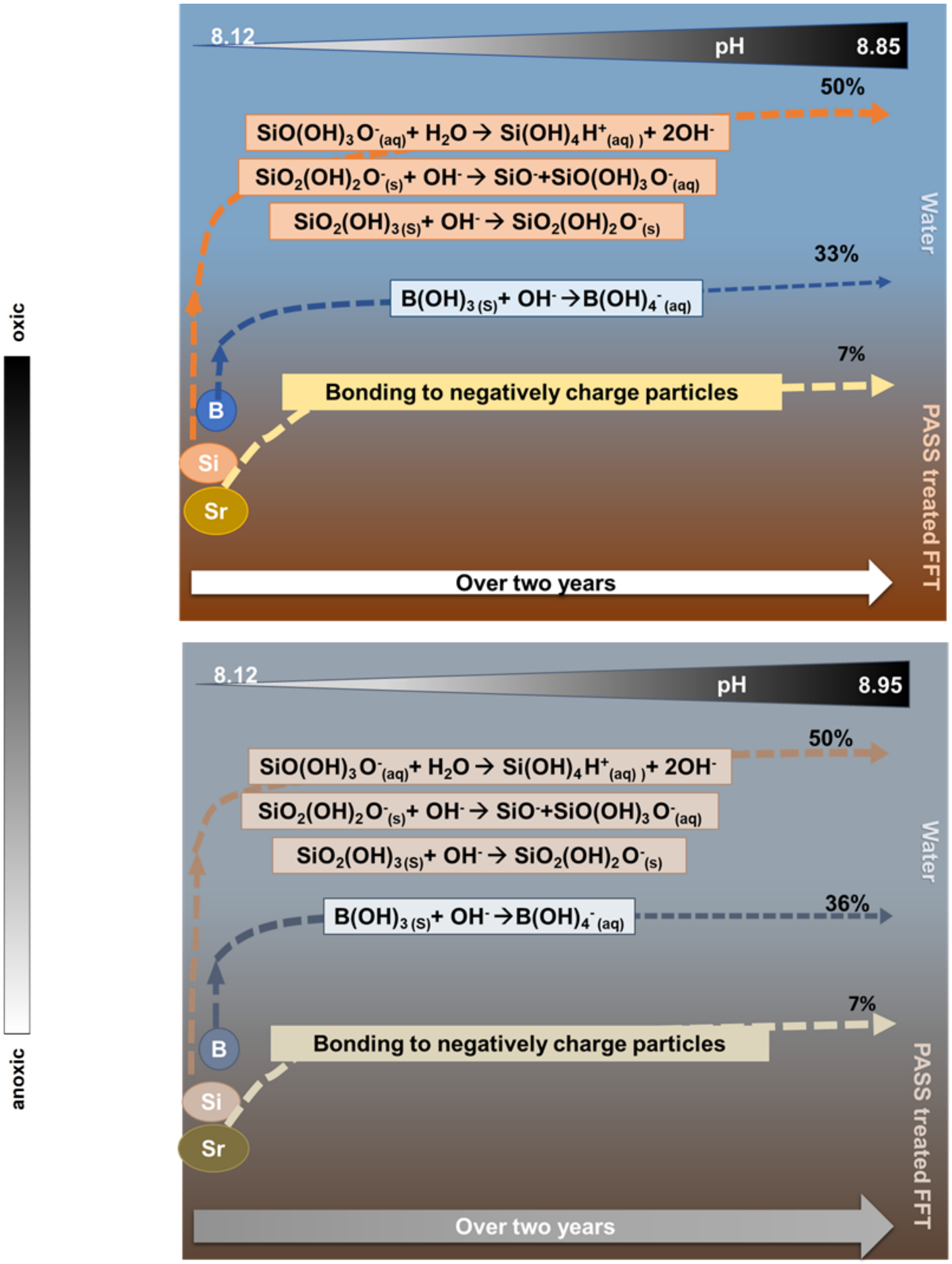

Fig.4.7 A schematic representation of the fate of trace elements in oxic and anoxic columns over time (the relative change of components are determined in capping water).

#### 4.3.1.2 The fate of cations and anions in pit lake models

In this study, primary cations and anions were also quantified. The concentrations of $Cl^-$ were 227.8 ± 0.07 mg/L, $SO_4^{2-}$ 114 ± 0.08 mg/L, $Ca^{2+}$ 39.4 ± 4 mg/L, $Mg^{2+}$ 16 ± 0.01 mg/L, $Na^+$ 353.8 ± 0.01 mg/L, and $K^+$ 7.76 ± 0.083 mg/L. Notably, these concentrations differ from the data previously reported for BML lake water (White, 2017; White & Liber, 2018). In comparison to the water composition of BML lake (Table 2.6), the concentration of cations and anions in this study was generally lower, with the exception of $SO_4^{2-}$, $Ca^{2+}$ and $Mg^{2+}$. In the lake water samples, ions such as Fe, Li, Cu, and Al were below detectable levels, and their concentrations remained undetected in subsequent pit lake models over time.

**Anions:** $SO_4^{2-}$ concentration was monitored over a two-year period (Fig. 4.8). In the initial phase, there was a pronounced increase in $SO_4^{2-}$ concentration under both oxic and anoxic columns, i.e., 10% and 27%, respectively. As the study progressed, the oxic columns showed a further increase in $SO_4^{2-}$ levels by 13%, whereas the concentration change was comparatively less in the anoxic systems which was increased from 29% to 36%. This observation aligns with the fact that alum pre-treatment of the tailings could release $SO_4^{2-}$ into the capping water over time. A prior study on FFT treated with sulfate-containing coagulants (gypsum and alum) reported an increase in $SO_4^{2-}$ concentration in the released water (MacKinnon et al., 2001). The less release of $SO_4^{2-}$ in anoxic columns could be attributed to high initial increase in sulfate levels during the commissioning phase, potentially resulting in an insufficient $SO_4^{2-}$ availability for subsequent release. An alternative explanation for the reduced release of $SO_4^{2-}$ under anoxic columns could be the presence of sulfate reduction bacteria (SBR). The more pronounced SBR activity under anoxic condition could use $SO_4^{2-}$ as an electron acceptor and reduce it to hydrogen sulfide, which can be further oxidized to elemental sulphur (Fig. 4.9) (Chang et al., 2008; Kinnunen et al., 2018). Regarding $Cl^-$, an initial surge in concentration was recorded, as observed previously, which was gradually increased over time. Regarding $Cl^-$, an initial surge in concentration was recorded, as observed previously, which was gradually increased over time (Dompierre et al., 2017; Kuznetsov et al., 2023). Specifically, there was an increase of 72% and 104 % $Cl^-$ under oxic and anoxic columns within the first year, respectively. Following that, there was a slow release of $Cl^-$ from FFT to capping water in the second year (Fig.4.8). Apparently, $Cl^-$ was mainly transported from pore water (801.90 mg/L) of FFT to capping water via advection and diffusion as FFT consolidate and strong concentration gradient between pore water and capping water influence the release, respectively. A similar observation was made previously by Dompierre et al. in a full-scale demonstration EPL in northern Alberta (Dompierre et al., 2017). The high hydraulic conductivity of PASS-treated FFT may also result in an accelerated chemical mass flux to capping water during the early stages of EPL system (Cossey et al., 2021), which ultimately leads to an increased release of $Cl^-$ in short term. Biagi et al. made a similar observation reporting a significant release of $Cl^-$ in the capping water of constructed wetland system carrying chemically treated FFT during the initial years of operation (2013-2015) (Biagi et al., 2019). In this study, a slow release in the second year of the column' operation highlights that the system was working efficiently compared to earlier EPL systems in which a continuous and significant $Cl^-$ flux was observed when untreated FFT was used over a three-year monitoring period (Kuznetsov et al., 2023).

**Cations:** In this study, $Na^+$ concentration was increased by 42% and 52 % under oxic and anoxic columns over time (Fig. 4.10). The release of $Na^+$ in the capping water can be directly attributed to their high dissolved concentrations in tailings' pore water, which is due to the Clark's hot water extraction process (CHWP). The CHWP uses caustic hot water (NaOH) to extract bitumen from oil sands, resulting in the introduction of soluble salts into the tailings including $Na^+$ (Biagi et al., 2019).

No correlation was observed between $K^+$ and $Na^+$ which is also observed previously in similar systems (Cilia, 2018; Dompierre et al., 2017) (Fig. 4.10). During the commissioning phase, $K^+$ concentration increased by 27% - 43%. The variation is likely attributed to the heterogeneity of the FFT used in this study (section 4.3.2). However, as the study progressed, the $K^+$ concentration started to change randomly over time, without a clear trend. This might be due to $K^+$ in in-situ reactions, such as ion exchange at clay surfaces in the FFT (Dompierre et al., 2016) or the nature of biogeochemical processes involving potassium uptake, release, and transformation (Kuznetsov et al., 2023) (Fig. 4.11).

For the lower ionic-strength ions, minimal changes were seen in $Ca^{2+}$ concentration during the first three months of monitoring for the oxic columns. In anoxic columns, $Ca^{2+}$ increased by 25% during the initial phase of operation. These differences were not likely due to DO conditions, but caused by the heterogeneous nature of FFT used in the columns as explained previously. It is crucial to mention that all precautions were made to homogenize the FFT but technical limitations and large-scale setup hindered the overall homogenization process efficiently. As time progressed, the concentrations declined by 33% which was further reduced to ~50% in the oxic and anoxic columns, respectively. The negative surface charge of the particle could have increased $Ca^{+2}$ bonding on particles as explained previously (Motta et al., 2018; Pourrezaei et al., 2014). Also, the interaction between PAM/AM and $Ca^{+2}$ can also facilitate flocculation and precipitation synergistically on negatively charged particles (Motta et al., 2018; Pourrezaei et al., 2014). This influence was stronger in the anoxic columns, where anaerobic microbial communities, particularly SRB, and by-products of PASS-treated FFT ($SO_4^{2-}$), can induce calcium carbonate precipitation (Castro-Alonso et al., 2019; Mitchell et al., 2019) (Fig 4.11). In addition to capping water, we further investigated the effect of precipitation in the FFT deposits. To this end, FFT analysis were conducted using XRD. Specifically, low calcium-bearing minerals were observed in the 18th month under the anoxic columns. The hydroxyl apatite ($Ca_5(PO_4)_3(OH)$) and hydrocalumite [$Ca_4Al_2(OH)_{12}(Cl,CO_3,OH)_2 \times 4H_2O$] were prominent (Milagres et al., 2017). An almost steady trend of $Mg^{2+}$ was observed in capping water for both oxic and anoxic columns. Specifically, at the end of the study period, it was decreased for both oxic and anoxic columns by only 1% (Fig. 4.10). A relatively stable trend of $Mg^{2+}$ and decreasing trend of $Ca^{+2}$ exhibited an efficacy of PASS-treatment of as compared to other the EPL model system which displayed an accelerated flux of these ions in the presence of untreated FFT (Cilia, 2018; Kuznetsov et al., 2023)

