# A Systematic Review on Naphthenic Acids in Soil: Environmental Fate and Remediation Challenges from Analysis to Cleanup

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**Abstract:** Naphthenic acids (NAs) are a group of complex organic compounds naturally present in crude oil, characterized as persistent, toxic, and difficult-to-degrade organic pollutants. Although the concentrations of NAs typically exceed polycyclic aromatic hydrocarbons by several orders of magnitude, NAs have emerged as critical soil pollutants. Soil biodiversity, agricultural safety, and human health are significantly threatened by their presence. The increased concern about NAs leaching into groundwater has raised the need for investigation in that direction, but more often than not studies focus on the aquatic environment, thereby leaving a lot of unknowns pertaining to their fate and transport in a heterogeneous soil matrix. In this regard, the present review thoroughly synthesizes and evaluates recent advances in the field of NAs in soil systems focusing on analytical techniques, environmental fate, and remediation technologies. Important findings include the urgent need for standardised analytical protocols to deal with the complex mixtures of NAs, the limited mechanistic understanding of the migration and transformation of NAs across soil types and the need for predictive adsorption-desorption models. Significant uncertainties remain regarding the efficiency of degradation strategies, particularly in relation to the effects of plant-microbe interactions. Moreover, we highlight three key areas of research that require urgent attention: the creation of soil-tailored analytical frameworks; the understanding of molecular interactions in the rhizosphere and their potential application in bioremediation; and the incorporation of process-based models into remediation design. This review seeks to guide future research, policy development and advancement of technologies to remediate soils contaminated with NAs by bringing together current understanding and laying down a pathway forward.

**Keywords:** Oil sands; Oxidative stress; Analytical standardization; Distribution; Biodegradation

## 1. Introduction

Due to oil spills and the discharge of oily wastewater, activities related to oil extraction, transportation, and refining can lead to soil pollution, thereby posing risks to the environment and human health (Meulen et al., 2025; Yuan et al., 2022). Research into petroleum-polluted soils has largely focused on polycyclic aromatic hydrocarbons (PAHs) in the past. Nevertheless, the improvement of analytical methods showed that naphthenic acids (NAs) are a group of naturally toxic petroleum compounds that constitute 2 to 4% of crude oil by mass (Valente et al., 2024) are often present in contaminated sites at concentrations 10-30 times higher than PAHs. NAs concentrations have been found to exhibit significant toxicity. Moreover, the natural NAs have half-lives of about 12.9-13.6 years in tailing ponds. NAs have been a critically neglected group of emerging soil contaminants (Zan et al., 2019). The first definition of NAs was developed in the 1960s. Previously, NAs were defined as a complex, containing alkyl-substituted acyclic and cycloaliphatic carboxylic acids that have the general formula of $C_nH_{2n+z}O_2$ (Figure 1(a)). In this formula, ‘n’ represents the carbon number (generally 5-33); and ‘z’ represents the hydrogen deficiency caused by ring structures, which is a negative even integer (Grewer et al., 2010; Whitby, 2010; Gheorghe et al., 2025). Nonetheless, there have been additions to this definition. The International Union of Pure and Applied Chemistry (IUPAC) says that real-use NAs mixtures may present structures with aromatic rings, unsaturation and heteroatoms (nitrogen, sulfur, and oxygen; NSO) (Headley et al., 2013; Barros et al., 2022;). Moreover, the discovery of oxidized naphthenic acids (ox-NAs) NAs with the formula $C_nH_{2n+z}O_x$, where x is equal to and higher than 3. This includes diacids ($O_4$ class) (Figure 1(b)) and tetra-acids (such as $C_{80}$ hexacyclic acid; they would be $O_8$ class) (Figure 1(c)). This has also contributed to their identification. They are implicated in difficult-to-manage calcium naphthenate deposits (Lutnaes et al., 2017; Negris et al., 2024). The unique structure of such substances complicates their analysis and moreover affects their environmental behaviour and persistence in soil, as a result, risk assessment and remediation efforts are challenging.