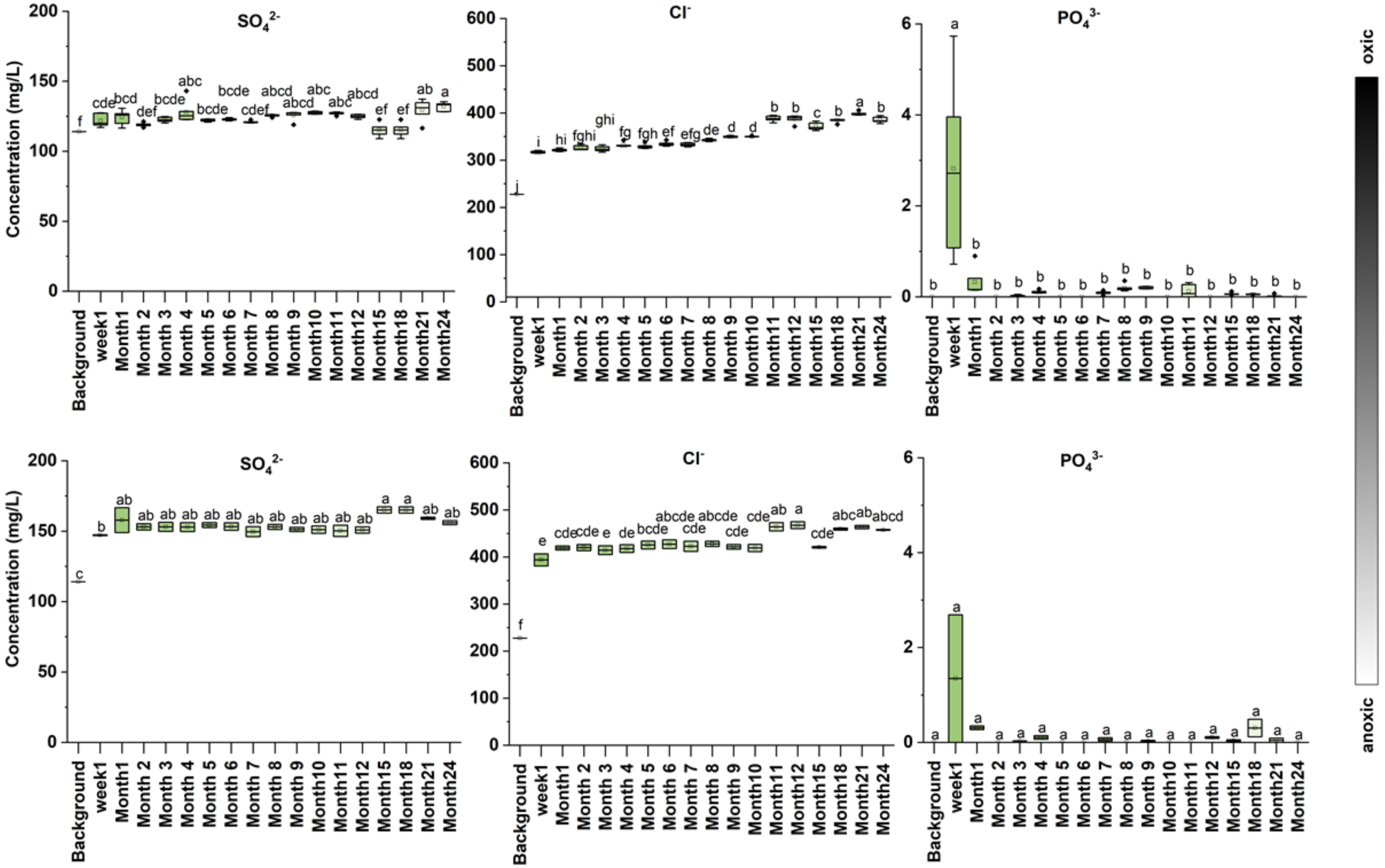

Fig.4.8 The concentration of anions in capping water in oxic and anoxic columns over time, SO$_4^{2-}$, Cl$^-$ and PO$_4^{-3}$

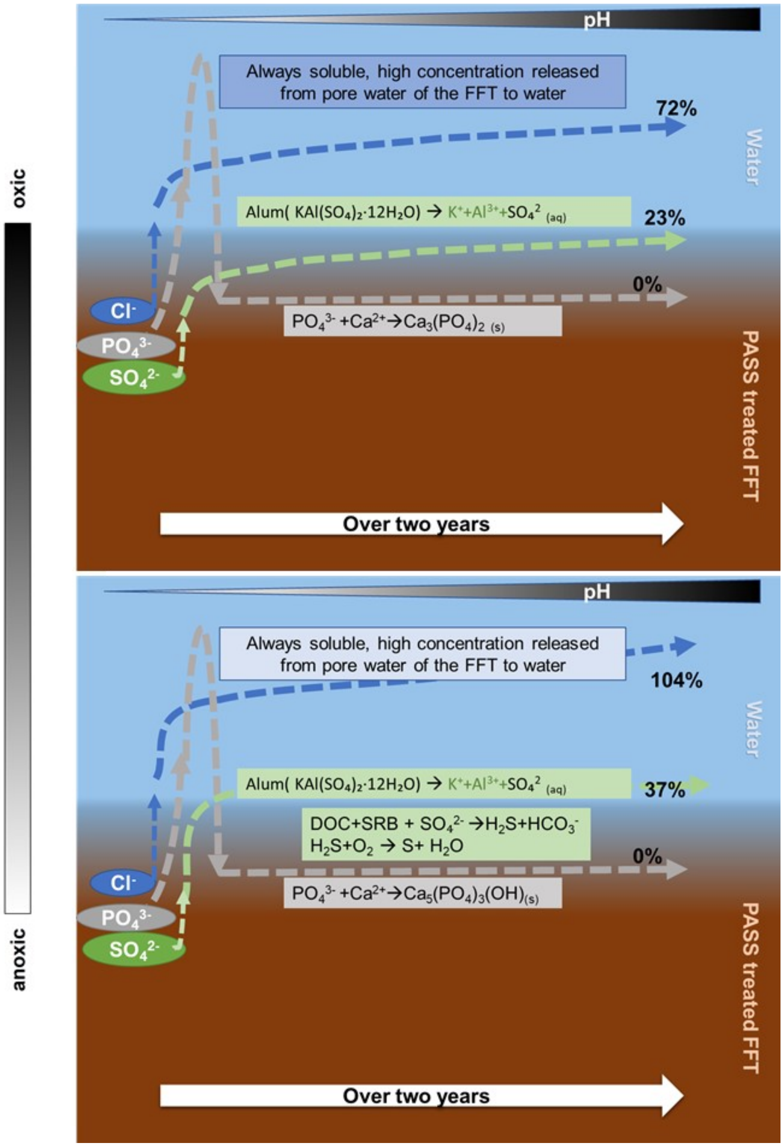

Fig.4.9 A schematic representation of the fate of $SO_4^{2-}$, $Cl^-$ and $PO_4^{-3}$ in oxic and anoxic columns over time (the relative change of components are determined in capping water).

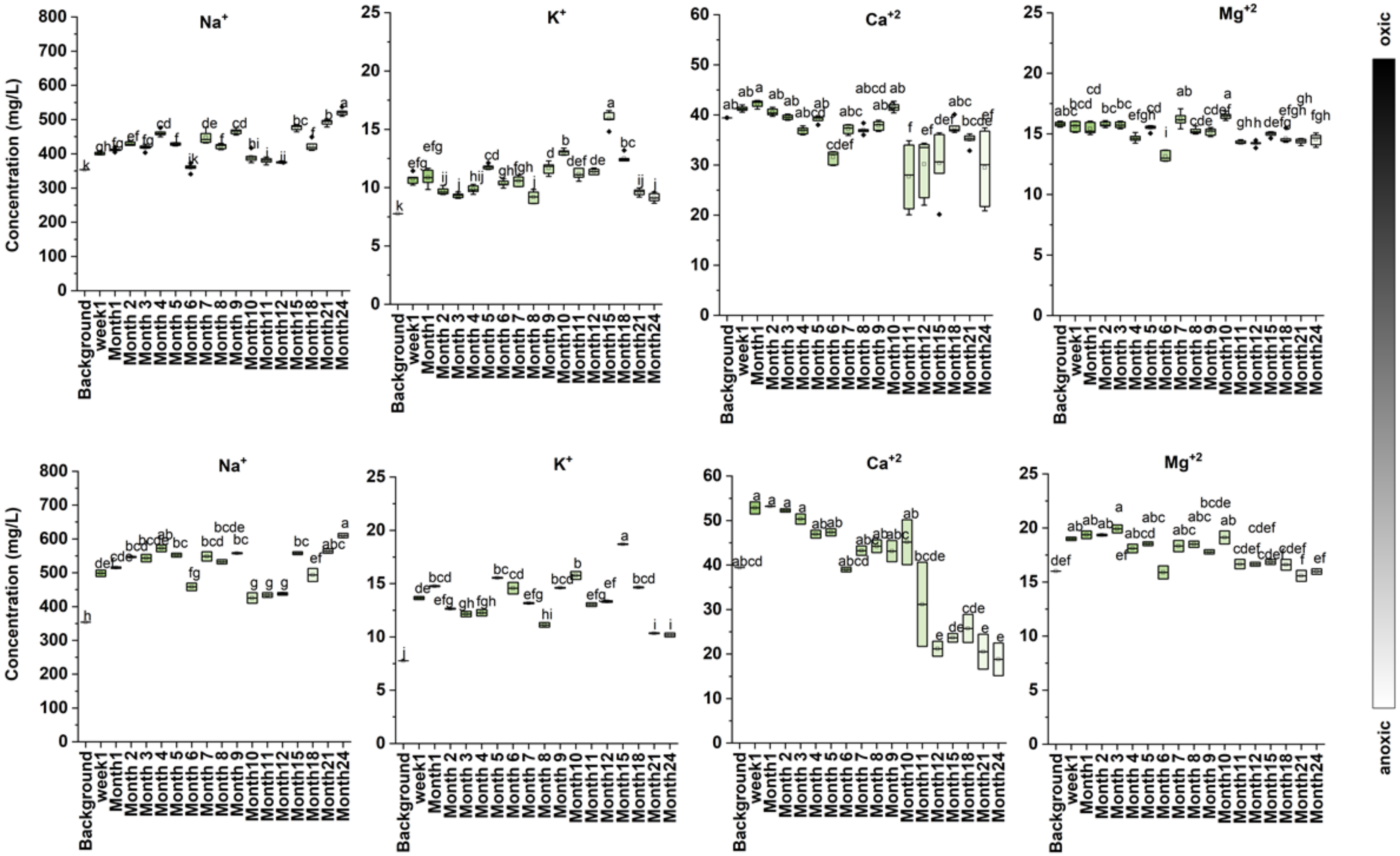

Fig. 4.10 The concentration of cations in capping water in oxic and anoxic columns over time, ,$Na^+$, $k^+$, $Ca^{2+}$and $Mg^{2+}$.

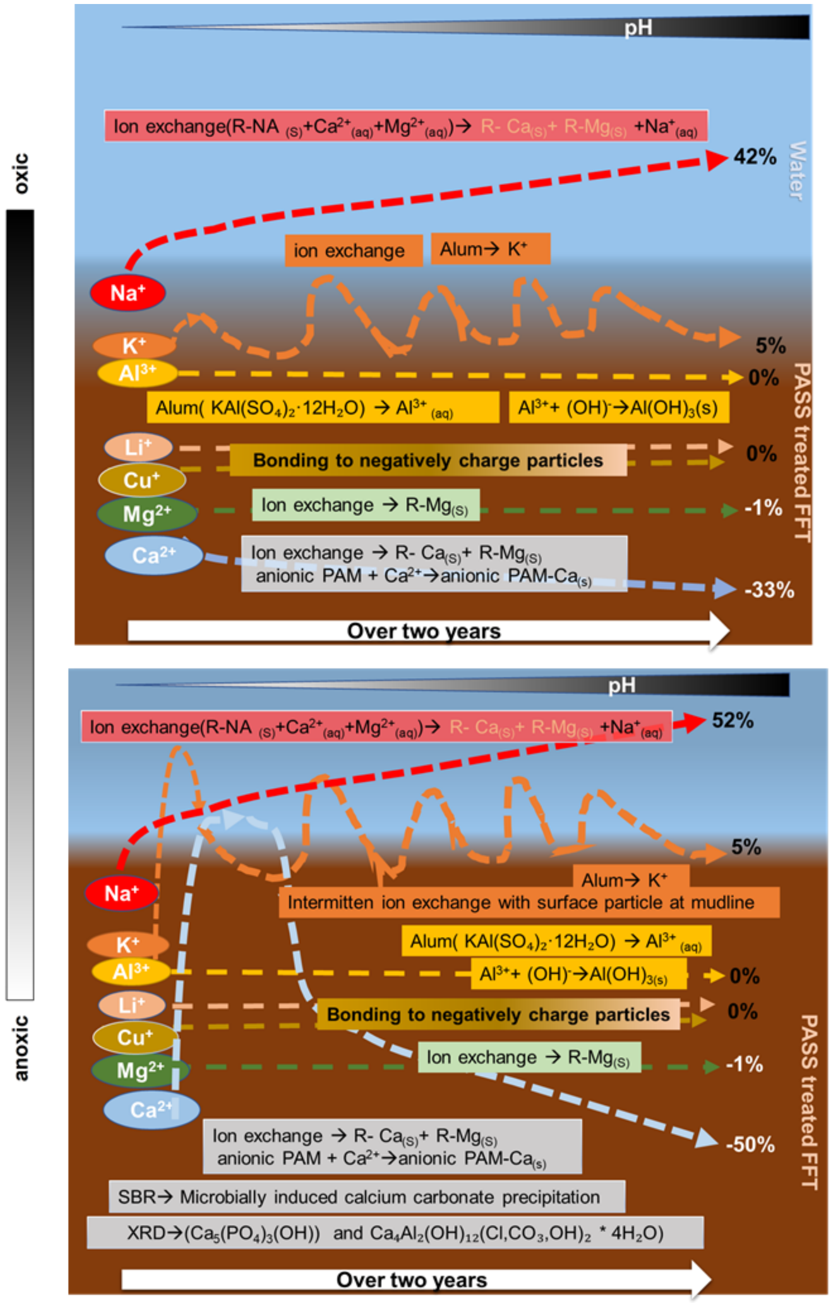

Fig.4.11 A schematic representation of the fate of cations in oxic and anoxic columns over time (the relative change of components are determined in capping water).

#### 4.3.1.3 The fate of NAs PASS-treated FFT and capping water.

The fate of classical NAs species in the capping water of column study was also studied (Fig. 4.12). It was observed that concentrations of NAs increased significantly for both oxic and anoxic columns during column commissioning phase. Specifically, NAs concentrations increased by 18% under oxic columns and 32% under anoxic columns during the commissioning period (variation stemmed from the heterogenic characterization of FFT). Following that, over the next 11 months, concentrations gradually reached 37% and 55% in the oxic and anoxic columns, respectively. The initial increase of NAs concentration could be attributed to the chemical pore water advection and diffusion flux from pore water of FFT (52.30 mg/L) to capping water. A previous study reported similar effects in different EPL (Dompierre et al., 2017). Furthermore, the initial increase in NAs could be attributed to the high pH of the capping water, given that the calculated pKa value for total NAs is 3.9, as determined by Huang et al. (Huang et al., 2017).This would imply that dissociation occurs more readily under alkaline conditions. As the study progressed, a steady decrease in NAs concentration was observed. At the end of the observation, concentrations were lower (10%) than the original level for oxic columns and 20% higher for anoxic columns. This decreasing trend is potentially related to the biochemical transformation of dissolved organics including NAs in the columns (Cossey et al., 2021; White, 2017). The lower decrease trend in anoxic columns implying less microbial activity, potentially reflecting a low level of oxygen consumption by biological processes. As of today, several studies have reported the natural attenuation of NAs in OSPW under aerobic and anaerobic columns over extended time (Cossey et al., 2021). In the reclamation site such as pit lake and wetlands, the aerobic degradation of NAs species likely is more pronounce in the uppermost layer of capping water and anaerobic degradation of NAs may happen in tailings where oxygen hardly penetrated (Cossey et al., 2021). Regarding the potential biodegradation of NAs species several pathways have been proposed. The biodegradation of aliphatic, alicyclic, and aromatic carboxylic acids includes β-oxidation, combined α- and β-oxidation, and aromatization pathways (Johnson et al., 2011).

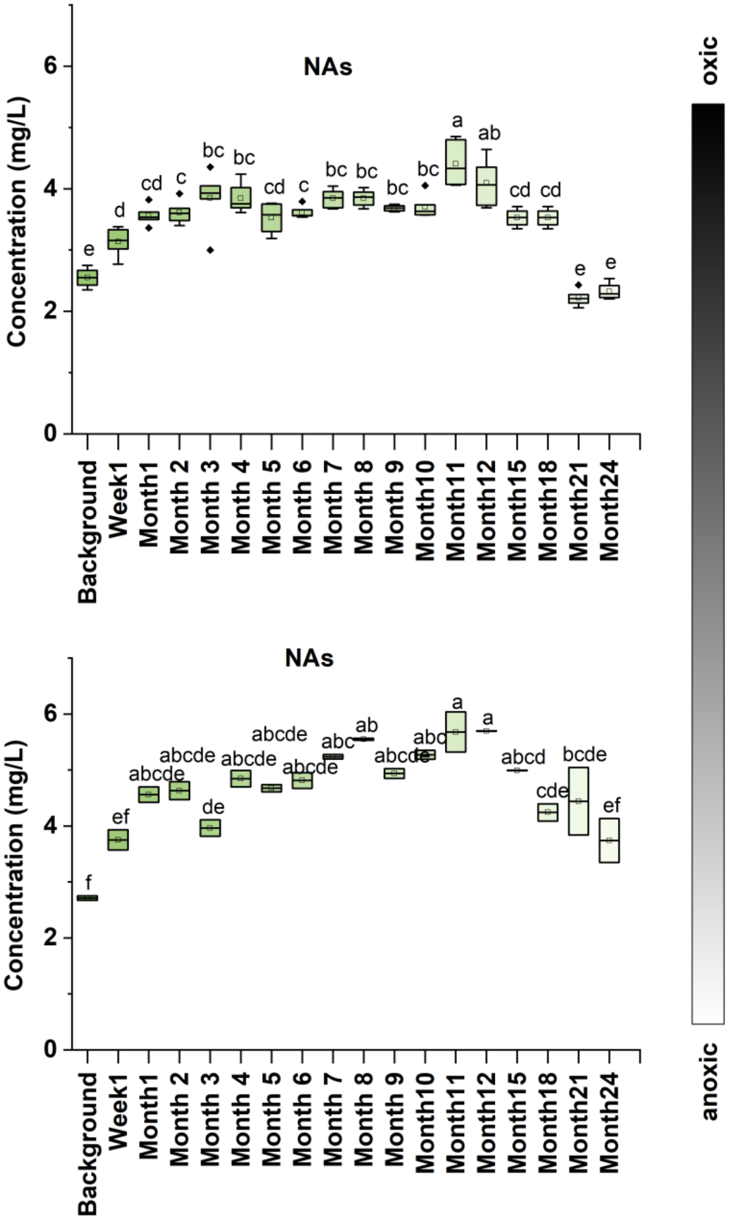

Fig. 4.12 The concentration of classical NAs in capping water in oxic and anoxic columns over time.

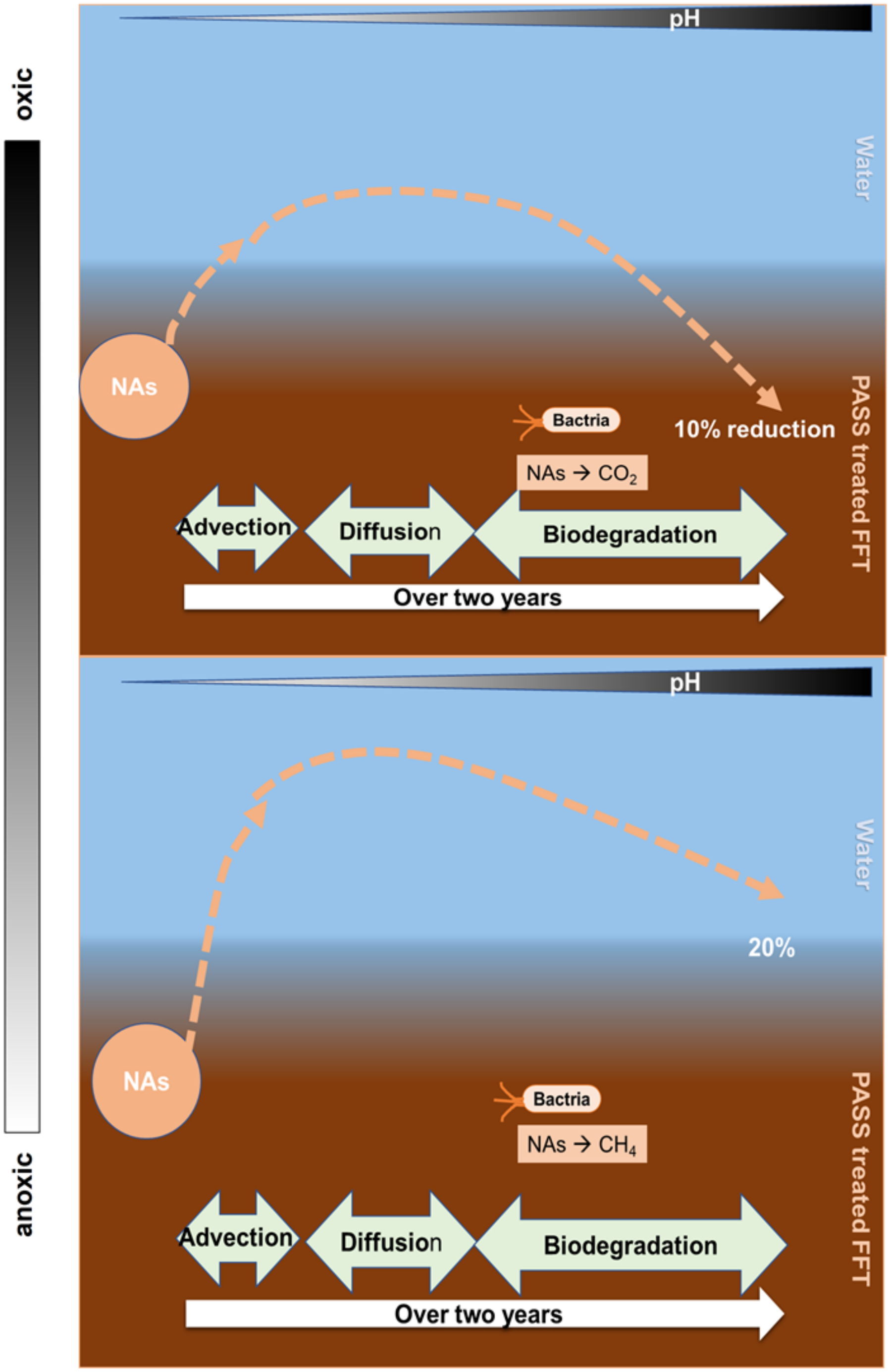

Fig. 4.13 A schematic representation of the fate of classical NAs in oxic and anoxic columns over time (the relative change of the component are determined in capping water).

### 4.3.2 Study II

#### 4.3.2.1 Chemical advective flux analysis from PASS-Treated FFT to capping water

The long-term monitoring indicated that the chemical flux in the capping water was sharp in the commissioning phase (Study 1). This is likely due to the high hydraulic conductivity of PASS-treated FFT as discussed previously (Cossey et al., 2021). Additionally, the migration of contaminants could have been affected by the initial characteristics of the lake water and FFT, specifically, the difference in concentration gradient (Cossey et al., 2021; Dompierre et al., 2017). To address these questions, bench-scale experiments were conducted that provided further insights into the initial and intermittent variations of Lake Miwasin on the mobility of chemical compounds.