The environmental importance of NAs is highly supported by their multi-faceted and high toxicity to a variety of organisms in a soil environment owning to the risks they pose. A crucial way by which NAs generate toxicity is by inducing oxidative stress, suggesting that NAs may generate reactive oxygen species (ROS) that overwhelm the antioxidant defences of organisms and generate damage. Moreover, NAs are potentially multi-toxicity and pose environmental threats. In vegetation, NAs disrupt essential physiological functions such as water root transport, stomatal conductance, and transpiration. Changes in root exudate profiles (e.g., organic acids, amines) and induction of oxidative stress severe enough to damage the respiratory chain and accelerate senescence (Kamaluddin et al., 2002； Jia et al., 2023). Animals can suffer from mortality, developmental defects, immunotoxicity and organ damage due to exposure which is mainly through ROS-mediated DNA and cellular damage (Bartlett et al., 2017). Moreover, Certain NAs fractions have been recognized as estrogen receptor agonists and exhibit anti-androgenic properties, suggesting that they act as potential endocrine disruptors. Toxicity data from animal studies indicate that the oral $LD_{50}$ in rats ranges from 3.0 to 5.2 g kg$^{-1}$, where $LD_{50}$ refers to the median lethal dose required to cause death in 50% of test animals (Reis et al., 2023). Surfactant-like properties of NAs cause disruption of the cell membrane and cell lysis of living organisms in microbial communities. This leads to a delay in growth and metabolism of susceptible species. In summary, NAs have negative effects along the soil trophic network-from microbes to plants and animals-largely by causing cellular damage and interference with key metabolic processes. This wide-ranging toxicity emphasizes the necessity of understanding the behaviour of these chemicals in soil matrices and the consequent need to develop measures to combat their ecological and health effects, this serves as justification for the present review.

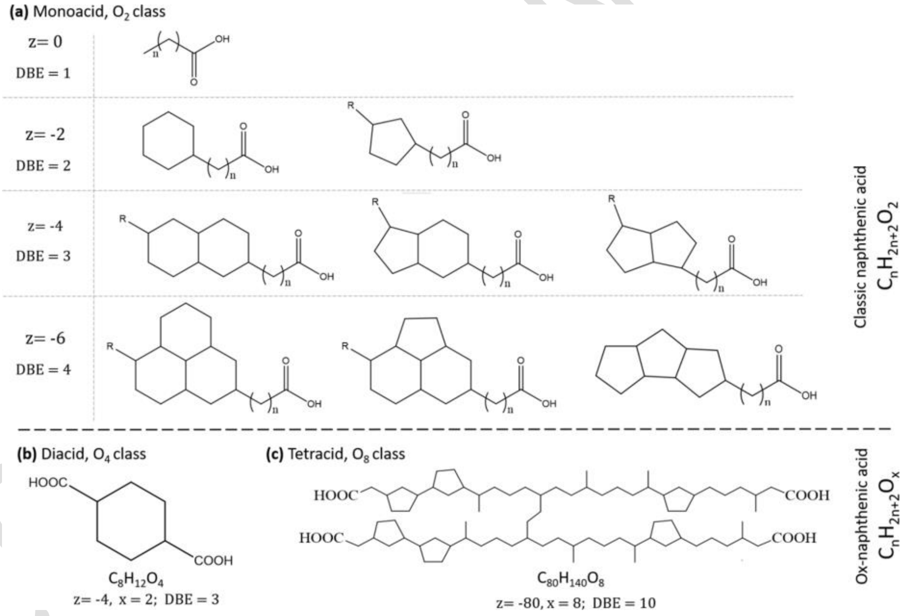

Figure 1 (a) Some chemical structures of naphthenic acids present in crude oil, where DBE (double bond equivalent) represents the number of rings and double bonds, R the alkyl chain, and z hydrogen deficiency (adapted from (Headley et al., 2013; Terra et al., 2017)); (b) cyclohexane di-1,4-carboxylic acid (Frank et al., 2009), and (c) $C_{80}$ hexacyclic acid (Sutton et al., 2010).