#### 4.3.2.2 Intermittent variable: effect of internal mixing because of lake turnover

To study the effect of lake turnover, the fate of the tracer element ($Cl^-$) was demonstrated in both the pore water of the FFT and the capping water (Fig 4.14a). The $Cl^-$ concentration was decreased in the FFT (24-26 % decrease), but increased in the capping water (36-38% increase) in both presence and absence of the turnover conditions. The $Cl^-$ concentration in FFT and capping water were similar for both turnover conditions in this study, implying that lake turnover likely had no direct influence on the mass flux in the presence of PASS-treated FFT. Previously, it was argued that chemically treated tailings can minimize the risk of fines re-suspension (Hyndman et al., 2018), likely resulted in limiting the extra chemical release during the lake turnover because of vertical mixing in the lake. Moreover, both turnover conditions had a chemical advective flux of 0.002 $m^3m^{-2}d^{-1}$, similar to BML's second year of operation (Dompierre et al., 2017). However, the initial advection flux in BML lake was twice as high as in the current study (Dompierre et al., 2016), indicating that PASS treatment likely reduced the chemical advection flux from FFT to capping water. In this study, dimensionless Peclet number was used to verify chemical flux measurement assumptions (Cilia, 2018). The measured Peclet number of 7.05 (>1) confirmed the study's hypothesis and indicated that advection flow transfer controls chemical mass transfer primarily during the model EPL's commissioning phase (Cilia, 2018).

#### 4.3.2.3 Initial variable: effect of lake water characterization and solid content of PASS-treated FFT

Replacing Lake water with ultrapure water dramatically changed $Cl^-$ concentration trends in both FFT pore water and capping water in the current study (Fig 4.14b). Correspondingly, chemical advection flux increased from 0.002 to 0.0028 $m^3m^{-2}d^{-1}$ (40%) when fresh water was presented as capping water instead of lake water (Peclet number =9.87). As expected, the higher concentration gap between FFT pore water and ultrapure capping water explained the higher chemical advective flux. These results imply that using a mixture of fresh water and OSPW, like Miwasin Lake, instead of fresh water, was a better choice to minimize the high initial advective flux.

As it was observed in section 4.3.1, the heterogenous solid content of the oxic and anoxic columns caused different chemical flux in the commissioning phase. In this part of the study, the effect of solid content of tailings was evaluated by comparing the original FFT and 20% diluted FFT. A 20% diluted FFT solid content increased the release of $Cl^-$ from the FFT (Fig 4.14c). Here, the chemical advective flux was 0.0024 $m^3m^{-2}d^{-1}$ (Peclet number = 10.47), which is 20% higher than the original FFT. These findings support the hypothesis that using tailings with varying solid content ratios results in different chemical advective fluxes, particularly during commissioning phase. Hence, using original tailings samples with a higher solid concentration leads in a lower initial chemical flow, as found in section 4.3.1 for oxic column versus anoxic column.

#### 4.3.2.4 Comparison of chemical advection flux: conservative model vs. recalcitrant organic pollutant from PASS-treated FFT to capping water

In this study, the advection flux of NAs was 0.0012 $m^3m^{-2}d^{-1}$ (Peclet number = 4.11), which is significantly lower than the chemical advection flux derived from $Cl^-$ (0.0020 $m^3m^{-2}d^{-1}$). This indicates that PASS treatment of FFT increased chemical immobilization of NAs on FFT particles and reduced the NAs flux into the capping water. The might be due to the presence of alum and PAM. Principally, alum forms cation bridge between negatively charged NAs and negatively charged clay particles (Omotoso et al., 2021); whereas, PAM could also facilitate the hydrogen bonding between NAs and amid functional group (Pourrezaei et al., 2014), leading to an overall reduction of NAs flux (Fig. 4.1).

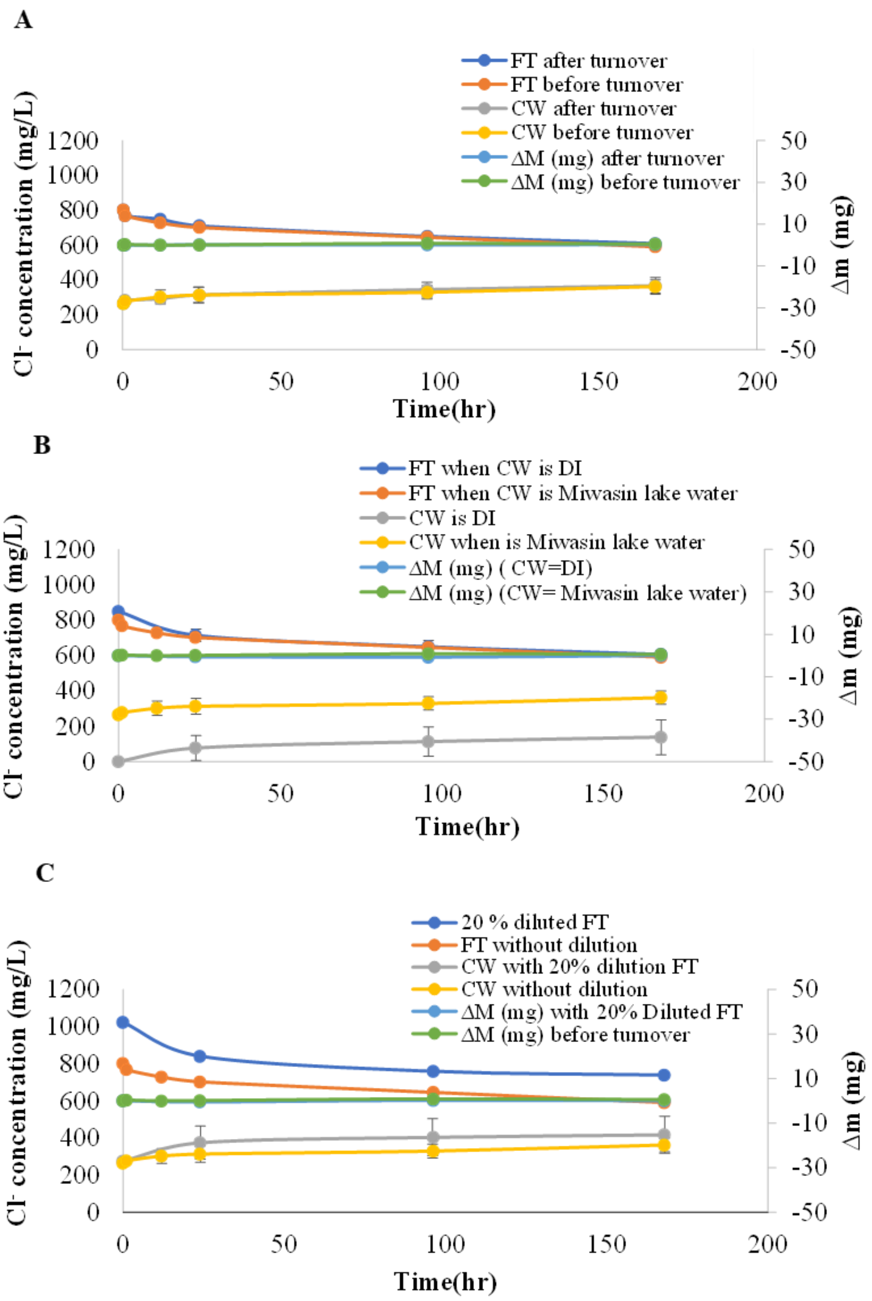

Fig. 4.14 Cl$^-$ concentration, Δm in PASS-treated FFT and capping water a) effect of turnover, b) effect of water quality, and c) effect of solid content of tailings.

## 4.4 Conclusion

In this study, it was found that PASS treatment of FFT within Lake Miwasin could achieve significant reductions in the mobility of specific metals, ions, and organic compounds ($PO_4^{-3}$: 100%, $Ca^{2+}$: 33%, $Mg^{2+}$: 1%, $Fe^{3+}$: 100%, $Li^{+}$: 100%, $Cu^{+}$: 100%, $Al^{+3}$:100%, and classical NAs: 10%) over two successive years. The higher chemical fluxes toward the capping water in commissioning phase were evident. A detailed study at the commissioning phase of model EPL system confirmed that advection mass transfer mechanism mainly controlled the migration of contaminants from the FFT to capping water. The chemical advection flux was 0.0020 $m^3m^{-2}d^{-1}$, 50% lower as compared to Base Mine Lake, the first established commercial-scale EPL. PASS pretreatment for FFT significantly reduced advection of NAs (0.0012 $m^3m^{-2}d^{-1}$), and minimized intermittent additional mass flux under comparable vertical mixing conditions in Lake Miwasin during the lake turnover period. Aside from FFT PASS treatment, directly covering the EPL with fresh water (by 40%) and filling it with more fluid (20%) FFT (by 20%) increases chemical mass flux in the early stages of closure system establishment. Regarding the primary finding on the flux of COPCs in this study, filling the EPL system with PASS-treated FFT demonstrates the potential to accelerate reclamation process, despite the possibility of varying outcomes under different field conditions. In addition, careful management of early stages and long-term monitoring can improve the overall performance of PASS treatment of FFT in this reclamation site in the oil sands mining.

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# 5 Chapter 5: Desorption and Migration of Dissolved Organics from Oil Sands Tailings to Capping Water: Demonstration Pit Lake

## 5.1 Introduction

The expansion of oil sands mining projects to meet the rising energy demand has led to an increase in the volume of tailings, making their management a critical concern (AER, 2020). Accordingly, the oil sands industry in Alberta, Canada, has generated more than 1.3 billion $m^3$ of FFT, which are stored in FFT ponds, covering a total area of 100 $km^2$ (Kuznetsova et al., 2023). Therefore, effective management of FFT is necessary to safeguard the environment and ensure the sustained viability of Alberta's oil sands industry in the long term (Charette, 2010). Oil sands FFT contain a mixture of water, sand, clay, residual bitumen, and toxic organic compounds including NAs (Allen, 2008).

Oil sands companies are not allowed to discharge oil sands FFT into the environment (Allen, 2008; Wilson et al., 2018). Directive 085 issued by the Alberta Energy Regulator (AER), "Fluid Tailings Management for Oil Sands Mining Projects," under the tailings management framework (TMF) mandates the progressive treatment and reclamation of FFT during the project's lifespan and also that all FFT be ready to reclaim a decade after the project's mine life. Several strategies are being developed to achieve these reclamation goals. The TMF considers end pit lake (EPL) as a potential reclamation strategy to facilitate the incorporation of FFT into the oil sands mine closure landscapes (AER, 2015).

Ongoing research endeavors are presently focused on investigating the potential for transforming EPL into self-sustaining aquatic ecosystems or boreal lake ecosystems (An et al., 2013; Charette, 2010; Dompierre et al., 2016). This includes studying the geochemical stability of the FFT that can provide insights into the lake's water quality during long-term storage (Dompierre et al., 2017; Samadi, 2019; White, 2017). As of today, Base Mine Lake (BML) and Lake Miwasin are the only two demonstrated EPL projects executed by the oil sands industry in Alberta, Canada (Clemente & Fedorak, 2005; Suncor, 2019; Syncrude, 2019b). Prior investigations on BML involved biogeochemical analysis of untreated FFT and water quality evaluation, revealing a decline in lake water toxicity over time. However, significant releases of contaminants of potential concerns (COPCs) and toxic organic constituents from untreated FFT into the lake water were observed (Clemente & Fedorak, 2005; COSIA, 2021a; White, 2017).

In 2016, Suncor established Lake Miwasin to implement Permanent Aquatic Storage Structure (PASS) treatment technology to accelerate dewatering and chemically immobilize COPCs for enhanced geochemical stability of FFT (COSIA, 2021a; COSIA, 2018b; Cossey et al., 2021). To this end, an average dosage of ~1200 ppm of alum (a coagulant) and ~1500 g/tonne clay of polyacrylamide (PAM, a flocculant) was added in FFT. Geochemically, when alum interacts with the clay surface charge, inter-particle electrostatic forces cause clay particles to aggregate, which entrap fine particles and remove the total suspended solids (TSS). Further, a thorough mixing of an adequate amount of alum results in a decrease in pH. The drop in pH is followed by the formation of aluminum cation ($Al^{3+}$) bridges between negatively charged organic compounds and clay particles, resulting in the production of immobilized complexes (Omotoso et al., 2021). This process facilitates the precipitation of the dissolved organics such as NAs and facilitates their removal from the slurry, thus, minimizing the risk of seepage. As such, PAM helps form polymer chains that effectively bind particles together, facilitating the creation of larger flocs (Li et al., 2023b). This process aids in the sedimentation of suspended solids and enhances the clarity of the supernatant water (Omotoso et al., 2021). Additionally, the formation of hydrogen bonds between polar substances, such as NAs, and the amid functional group of PAM can contribute to the stability of polar organic COPCs on PASS-treated FFT particles. As a result, the desorption of DOC is expected to be minimal (Pourrezaei et al., 2014). This may enhance the dewatering efficiency and reduce the water content of the FFT, ultimately improving the effectiveness of the PASS treatment process.

At Lake Miwasin, diffusion and desorption are believed to be the primary mechanisms of chemical mass transfer similar to other pit lake closure landforms (Samadi, 2019). However, the rate and mechanism of desorption of organic constituents from the treated FFT to the lake water remain unclear. A comparison between the initial concentration of organic contaminants in PASS-treated FFT and their desorption capacity may serve as a valuable indicator to understand the effectiveness of PASS treatment for FFT management. In this study, we examined the desorption kinetics of DOC and NAs to decipher the movement of organic constituents from FFT deposits to the lake water. Specifically, the study aimed to achieve the following objectives: (1) investigate the desorption rate of DOC from FFT to lake water; (2) assess desorption kinetics models to understand the governing mechanisms of the desorption process; (3) examine equilibrium using isotherm models to identify the most suitable fit; and (4) evaluate the influence of factors such as lake water salinity, DOC concentration, hardness, chemical amendment by-products, and temperature fluctuations on the desorption capacity of NAs and DOC. We hypothesized that the implementation of the PASS treatment onto FFT within Lake Miwasin impedes the desorption of DOC from the FFT solid content. Mechanistically, we postulated that high alum dosage (~1200 ppm) can be the primary driver for NAs precipitation or adsorption led by hydrogen bonding between PAM and polar organic compounds (e.g., NAs).

## 5.2 Material and Methods

### 5.2.1 Chemicals and materials

Methanol, sodium chloride (NaCl), sodium sulfate ($Na_2SO_4$), potassium chloride (KCl), hydrochloric acid (2N) and calcium chloride ($CaCl_2$) were purchased from Fisher Scientific (Pittsburgh, PA, USA). High-performance liquid chromatography (HPLC) grade formic acid (99.9%) was obtained from Fluke. Humic acid (HA) and potassium sulfate ($K_2SO_4$) were purchased from Sigma. In addition, all reagents were of analytical grade and all solutions were prepared using Ultra-pure water (Synergy UV, Millipore Sigma, USA).

### 5.2.2 PASS-treated FFT and lake water samples characterization

PASS-treated FFT and water samples were collected in August 2020 from the Lake Miwasin, Suncor Energy Inc., Alberta, Canada. The samples were stored at 4 ˚C in dark until processed for desorption experiments. The water quality parameters were subjected to several analyses whose results are presented in Table 4.1.

Accordingly, FFTs were characterized following a number of methods which is already explained in section 4.2.2.

### 5.2.3 Batch desorption study

Initial experiment indicated that fully saturated PASS-treated FFT particles have insignificant tendency for adsorption of extra DOC content of lake water after three-week, detailed information is addressed in Fig. 5.1a. Desorption isotherms and kinetics studies were performed in duplicate batch mode in 200 mL conical flasks. Simulated lake water was prepared (6.5 mmol/L NaCl and, pH =8.15) as per the Lake Miwasin conditions which was later added to flasks containing different dosages of FFT. This produced selective FFT/ liquid ratio of 1, 5, 20, 30, and 50 g/L. All flasks were instantly sealed with parafilm and then mechanically oscillated on a shaker (New Brunswick™ Innova® 2100 platform shaker, Eppendorf Inc., USA) at agitation speed of 200 rpm and temperature of 20 °C for a certain period (0.5 to 10 hours). Subsequently, centrifugation was performed at 9000 rpm for 10 min to separate the supernatant and solid residues.

Then, supernatant of samples was filtered through a 0.2 μm syringe filter (Basix™ Nylon Syringe Filters, Fisher Scientific, USA) and stored at 4 °C until further analysis.

For the desorption study, several investigations were conducted:

i. Influence of ion strength on the equilibrium desorption capacity (10 hours) was examined using simulated lake water with different conductivities, i.e., 2 μS/cm (NaCl 2), 700 μS/cm (NaCl 700), and 1800 μS/cm (NaCl 1800). Real Lake Miwasin water samples and ultra-pure water (DI) samples were included as positive and negative controls, which further supported a comprehensive analysis of the desorption behavior.

ii. Impact of main electrolytes in the lake water on the equilibrium desorption capacity (10 hours) was assessed using aliquot solutions of lake water namely NaCl, $Na_2SO_4$, KCl, $K_2SO_4$, and $CaCl_2$ at 1800 μS/cm, which is the conductivity level of Lake Miwasin.

iii. Effect of lake water temperature on the desorption capacity at equilibrium was investigated using simulated Lake Miwasin water samples (6.5 mmol/L NaCl, 700 μS/cm) at different temperatures ranging from 10 to 30 °C (seasonal effect).

#### 5.2.3.1 Desorption kinetics study

Pseudo-first order (PFO), Pseudo-second order (PSO), and intraparticle diffusion models were used to describe DOC desorption kinetics in the FFT (Table S1, Supportive Information).

The amount of desorbed DOC from FFT for each reaction time ($q_i$: mg/kg) was calculated by using the following equation:

$$q_i = \frac{(C_i)*V}{m} \qquad (1)$$

Where, $q_i$ is the amount of desorbed DOC from FFT at time t (hr); V is the volume of the solution (L); m is the mass of FFT (g), and $C_i$ is the concentration of DOC (mg/L).

#### 5.2.3.2 Desorption equilibrium study

The amount of desorbed DOC from FFT at equilibrium state ($q_e$) (mg/kg) was calculated by using the following equation:

$$q_e = \frac{(C_e)*V}{m} \qquad (2)$$

Where $C_e$ (mg/L) is the concentration of DOC in the aqueous medium at equilibrium time.

The experimental data were finally fitted to the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherm equations to investigate the thermodynamic property and desorption mechanism of DOC and NAs from FFT (Table S2).

#### 5.2.3.3 Distribution coefficient ($K_d$) and organic carbon water partition ($K_{OC}$) coefficients

The adsorption-desorption distribution coefficient ($K_d$) is used to estimate the mobility of compounds in soil, sediment, and sludge (OECD, 2000). $K_d$ is often normalized to the organic content of the matrix to obtain the organic carbon-water partition coefficient ($K_{oc}$) (Kögel-Knabner et al., 2000). $K_{oc}$ is a crucial parameter used to predict the environmental fate of a chemical in the sediment matrix (Reategui et al., 2021). High values of $K_{oc}$ (of the order of 2000 or more) indicate that at equilibrium, a preponderance of the chemical is bound to the solid phase surface and thus has a low tendency to migrate to solvent. Conversely, lower value of $K_{oc}$ ($2000 \leq K_{oc}$) indicates that the chemical will exhibit high mobility within the sediment (Bian et al., 2022). The single point $K_d$ was calculated as follows:

$K_d = q_{eq} / C_e$ (Eq. 4)

$K_{oc}$ was calculated based on a linear distribution coefficient normalized to organic carbon, which could be described as $K_{oc} = K_d/f_{oc}$, where $f_{oc}$ is the fraction of soil organic carbon.

### 5.2.4 Analytical

Both solid-phase extraction and UPLC-TOF-MS technique were applied to assess the concentration of extracted NAs during the desorption study. Initially, samples were acidified using hydrochloric acid to achieve a pH of less than 2. Then, co-polymer-based sorbent Oasis HLB

(Waters, MA, USA) cartridges were conditioned using an SPE manifold. The cartridges were washed with 10 mL of methanol followed by 20 mL of Milli-Q water. Next, the acidified supernatant samples were passed through the conditioned OASIS HLB cartridge at a flow rate of 5 mL/min. The cartridges were further washed with 40 mL of acidified water (pH = 2) following drying under a nitrogen gas flow for 20 minutes. To elute the analytes, the OASIS HLB cartridge was first prewashed with 20 mL of methanol, and then 20 mL of acidified methanol (formic acid: methanol = 1:10, v/v) was used for final elution. The extracts were air-dried under a fume hood and reconstituted using a solution of water: methanol (1:1, v/v) to a volume of 5 mL. For quantification of NAs, 0.5 mL of the reconstituted samples were subjected to analyses on UPLC-TOF-MS. The chromatographic separation was performed using a UPLC (Waters, ON) coupled with a high-resolution TOF-MS (Synapt G2, Waters, ON), which operated in negative electrospray ionization (ESI) mode. The MS was equipped with a Phenyl BEH column, and myristic acid-1-$^{13}$C was used as the internal standard. The sample analysis and data acquisition have been previously described (Huang et al., 2018). DOC was determined by using a Shimadzu total organic carbon analyzer. To study the influence of FFT dosage, ion strength, different electrolyte and temperature on desorption, ANOVA (Tukey's multiple comparison test; overall confidence level = 0.05) were performed on the datasets using OriginPro software (OriginLab Corporation).

## 5.3 Result and Discussion

### 5.3.1 Characterization of PASS-treated FFT

Table 4.3 summarizes the physicochemical properties of PASS-treated FFT. First, the Dean Stark analysis revealed that PASS-treated FFT contained 52.21% water, 47.32% solids, and a notably low (0.47%) bitumen content. The solid content of PASS-treated FFT was similar to a previous study that used centrifugation combined with PAM treatment on MFT (Gumfekar et al., 2019). Regarding the water content, PASS-treated FFT had comparatively less water than untreated FFT (70-80%), mature fine tailings (MFT) (60-70%), and centrifuged FFT (60-65) (Allen, 2008; Botha & Soares, 2015). The low water content in PASS-treated FFT suggests the effectiveness of PASS treatment towards dewatering of FFT.

We further assessed the total organic matter (TOM), TOC, DOC, and NAs content of FFT, which were found 12.7%, 8.1%, 1.15%, and 0.011%, respectively (Table 4.2). Apparently, lower concentrations of NAs indicate that a substantial amount of other forms of organic carbon were present which required further characterization. Therefore, we performed surface characterization of PASS-treated FFT by using FT-IR (Fig. 4.1). Notably, we observed broad absorption bands at 600-800, 900-1100, 2850-2940, and 3600-3700 cm$^{-1}$, corresponding to C-H aromatic bending (Reddy et al., 2020), carboxyl (C=O) and C-N stretching vibrations (Liu et al., 2018; Zhao et al., 2005), stretching vibrations of O–H groups (carboxylic acid) (Hu et al., 2006), and N–H bending vibrations of secondary amines (Gwon et al., 2010), respectively (IR spectrum, 2020). This reflects the presence of PAM, residual acrylamide monomer (AM, impurity of PAM preparation), hydrocarbons, and carboxylic acids on the particles of PASS-treated FFT. Furthermore, N-H could have also facilitated the hydrogen bonding between surface of PASS-treated FFT particles and the hydroxyl groups of NAs (Pourrezaei et al., 2014).