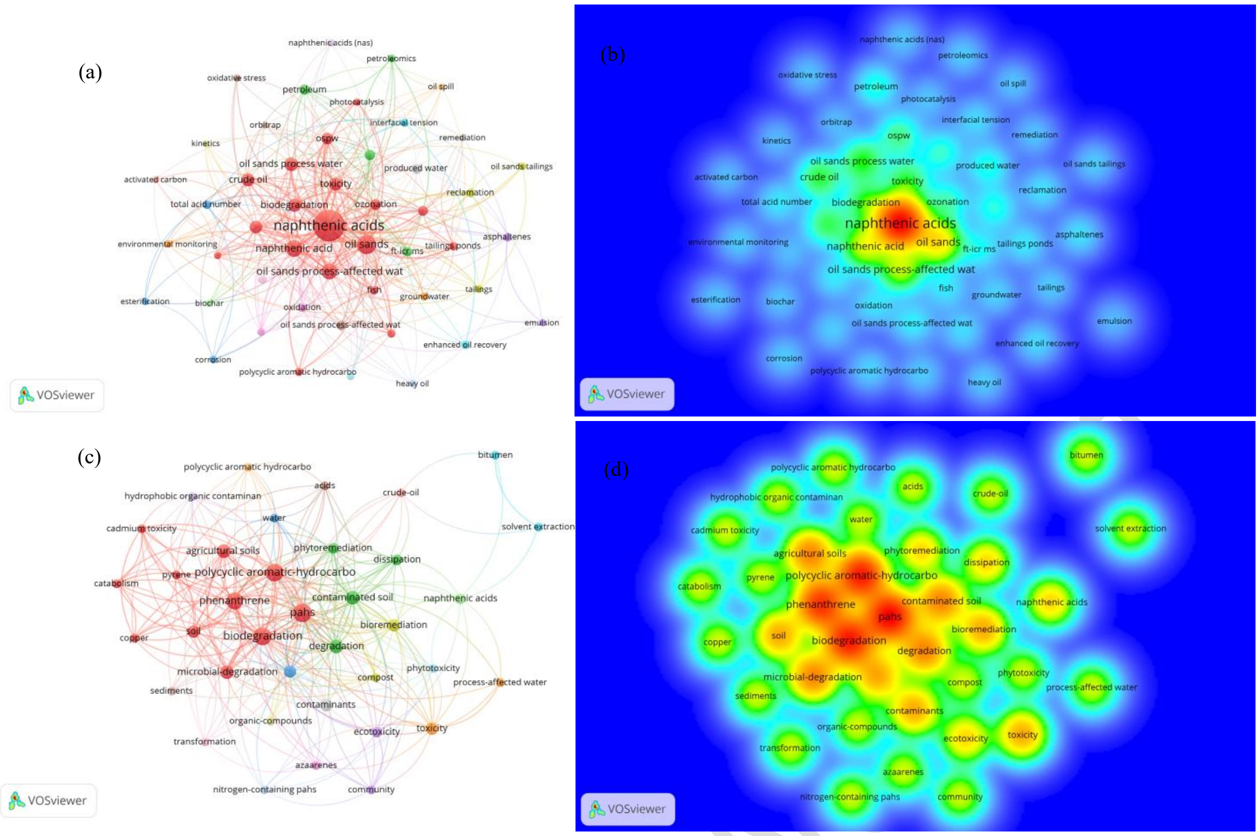

Figure 2 Keywords density visualization map for NAs (a; b) and NAs in soil (c;d).

This review aims to clearly define the scope and substantiate the identified research gaps through a structured and transparent literature analysis. To ensure methodological rigor, a systematic search was conducted using the Web of Science Core Collection database for publications available up to December 2025. The search was performed using the keywords “naphthenic acids” and “naphthenic acids in soil”. The initial search using “naphthenic acids” yielded 1316 publications. A refined search using “naphthenic acids in soil” returned 71 articles. These records were further screened based on relevance to soil systems. Studies focusing exclusively on aquatic environments without clear implications for soil processes were excluded. Additional inclusion criteria considered studies addressing analytical methods, environmental behavior, toxicity, and remediation of NAs in soil. After screening titles, abstracts, and full texts, a subset of relevant studies was selected for detailed analysis. The keyword co-occurrence analysis confirms that most existing literature is concentrated on oil sands, oil sands process water, and biodegradation (Fig. 2(a) and (b)), whereas soil-related studies remain limited. The keyword network for soil-focused studies (Fig. 2(c) and (d)) highlights associations with PAHs, bioremediation, and toxicity. Notably, although NAs often occur at higher concentrations than PAHs and present greater remediation challenges, their behavior in soil systems remains underexplored, with important implications for groundwater and agricultural safety. Based on this analysis, three major scientific bottlenecks are identified: (1) the absence of standardized analytical approaches for complex NAs mixtures in soil; (2) limited mechanistic understanding of their migration and transformation in heterogeneous soil matrices; and (3) the lack of effective, mechanism-based remediation strategies for NAs-contaminated soils. Accordingly, this review addresses the central question of how the structural characteristics and environmental behavior of NAs govern their persistence in soil systems and influence the effectiveness of different remediation strategies. In response, this review provides a structured and critical synthesis of current knowledge on NAs in soil systems, including analytical techniques, environmental behavior, and remediation strategies. By identifying limitations in existing approaches and highlighting key research priorities, this work aims to support future research, technological development, and policy-making related to NAs-contaminated soils.

## 2. Analytical Methodologies for NAs in Soil: Challenges and Techniques

The accurate measurement of NAs in soil is important for risk assessment and remediation but presents unique problems in terms of analysis. The first is the challenge that NAs are complex mixtures consisting of potentially thousands of isomers and homologs and for which standards are not available for most constituents (Barros et al. 2022). The soil environment creates ‘co-extracted interferents’ that are organic and inorganic and difficult to quantify. As a result, absolute quantification is unattainable; indeed many methods are semi-quantitative by default since they use a commercial surrogate mixture as a standard (Scott et al., 2008a). Methods for determining NAs have been widely developed and applied worldwide, primarily focusing on the assessment of their concentrations and structural characteristics. The total acid value generally characterizes the NAs concentration in crude oil with respect to concentration determination. Different methods of structural composition analysis are being utilized. (Yen et al., 2004). Both gas chromatography (GC) and liquid chromatography (LC), for chromatography, have been established literature precedents for pre-separation of NAs to lower sample complexity before mass spectrometry. As an example, the characterization of NAs in a number of applications has been done by GC×GC-TOF/MS. In the same vein, the fingerprints analysis of NAs has been achieved through GC-FT-ICR MS with electron as well as chemical ionization. In addition, high-performance liquid chromatography (HPLC) or ultra-performance liquid chromatography (UPLC) in conjunction with high-resolution mass-spectrometry (HRMS) has also been widely used for NAs analysis (Chen et al., 2024).

### 2.1 Non-Specific Aggregate Parameter: Total Acid Number (TAN)

NAs content in a soil petroleum mixture can be assessed by the Total Acid Number method, where oil sample is titrated with KOH to determine the mg of KOH requisite for neutralizing 1 g of oil. Nevertheless, it should be noted that the method also considers the presence of other acid petroleum compounds, making it difficult to define the NAs content actually present in soil (Barros et al., 2022).

### 2.2 Spectroscopic and Chromatographic Techniques

The assessment of absorbance of carboxyl groups in the infrared spectrum is used for Fourier-transform infrared spectroscopy (FTIR) analysis of NAs. The detection limit is usually about 1 mg $L^{-1}$, but it is not possible to identify NAs content accurately through specific functional group peak detection. The FTIR measure adopts the standard quantitative procedure involving methylene chloride extraction from acidified samples. The FTIR analysis of NAs primarily targets the characteristic stretching vibrations of the carboxyl groups (-COOH), particularly the C=O carbonyl stretching band. In reality, the data refers to the organic matter extracted from the acid, which does not perfectly match the chemical formula of NAs (Clemente et al., 2005; Grewer et al., 2010).