### 5.3.2 The DOC desorption kinetics

The findings of the primary study indicate that PASS-treated FFT has a minimal ability to adsorb NAs and DOC from lake water. Due to the process of bitumen extraction which contributes to waste stream of FFT in high pH, it was anticipated that hydrophilic carboxylates such as NAs will exhibit a low tendency to adsorb on saturated porous media of FFT and the migration of DOC and NAs is partially emerged from the solid content of FFT to the liquid phase (Wan et al., 2014). To investigate the kinetics of DOC desorption, a study was conducted using 5 g/L of FFT at various contact times between 30 min and 24 h (Fig 5.1b). It was observed that the desorption process reached equilibrium at 10 h, leading to a 3.4 mg/L increase in DOC concentration in the synthesized lake water sample. Interestingly, within just 2 hours of contact time, the concentration of DOC in the synthesized lake water sample increased from 0 to 1.9 mg/L, which is 56% of the equilibrium condition. The desorption capacity at equilibrium was found to be 0.67 mg DOC /g PASS-treated FFT. Comparing the initial DOC concentration of the FFT, it was observed that only 5.82% of the total DOC in PASS-treated FFT have a chance to be released in the capped water.

The parameters of the kinetics study for pseudo-first-order (PFO), pseudo-second-order (PSO), and intraparticle diffusion models have been calculated (Table 5.2). The intraparticle diffusion model exhibits the highest correlation coefficient as compared to PFO and PSO (Fig. 1c, Table 5.1). The intraparticle diffusion rate of DOC from the FFT fitted intraparticle diffusion model was 0.2 mg DOC/g FFT /$h^{1/2}$. Since, the intraparticle diffusion model is linear, based on the Weber and Morris theory, diffusion of DOC between the particles of FFT only has played a significant role in controlling the desorption kinetics. Further, the boundary layer between FFT and the aqueous solution is not limiting the desorption process (Seidensticker et al., 2017; Weber Jr & Morris, 1963). The adsorption kinetics study of several PAHs component (anthracene, acenaphthene and fluoranthene) on granular activated carbon also indicated that intraparticle diffusion is only limiting the adsorption rate of contaminants on adsorbent (Valderrama et al., 2008). However, the rate constant for intraparticle diffusion of desorption in this study is significantly lower than the rate constant for intraparticle diffusion of adsorption for anthracene, acenaphthene and fluoranthene by 96 %, 97% and 96%, as reported by Velderrama et al..

Theoretically, the computed R square value is reasonable (80%) for all kinetics models regarding the complexity of PASS-treated FFT characterization. However, the experimental desorption capacity at equilibrium was not in line with the calculated desorption capacity predicted by PFO or PSO kinetics models (as shown in Table 5.1). Solely the Intraparticle diffusion model was able to accurately predict the equilibrium capacity ($q_e$(IDP)= 0.65 mg/g). This finding also suggests that desorption of DOC from the FFT particles is not controlled by the concentration difference between the adsorbate in the bulk phase and on the particle surface (bulk diffusion) nor chemisorption in the boundary layer (film diffusion). It is mainly controlled by intraparticle diffusion. Similarly, Islam et al. favored the intraparticle diffusion model over the PSO model for studying adsorption kinetic due to its stronger correlation with experimental data, despite both models having high R-squared values. (Islam et al., 2018).

Table 5.1 Calculated kinetics parameters for FFT desorption.

| **Kinetic model** | **Parameter** | **Value** |
|---|---|---|
| Pseudo first order | $q_e$ (mg/g) | 0.56 |
| | $k_{PFO}$ ($h^{-1}$) | 0.23 |
| | $R^2$ | 0.81 |
| Pseudo second-order | $q_e$ (mg/g) | 0.81 |
| | $k_{PSO}$ (g/mg/h) | 5.17 |
| | $R^2$ | 0.87 |
| Intraparticle diffusion | I | 0.04 |
| | Ki (mg/g/$h^{1/2}$) | 0.21 |
| | $R^2$ | 0.98 |

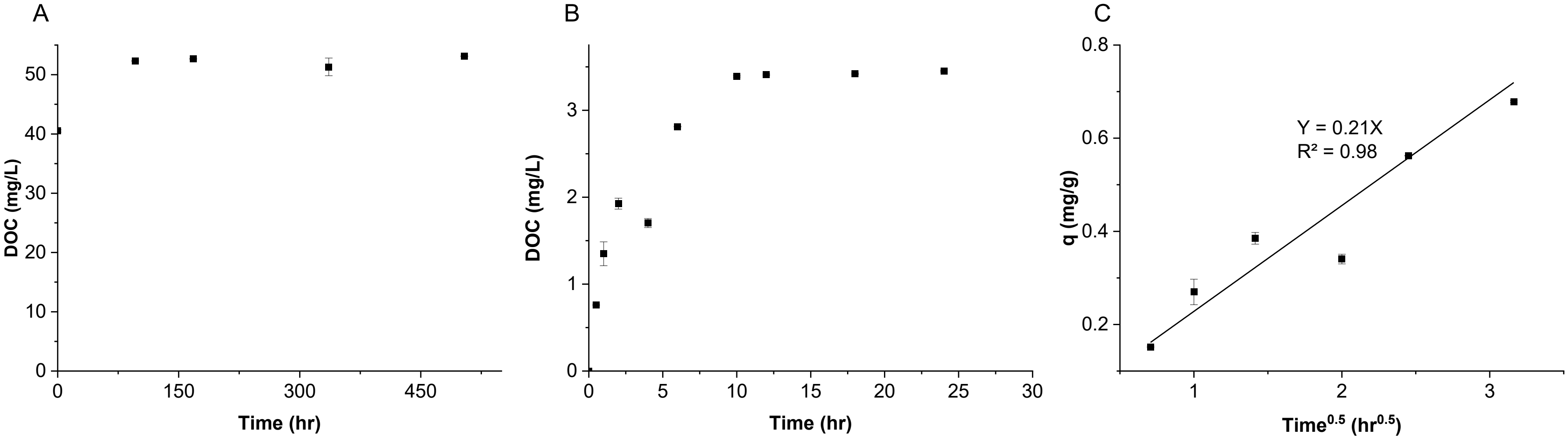

Fig. 5.1 a) Effect of contact time on DOC concentration of 5 g/L dosage of PASS-treated FFT for lake water, b) Effect of contact time on DOC concentration of 5 g/L dosage of PASS-treated FFT for simulated lake water c) Intraparticle diffusion kinetics model plot for PASS-treated FFT.

### 5.3.3 Effect of dosage and DOC desorption isotherm

The results showed that the FFT dosage substantially affected the desorbed concentration of DOC (Fig. 5.2a). Specifically, desorbed DOC concentration increased from 0.98 to 13.1 mg/L with an increase in 1 to 50 g/L of FFT. These results corroborate with the kinetics desorption explained above. In the absence of any limitations imposed by the boundary layer (discussed in section 5.3.2), an increase in FFT dosage is expected to yield a larger surface area available for desorption and subsequently higher DOC desorption.

The Langmuir, Freundlich, Temkin, and D-R isotherms were also applied to the experimental data (Table 5.2). Both Freundlich and Temkin isotherms showed high correlation coefficients for PASS-treated FFT. However, the Temkin isotherm showed the best-fitted correlation coefficient (0.91) as compared to the other isotherm models (Table 5.2, Fig. 5.2b-c). The Temkin isotherm model assumes that the heat of adsorption (or the adsorption energy) of the molecules in the layer will decrease linearly with increasing coverage (Salehi et al., 2010). Consequently, it can be assumed that all DOC compounds, regardless of their chemical structure or functional groups, interact with the PASS-treated FFT in a relatively similar manner in terms of binding energy (Auta & Hameed, 2011; Kim et al., 2004; Salehi et al., 2010). The Temkin model parameters of binding energy and isothermal constant were found to be −12.8 KJ/mol and 0.01 L/g, respectively. Since the calculated binding energy was lower than 8 KJ/ mol, DOC could have physically desorbed from FFT's surface (Gupta et al., 2017). Moreover, the desorption process was determined to be endothermic in terms of negative bonding energy (Hadi et al. 2010, Nollet et al. 2003), implying that increasing temperature may increase the desorption of DOC from PASS-treated FFT.

Table 5.2 Calculated isotherm parameters for FFT desorption.

| **Isothermal model** | **Parameter** | **value** |
|---|---|---|
| Langmuir | $q_m$ (mg/g) | 0.28 |
| | $k_{ads}$ (L/mg) | -9.75 |
| | $R^2$ | 0.52 |
| Freundlich | 1/n | -0.37 |
| | $K_f$ (L/g) | 1.00 |
| | $R^2$ | 0.82 |
| Temkin | b (KJ/mol) | -12.8 |
| | $K_T$ (L/g) | 0.01 |
| | $R^2$ | 0.91 |
| D-R | $q_d$ (mg/g) | 0.32 |
| | β (mol2/J2) | 0.00 |
| | $R^2$ | 0.59 |

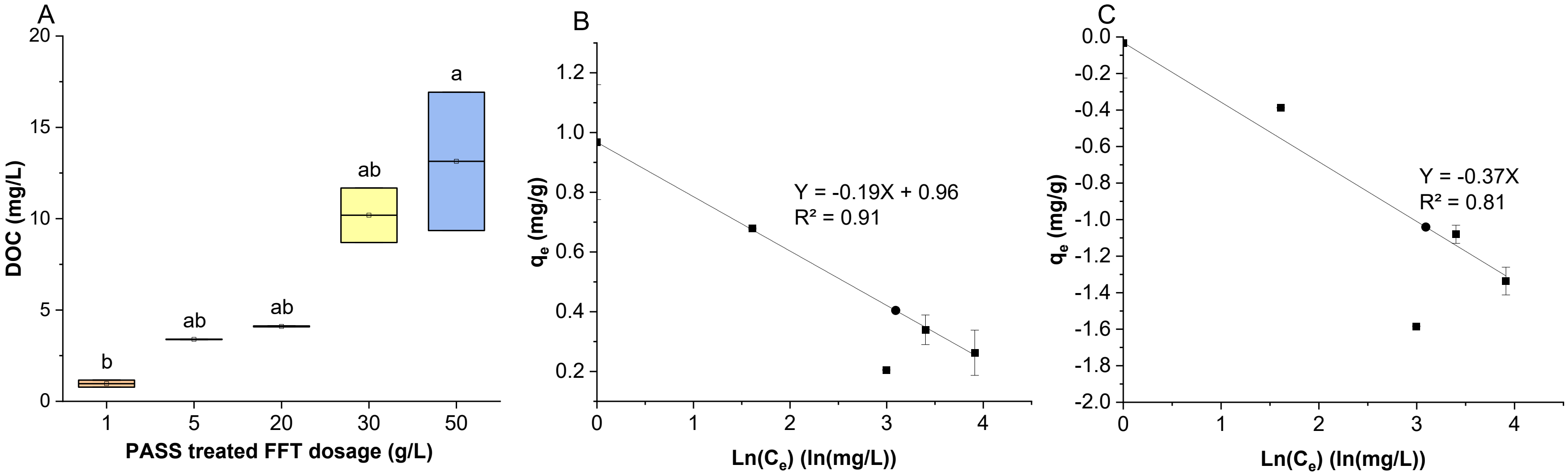

Fig. 5.2 a) Desorption of DOC as a function of PASS-treated FFT dosage, b) Isothermal desorption models plot of Temkin for FFT c) Isothermal desorption models plot of Freundlich for FFT.