The determination of NAs using HPLC analysis is 2-nitrophenylhydrazine (NPH) derivatives of carboxylic acids prepared in an aqueous medium using coupling agent 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) (Miwa et al., 2000). FTIR gives a concentration that is about 11% greater than HPLC according to the research. Also, HPLC uses less man-hours than FTIR and does not use chlorinated solvents. The method has shown to be more effective and accurate with a detection limit of approximately 5 mg $L^{-1}$. Yen et al. (2004) demonstrated enhanced HPLC detection of low NAs concentrations (approximately 5 mg $L^{-1}$) in oil sands, which was also simpler, faster, and more precise than FTIR. HPLC-HRMS coupling gives the best compromise between price, feasibility and resolution. Analyzing NAs with LC-MS allows more information about oxidized NAs ($O_2$-$O_6$) to be obtained than GC-MS (Huang et al., 2021). When low concentration NAs in crude oil do not have a chromophore, application of preconcentration, separation and esterification procedures is required for their chromatographic analysis in order to improve volatility, reduce polarity and enhance detection sensitivity (Barros et al., 2022).

### 2.3 Mass Spectrometric (MS) Techniques and Hyphenated Methods

The term MS refers to the technique that NAs must undergo to separate out the components of a NAs mixture. In that way, one is able to show the spectra of each individual NAs isomer based on the relative responses of each mass which corresponds to their n and z values (Gheorghe et al., 2025). Although direct MS methods afford considerable information, group type analysis may not fully resolve all constituent isomers and diastereomers within complex mixtures (Porto et al., 2021). Mass spectrometry concentrates on the typical sample ion and requires initial ionization into ions. There are several ionization sources that can efficiently ionize NAs, including electron ionization (EI), chemical ionization (CI), negative ion electrospray ionization (ESI), field desorption (FD), and atmospheric pressure chemical ionization. The molecular composition of NAs can be unequivocally determined when these ionization sources are coupled to their mass spectra (Zhan et al., 2000; Merlin et al., 2007). Moreover, the quadrupole time-of-flight mass spectrometry (QTOF-MS), Orbitrap MS and FT-ICR MS are certainly offering a high resolution than above all mentioned MS detectors, but costly. According to Wang et al. (2019) the identification of NAs in refinery wastewater through the derivative reagent was achieved using QTOF-MS utilizing a derivative method to generate characteristic fragments. Using their identification approaches, the authors identified 70-126 classical NAs, 30-68 oxidizing NAs, and 54-60 nitrogenous NAs.

Electrospray ionization mass spectrometry (ESI-MS) is a soft ionization technique that converts ions in solution into gas-phase ions to study them in mass spectrometry. For instance, Clemente extracted from aqueous samples naphthenic acids by solid-phase extraction on a divinylbenzene-based polymeric sorbent (ENV+), a modified styrene-divinylbenzene material used for solid-phase extraction. Sorbent with acetonitrile and analyzed by ESI/MS were eluted these acids (Clemente et al., 2005). The detection limit assessed on a 500 mL water sample is 0.01 mg $L^{-1}$ (Sakin et al., 2011). One of the major challenges of ESI is the matrix effect which can compromise its quantitative ability with the presence of salts and coelutes (Oetjen et al., 2017).

Gas Chromatography-Mass Spectrometry (GC-MS) is a key technique for the qualitative and quantitative analysis of complex mixtures of NAs such as linear, tricyclic and pentacyclic carboxylic acids. It is advantageous in determining sources as well as the degradation stages of NAs contamination. The derivatization of polar NAs to enhance their volatility and detectability is a vital prerequisite for GC-MS analysis. Typical reagents for converting NAs to (tert-butyldimethylsilyl)

TBDMS esters are N-methyl-N-(tert-butyldimethylsilyl) trifluoroacetamide (MTBSTFA). The fragmentation caused by electron ionization of such derivatives provides the characteristic $[M+57]^+$ ions (where M is the molecular mass of the TBDMS ester), which corresponds to the $[\text{naphthenate+dimethylsilyl}]^+$. The pattern of fragmentation that has been appearing on the spectra allows to correlate the peaks with certain numbers C (carbon) and Z (hydrogen deficiency). This is of interest for the characterisation and semi-quantification of components in complex mixtures of NAs (Clemente et al., 2005). According to Scott et al. (2008a), the detection limit of GC-MS method is 0.01 mg $L^{-1}$.

Comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC×GC-TOF/MS) is a significant advance for countering the co-elution and incomplete separation associated with one-dimensional GC-MS. With the first dimension column, the second column provides modulators that trap, focus and reinject effluents. As the second column is orthogonally selective, separation is undertaken here inside a second column. Not only does this improve resolution, but it also enhances peak capacity in two-dimensional chromatography.

According to Bowman et al. (2020), GC×GC-TOF/MS can be used to identify a wide range of components present in oil sands tailings water, such as adamantane, dicyclic, (alkylated) monocyclic and even thiophene carboxylic acids. An analytical question that must be addressed when GC-MS is used is the need to differentiate between esters produced synthetically during derivatization (e.g. methyl esters) and esters that occur naturally in environmental samples. One more ionization mode that is frequently utilized in GC-MS is EI. The mass spectrum is well reproduced and contains more information on fragment ions, which is beneficial for predicting the structure of unknown substances. EI has advantage as it is easy to implement. The drawback of EI is that the intensity of the molecular ion peak is weak or nonexistent when the molecular stability of the sample is poor (Chen et al., 2024).

Even with modern methods on the rise, traditional GC-MS is still more practical. Headley et al. note the benefits of operational simplicity, availability, and reliability. Moreover, work (Headley et al., 2013) shows it can track gross changes in NAs concentrations and broad shifts in composition. Accordingly, overview analysis is an accessible and effective technology for many monitoring and screening applications.

### 2.4. Synthesis and Method Selection for Soil Analysis

The choice of analytical method involves trade-offs among resolution, sensitivity, cost, and operational convenience. Previous studies have often reported an inverse relationship between analytical resolution and measured NAs concentrations (Ross et al., 2012), however, this trend is not universal. To compare analytical techniques for NAs, representative data from the Alberta oil sands region in Canada are summarized in Table 1. In general, higher-resolution methods (e.g., HPLC-HRMS, GC×GC-TOF/MS) tend to provide more selective and interference-free measurements, often resulting in lower reported concentrations. In contrast, less selective techniques (e.g., FTIR, TAN) may yield higher apparent concentrations due to contributions from non-NAs organic acids (Han et al., 2009; Vander et al., 2023). However, the magnitude and even direction of these differences vary across samples. For example, in the Suncor South Tailings Pond sample, the concentration measured by HPLC-TOF/MS is slightly higher than that obtained by FTIR. Such discrepancies likely reflect differences in sample matrix, co-extracted compounds, and method-specific sensitivity and calibration. Furthermore, the ratio between low and high-resolution measurements varies substantially among different environmental matrices (e.g., river water vs. tailings pond water), indicating that matrix effects play a critical role in influencing analytical outcomes. This variability has important implications for environmental monitoring, as differences in analytical selectivity and matrix interference may lead to inconsistent concentration estimates across studies. These variations highlight the importance of accurate analytical characterization, as they directly determine the feasibility and efficiency of subsequent remediation strategies.

For soil analysis, which represents a complex matrix, GC-MS is a widely used and practical option for determining total NAs and broad compositional profiles, offering good sensitivity, reliability, and operational simplicity (Table 2) (Gheorghe et al., 2025). When detailed molecular characterization is required, higher-resolution techniques such as HPLC-HRMS or GC×GC-TOF/MS are preferred, although they require more advanced instrumentation and expertise. The selection of analytical methods should be aligned with the objectives of the study. For example, total NAs burden can be assessed to evaluate overall contamination, whereas source identification and transformation analysis require careful consideration of soil matrix effects. Appropriate quality control measures, including the use of internal standards and effective sample cleanup procedures, are essential to ensure data reliability.