### 5.3.4 Fate of DOC and NAs based on $K_{oc}$

To assess the fate of DOC and NAs in capped water, $K_d$ and $K_{oc}$ were calculated using $C_e$ and $q_{eq}$ (eq. 4 and Table 5.3). The $K_{oc}$ value for both DOC and NAs were 2500 L/kg, which represents a normalized $K_d$ with respect to organic matter on solid particles (Bian et al., 2022). The fact that DOC and NAs have similar organic carbon coefficients ($K_{oc}$) indicates their similar binding potential to FFT particles (Mojiri et al., 2020), implying of a similar transport behavior (Marimoutou et al., 2023). Thus, DOC can be used as a proxy for the migration behavior of NAs from tailing deposits to the capped water. Moreover, the high $K_{oc}$ value of DOC (>2000 L/kg) suggests that DOC and NAs had limited partitioning and migration to lake water and strong binding to PASS-treated FFT particles (Güler & Tuncel, 2022; Peng et al., 2002; Scheytt et al., 2005). The comparison of $q_{eq}$ values for DOC and NAs with initial PASS-treated FFT characterization further confirmed that at the optimum conditions, a low concentration of NAs (39%, 11 mg/L) and DOC (6%) is desorbed (Table 4.2; Table 5.3). Consequently, it can be implied that utilizing this form of FFT in a self-sustaining closure system i.e. end pit lakes might not have significant environmental implications for the capped water, as organic contaminants are likely to remain bound within the sediment for an extended period after the closure system is established (Güler & Tuncel, 2022). This observation becomes prominent in pit lake systems when the consolidation rate decreases over time reflecting that advection flux is not the primary mass transfer mechanism. A separate study indicated an initial advection flux of NAs was notably low, i.e. 0.0012 $m^3m^{-2}d^{-1}$ (Chapter 4).

Table 5.3 Value of $K_d$, $K_{oc}$, $f_{oc}$ and $q_{eq}$ for DOC and NAs content in PASS treated FFT particles.

| **Parameter** | **$K_d$ (L/Kg)** | **$K_{oc}$ (L/Kg)** | **$f_{oc}$** | **$q_{eq}$ (mg/Kg)** | **$C_e$ (mg/L)** |
|---|---|---|---|---|---|
| DOC | 200.00 | 2500.00 | 0.08 | 678.00 | 3.39 |
| NAs | 200.00 | 2500.00 | 0.08 | 22.00 | 0.11 |

### 5.3.5 Effect of temperature on desorption of DOC

Results of desorption experiment at different temperatures (10-30°C) under similar conditions are presented in Fig 5.3a. Briefly, changes in desorption capacity at equilibrium were insignificant throughout the experimental temperature range. This is expected when the intraparticle diffusion exclusively governs the desorption processes at temperatures below 30 °C (Al-Ghouti et al., 2005). However, it should be noted that by increasing the temperature beyond this range might promote faster diffusion within the porous structure and potentially increase the desorption capacity (Al-Ghouti et al., 2005). In the context of end pit lakes, we can state that the diffusion of organic pollutants from PASS-treated FFT into water solution remains remarkably stable, with moderate changes due to seasonal variations.

### 5.3.6 Effect of ion strength on desorption of DOC

Original water samples from Lake Miwasin showed that sodium and chloride ions were prominent; therefore, experiments were conducted to investigate the effect of ionic strength at varying concentration of NaCl (Table 4.1). To this end, we compared the effects of low ionic strength (2 µS/cm), moderate ionic strength (identical concentration of NaCl as in lake Miwasin Sample, 700 µS/cm), and high ionic strength (based on lake Miwasin total conductivity, 1800 µS/cm). Additionally, a sample of Lake Miwasin water was also used as a positive control. DOC desorption capacity at equilibrium was examined in terms of conductivity (ionic strength) at pH=8.15 ( Fig. 5.3b). The impact of ionic strength in terms of concentrations of NaCl concentration was insignificant on the desorption of DOC. Earlier studies also displayed that an increase in ionic strength have minimal effect on organic compound desorption in high-organic porous media like PASS-treated FFT (OM = 13%) (Conde-Cid et al., 2020; Engel & Chefetz, 2016; Guo et al., 2010; Lazo-Cannata et al., 2011). However, this behavior may not apply to the situations where the source of ionic strength differs (Guo et al., 2010; Jardine et al., 1989). A change in the source of ionic strength may explain why, as compared to the simulated lake water with NaCl, there was a notable decrease in the DOC desorption capacity when real lake water was used.

Further experiments were conducted at a steady conductivity of 1800 µS/cm and a pH of 8.15 to investigate the effects of various ions on desorption capacity of DOC from PASS-treated FFT (Fig. 5.3c). For NaCl, desorption capacity was higher in comparison to $Na_2SO_4$, KCl, $K_2SO_4$, and $CaCl_2$. The reduced desorption capacity potentially implies that DOC is more stable in saline lake water samples where the other tested ions dominate compared to $Na^+$ (Setia et al., 2013). Several studies proposed that replacing cations (e.g., $Na^+$) with $Ca^{2+}$ results in stronger covalent bonding with organic matter in sediment (containing clay), potentially reducing DOC desorption capacity (Marchuk et al., 2013; Mayes et al., 2012; Skyllberg & Magnusson, 1995). Similar behavior might result in a lower desorption capacity of DOC in the presence of KCl compared to NaCl in the simulated lake water sample (Marchuk et al., 2013). Moreover, minor variation in desorption capability between KCl and $K_2SO_4$ implies that cations could influence DOC stability in particles (Jones & Willett, 2006; Lee et al., 2003; Zhu et al., 2019). Overall, assessing effects of ionic strength in current study, the type of ions (mainly cations) had a more pronounced effect on DOC desorption from PASS-Treated FFT to capped water than their respective concentrations.

The desorption capacity for humic acid (HA) solutions was assessed to replicate the DOC concentration found in the water samples at Lake Miwasin (Fig. 5.3c). Desorption capacity was increased for HA solutions as compared to DI. This indicates that HA and organic matter complexation reduces the stability of DOC on particles, leading to an increase in DOC desorption from particle (Akkanen & Kukkonen, 2003; Pan et al., 2008; Seidensticker et al., 2017; Xu et al., 2018; Xu et al., 2016; Yu et al., 2023).

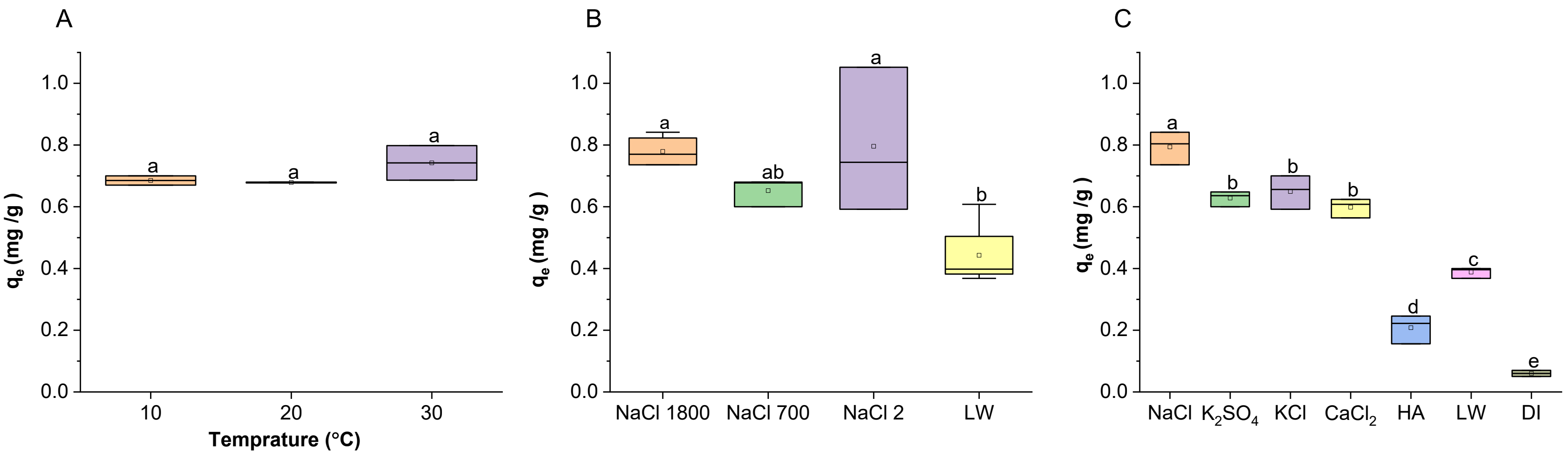

Fig. 5.3 a) Desorption capacity of DOC from FFT at equilibrium for different temperatures, b) Desorption capacity of DOC from FFT at equilibrium for desorption solutions with different ion strengths at constant pH, c) Desorption capacity of DOC from FFT at equilibrium for desorption solutions with different electrolyte at constant pH and conductivity[7].

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[7] LW= lake water, NaCl 1800= NaCl solution have conductivity of 1800 µs/cm

### 5.3.7 Implications

The present research examines the dynamics of DOC migration during the long-term storage of PASS-treated FFT within end pit lakes, emphasizing the case of Lake Miwasin. The data suggest that PASS-treated FFT remains resilient under various physical and chemical changes. This resilience is seen in its reduced tendency to release potentially harmful organic materials into the capped water. The study has implications in at least two domains:

- **Improved Environmental Solution**: PASS-treated FFT reduces the mobility of COPCs (i.e. NAs) and offers a progressive and environmentally friendly alternative for FFT management in pit lakes, compared to traditional FFT techniques. This approach corroborates the province's vision for sustainable end pit lakes and enduring aquatic integrity, based on TMF goals (AER, 2015).
- **Benefits for Industry Stakeholders:** For stakeholders like Suncor Energy Inc., the research is useful to understand contaminants desorption and migration during long-term pit lake management strategies. The investigation on tailings treatment behavior in pit lake system allows for a more proactive approach to environmental challenges tied to FFT deposition, potentially reducing costs associated with environmental remediation. The conducted research directly assists the stakeholders in following the specifications provided in the Water Resource Act and the Environmental Protection and Enhancement Act (EPEA)(AER, 2015). As a result, this allows the company like Suncor to better meet

both public and government expectations for protecting the environment, reducing risks, and responsibly managing pit lake.

## 5.4 Conclusions

Understanding the movement of organic compounds from FFT to lake water is vital for FFT management and reclamation of permanent aquatic closure. The treatment of FFT via the PASS method is environmentally advantageous and a step forward in FFT management. PASS-treated FFT accelerate dewatering; however, there is uncertainty regarding the stability. This study, a first of its kind, examines the release dynamics of DOC from such FFT. We observed that higher FFT dosage and lake water organic matter resulted in increased desorption of DOC, while temperature and conductivity had minimal effects. Specific electrolytes influenced DOC release, with sodium aiding its migration, while potassium and calcium play significant roles in controlling the desorption process from treated FFT particles. Desorption dynamics followed physically favorable patterns as represented by Temkin isotherms. Similarly, equilibrium desorption capacity was accurately predicted by the Intraparticle diffusion kinetic model. Importantly, only 5.82% of the DOC and 39.1% of NAs in PASS-treated FFT was potentially released under the conditions of the Lake Miwasin. Intraparticular diffusion mainly controlled the mechanism of desorption and the high distribution coefficient indicated that DOC and NAs have low tendency to migrate to capped water. Overall, this study highlights the considerable stability of PASS-treated FFT in relation to the physical and chemical conditions of the lake water, making them a promising alternative in FFT management strategies.