Overall, no single analytical method is universally optimal. Low-resolution techniques (e.g., FTIR, TAN) are suitable for rapid screening but may overestimate concentrations due to limited selectivity. In contrast, high-resolution methods (e.g., HPLC-HRMS, GC×GC-TOF/MS) offer greater specificity and structural insight, making them more appropriate for detailed characterization, albeit with higher complexity and cost. Importantly, matrix effects, especially in soil systems, can significantly influence analytical performance. Therefore, method selection should be guided by the study objective, sample matrix, and required level of chemical detail.

Table 1 compares the analytical techniques of NAs in different samples.

| **Source of NAs** | **sampling time** | **Test method** | **Concentration (mg L$^{-1}$)** | **Reference** |
|---|---|---|---|---|
| Syncrude West In Pit | 2009 | FTIR<br>HPLC-TOF/MS | 25.5<br>20.7 | (Lu et al., 2013) |
| Suncor South Tailings Pond | 2009 | FTIR<br>HPLC-TOF/MS | 11.0<br>12.9 | |
| Albian External Tailings Facility Pond | 2009 | FTIR<br>HPLC-TOF/MS | 8.3<br>6.8 | |
| Athabasca River, u/s from oil sands | 2011 | GC-MS | 0.17 | (Ross et al., 2012) |

|  |  |  |  |  |
|---|---|---|---|---|
|  |  | HPLC-TOF/MS | 0.00491 |  |
| Athabasca River, d/s from oil sands | 2011 | GC-MS | 0.1 |  |
|  |  | HPLC-TOF/MS | 0.016 |  |
| Steepbank River | 2011 | GC-MS | 0.26 |  |
|  |  | HPLC-TOF/MS | 0.00582 |  |
| Mclean Creek | 2011 | GC-MS | 7.94 |  |
|  |  | HPLC-TOF/MS | 0.0807 |  |
| Johnson Lake | 2011 | GC-MS | 0.22 |  |
|  |  | HPLC-TOF/MS | 0.0274 |  |
| Syncrude West in Pit | 2009 | GC-MS | 36 | (Grewer et al., 2010) |
|  |  | FTIR | 60 |  |
| Syncrude Demo Pond (Big Pit) | 2009 | GC-MS | 5.9 |  |
|  |  | FTIR | 14 |  |
| Suncor Pond 2/3 | 2009 | GC-MS | 47 |  |
|  |  | FTIR | 63 |  |
| Albian External Tailings Facility Pond | 2009 | GC-MS | 18 |  |
|  |  | FTIR | 35 |  |
| Athabasca River, Fort McMurray u/s from oil sands | 2009 | GC-MS | <0.03 |  |
|  |  | FTIR | 0.08 |  |
| Athabasca River, 30 m u/s from oil sands | 2007 | GC-MS | <0.01 | (Scott et al., 2008a) |
|  |  | FTIR | 0.29±0.08 |  |
| Athabasca River, d/s from oil sands | 2007 | GC-MS | <0.01 |  |
|  |  | FTIR | 0.26 |  |
| Consolidated tailings (CT)water | 2007 | GC-MS | 4.9 |  |
|  |  | FTIR | 18 |  |
| Tailings water | 2004 | GC-MS | 4 |  |
|  |  | FTIR | 17 |  |
| Tailings water | 2007 | GC-MS | 12 |  |
|  |  | FTIR | 34 |  |

Table 2 The detection limits of different test methods were compared.

| **Test method** | **Limit of detection** | **Reference** |
|---|---|---|
| FTIR | 1 mg L$^{-1}$ | (Clemente et al., 2005) |
| HPLC | 5 mg L$^{-1}$ | (Yen et al., 2004) |
| ESI-MS | 0.01 mg L$^{-1}$ | (Sakin et al., 2011) |
| GC-MS | 0.01 mg L$^{-1}$ | (Scott et al., 2008a) |