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# 6 Chapter 6: Conclusion and Recommendation

## 6.1 Dissertation Overview

Oil sands surface mining is associated with the production of large amounts of FFT, a mixture of water, minerals, and residual chemicals. The long-term storage of FFTs, as well as their potential impact on ecosystems, pose significant environmental challenges. To address these concerns, various reclamation strategies have been under exploration. One promising approach to sustainable tailings management is the establishment of EPL, which involves converting a closed-mine pit into an aquatic environment. However, concerns remain in EPL scenarios, particularly about the potential release of contaminants from FFT into the capping water. Furthermore, the dewatering of fresh FFT within the reclamation site can be lengthy, leading to sustainability concerns. The implementation of PASS tailings treatment technology could be an alternative approach to addressing environmental concerns for the EPL reclamation strategy. The initial expectation is that the use of this treated FFT within the EPL system will significantly improve the dewatering process and the capping water quality (by immobilizing COPCs, including NAs). However, there is a significant knowledge gap regarding the geochemical stability of PASS-treated FFT, specifically the fate of toxic ions, metals, and organic compounds.

Therefore, this dissertation systematically investigated for the first time the implications of PASS-treated FFT in the modeled EPL. The research journey began with an extensive characterization of FFT. In particular, in Chapter 2 for the very first time the extraction and cleanup conditions were optimized for the development of a method for analyzing NAs in FFT, a class of organic compounds commonly found in FFT. Subsequently, Chapter 4 explored both the short-term and long-term impacts of PASS-treated FFT on the mobility of COPCs within a demonstrated EPL system condition. Additionally, the chemical mass transfer in the early stage of EPL establishment was investigated through the exploration of advection-dispersion-decay processes from the treated FFT into the capping water. Further, the effect of factors such as the presence or absence of lake turnover conditions to evaluate water mixing effects, different consolidation ratios, and a comparison of water qualities, specifically contrasting lake water with fresh water, on chemical mass transfer were addressed.

Finally, Chapter 5 delivered a comprehensive analysis of desorption kinetics and mechanisms, shedding light on how DOC was released from the PASS-treated FFT solid content into the capping water. This study explored the release capacity of DOC from the treated FFT to the lake water sample under varying physical and chemical conditions within the EPL system. Additionally, this chapter reported the immobilization effectiveness of the treated FFT at a molecular level. The findings offered crucial insights on PASS treatment of FFT that contribute to sustainable tailings management practices.

## 6.2 Conclusion

This thesis addressed three main topics: the development of methods for characterizing NAs in FFT, the effects of PASS treatment on tailings within a model EPL system on COPC mobility, and the desorption behavior of DOC in treated FFT. The experimental results and analysis led to the following conclusions:

- An effective extraction and cleanup procedure for analyzing NA species in oil sands tailings was developed.

  - Among the tested extraction conditions, 0.5 M sodium hydroxide (NaOH) proved to be the most effective solvent, compared to ten other solvents.
  - Orbital shaking outperformed static conditions, with a 1.27 times higher effectiveness.
  - Extending the mixing time to over 40 minutes improved adequately NAs recovery by 32% compared to a 5-minute duration.
  - Using two extraction steps was adequate and increased the recovery rate of total NAs by 26% compared to a single extraction.
  - For the cleanup step, methanol/formic acid as the eluting solvent (43%) and methanol/water as the reconstitution agent (82%) with HLB cartridges yielded the highest NAs recovery.
- Using the optimized method, NAs were quantified in different oil sands tailings, ranging from 56.1 to 112.25 mg NAs/kg tailings, with PASS-treated FFT showing the highest levels.
- Classical NAs with carbon numbers of 16 and 18 were the most common NA species in all tailings.
- This novel methodology provided new insights for FFT treatment evaluation, innovative reclamation practice and monitoring the fate of NAs in FFT reclamation sites.

Investigation on the fate of COPCs during short-term and long-term storage of treated FFT in the EPL model's system:

- The release of potentially toxic elements, ions, and dissolved organics was reduced over time including $PO_4^{-3}$, $Ca^{2+}$, $Mg^{2+}$, $Fe^{3+}$, $Li^{+}$, $Cu^{+}$, $Al^{+3}$ and NAs by 100%, 33%, 1%, 100%, 100%, 100%, 100% and 10%, respectively.
- The long-term monitoring of system highlighted the higher chemical fluxes toward the capping water in the initial phase.
- A detailed study at the commissioning phase of the model EPL system confirmed that the advection mass transfer mechanism mainly controlled the migration of contaminants from the FFT to capping water.
- The use of PASS treatment for FFT significantly reduced chemical advection, particularly NAs.
- Intermittent additional mass flux via lake turnover caused by the seasonal change was not observed, implying that PASS treatment of FFT minimized the effect of internal mixing of lake on the mobility of the COPCs from the FFT to capping water.
- Aside from FFT PASS treatment, directly covering the EPL with fresh water and filling it with more fluid FFT increased chemical mass flow in the early stages of closure system establishment.

- Considering the final goal of the EPL system, the finding revealed that the implication of PASS-treated FFT accelerated the reclamation process in the EPL system with PASS-treated FFT, as has already been established in Lake Miwasin, even if field conditions have different results.

Investigation of DOC desorption behavior from the solid content of treated FFT into capping water under different conditions.

- Higher FFT dosage and capping water organic matter led to increased desorption capacity DOC.
- It was observed that the desorption process reached equilibrium at 10 h, leading to a 3.4 mg/L increase in DOC concentration in the synthesized lake water sample. The desorption capacity at equilibrium was found to be 0.67 mg DOC /g PASS-treated FFT.
- Temkin isotherms model best explained the desorption process and displayed that desorption dynamics followed physically favorable patterns.
- Temkin isotherm model parameters of binding energy and isothermal constant were found to be −12.8 KJ/mol and 0.01 L/g, respectively.
- The intraparticle diffusion kinetics model best described the desorption, in which the intraparticle diffusion rate of DOC process was 0.2 mg DOC/g FFT /h$^{1/2}$.

- The linear intraparticle diffusion model properly predicted the equilibrium desorption capacity of DOC as 0.65 mg/g of PASS-treated FFT
- The intraparticle diffusion model helped us to conclude that the desorption DOC was mainly controlled by pore diffusion and film diffusion between solid content of FFT and the aqueous solution is not limiting the desorption process.
- The intraparticle diffusion kinetics model was favorable and properly predicted the equilibrium desorption capacity of DOC as 0.65 mg/g of PASS-treated FFT.
- A small percentage (5.82%) of the DOC and less than half of NA species (39.1%) in PASS-treated FFT were potentially released. The distribution coefficient value of DOC and NAs was comparably high, indicating that DOC and NAs were mostly stable within the PASS-treated FFT deposition.
- Temperature and conductivity of the capping water had minimal effects on desorption behavior.
- Cation electrolytes ($K^+$ and $Ca^{2+}$) significantly inhibited the desorption process compared to $Na^+$ while anion one had no significant effect on the desorption process.
- In term of immobilization of organic compounds, the study demonstrated considerable geochemical stability of PASS-treated FFT under various physical and chemical conditions of the capping water, implying the treated FFT potential as a valuable choice in FFT management.

### 6.3 Recommendation

The developed method for characterizing NAs in FFT in this study could be suggested for use as a routine process for NAs characterization of a broader range of tailings samples. This approach helps identify trends and patterns in NAs composition across different types of tailings samples. Additionally, a broader range of tailings samples for NAs characterization and considering coupling this approach with advanced techniques like laser-induced breakdown spectroscopy (LIBS) would be beneficial for real-time monitoring of NAs in tailings. This integration could facilitate environmental assessment and continuous monitoring of NAs levels in different oil sands tailings reclamation areas.

This study is the first study that investigated the impact of PASS-treated FFT in terms of the fate of COPCs in controlled EPL systems. However, expanding the duration time of monitoring provide a more comprehensive understanding of COPCs flux and the performance of PASS-treated FFT in EPL system, particularly in term of biological aspect. In particular, the extension of monitoring duration enables more accurate understanding of the biodegradation of PASS treatment polymer by-products (PAM and AM) and NAs and the performance of PASS-treated FFT. Furthermore, to validate the efficacy of PASS treatment in operational EPL systems like Lake Miwasin, field observations could be compared with laboratory results, ensuring that the treatment continues to demonstrate its efficacy in practical, real-world scenarios.

Considering the observation of this thesis on the promising efficiency of PASS treatment in enhancing tailings management, it is beneficial to delve into alternative strategies that can complement or augment PASS treatment further. For example, the combination uses of PASS-treated FFT and other promising economical reclamation materials such as biochar or peat-mineral mix resulted from the surface mining of oil sands could be investigated to enhance and accelerate the reclamation period in passive tailing management strategy including EPL or wetlands.

By addressing these recommendations, this dissertation can contribute to the ongoing efforts to improve the environmental sustainability of oil sands tailings management and advance our understanding of the fate and impact of contaminants in oil sands reclamation sites.

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# Appendix: Supporting Information

## Tables

**Table S1** A description of desorption kinetics models used in this study.

| **Model** | **Linearized equation*** | **Parameters** |
|---|---|---|
| PFO (Pseudo-first order) | $\ln(q_e - q_t) = \ln q_e - k_{PFO} t$ | $q_e$–the amount of desorbed DOC from FFT at equilibrium (mg/g)<br>$q_t$– the amount of desorbed DOC from FFT at time t (mg/g)<br>$k_{PFO}$– PFO rate constant of desorption (h $^{-1}$) |
| PSO (Pseudo-second order) | $\frac{t}{q_t} = \frac{1}{k_{PSO} {q_e}^2} + \frac{t}{q_e}$ | $q_t$– the amount of desorbed DOC from FFT at time t (mg/g)<br>$k_{PSO}$– PSO rate constant of desorption (g/mg/h)<br>$q_e$ – the amount of desorbed DOC from FFT at equilibrium (mg/g) |

| | | |
|---|---|---|
| Intraparticle diffusion | $q_t = k_i t^{1/2} + I$ | $q_t$– the amount of desorbed DOC from FFT at time t (mg/g)<br>$k_i$ – Intraparticle diffusion rate constant (mg/g/h$^{1/2}$)<br>I – intercept (provides the extent of boundary layer thickness) (mg/g) |

**Table S2** A description of isotherm models investigated in this study.

| Model | Linearized equation* | Parameters |
|---|---|---|
| Langmuir | $\frac{1}{q_e} = \frac{1}{k_{ads} q_m C_e} + \frac{1}{q_m}$ | $q_e$ –DOC generate from adsorbent at equilibrium (mg DOC/g FFT)<br>$k_{ads}$ – Langmuir isotherm constant (L/mg DOC)<br>$q_m$ – maximum desorption capacity from adsorbent (mg DOC/g FFT)<br>$C_e$ – equilibrium concentration of desorbed DOC in solution (mg DOC/L) |
| Freundlich | $\ln q_e = \frac{1}{n} \ln C_e + \ln K_F$ | 1/n – the Freundlich exponent<br>$K_F$ – Freundlich constant (L/g) |
| Temkin | $q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$ | R – universal gas constant (J/mol/K)<br>T – liquid temperature (K)<br>b – constant related to the heat of desorption (J/mol)<br>$K_T$ – Temkin isotherm constant (L/g) |

| | | |
|---|---|---|
| Dubinin – Radushkevich (D-R) | $\ln q_e = \ln q_d - \beta \in^2$ | $q_d$ – D–R isotherm constant (mg DOC/g FFT)<br>β – constant related to free energy ($mol^2/J^2$)<br>∈ – Polanyi potential (J/mol) which is defined as $\in = RT\ln(1 + \frac{1}{C_e})$ |