## 3. Environmental behavior of NAs in soil

During the petroleum exploration, extraction, transportation and processing, NAs utilize petroleum as a carrier and has a crude oil leak and oil spill, accumulation of oily residues, sludge and waste, irrigation with oily effluents, sedimentation of oily particles, chemical contamination etc. (Zan et al., 2019; Hoang et al., 2021) (Figure 3(a)), leading to long-term and potentially irreversible impacts on soil ecosystems. Once introduced into soil, the environmental behavior of NAs is strongly governed by their chemical structure. Specifically, NAs with lower molecular weight and higher polarity tend to be more mobile, undergoing transport through processes such as dissolution, diffusion, and leaching. In contrast, higher molecular weight and more hydrophobic NAs exhibit stronger sorption to soil organic matter and mineral surfaces, resulting in reduced mobility but greater persistence. Structural features such as carbon number, degree of branching, and cyclicity also influence their susceptibility to transformation. For example, simpler and less sterically hindered NAs are more readily biodegraded, whereas more complex and highly branched structures tend to resist microbial degradation. In addition, acid–base properties and redox reactivity further control their speciation and toxicity in soil environments. NAs can interact with soil colloids through adsorption, be taken up and transformed by plants and microorganisms, or enter the food chain, where their effects may be attenuated or amplified. Environmental factors such as pH, temperature, salinity, oxygen availability, and microbial community composition further modulate these processes (Kannel et al., 2012), as summarized in Figure 3(b).

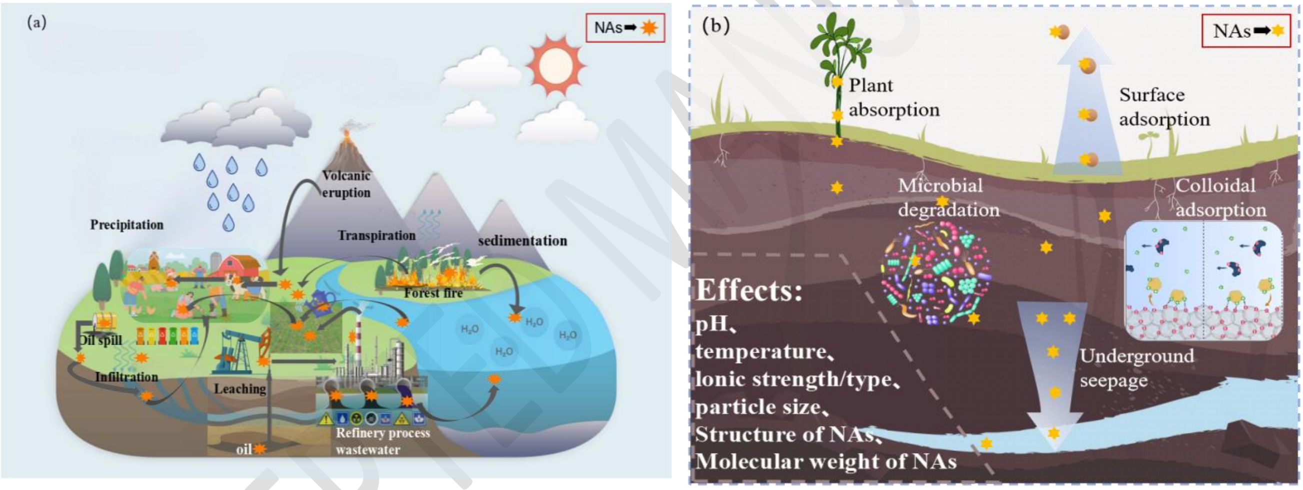

Figure 3 Pollution sources and environmental behavior of NAs. (a) pollution sources; (b) environmental behavior.

### 3.1 Distribution of NAs in soil

NAs are mostly found in the surface soil layers 0-20 cm. Contaminants that become adsorbed to soil particles or retained in capillary pores can only migrate very little and thus extremely difficult to control. In contrast, dissolved or separate NAs that are retained in non-capillary pores have high mobility and pose a risk for pollution (Gheorge et al., 2025). NAs predominantly occur at Athabasca in Canada where there are large quantities of oil sands. Other occurrences include Orinoco in Venezuela, California, Utah, and Wyoming in the United States, Siberia in Russia, as well as other oilfields in China e.g. Tarim, Qaidam, and Changqing. According to reports, NAs is severely polluting oil refineries, chemical plants, and gas station in the U.S. and U.K. The Netherlands has experienced more than 100 000 oil pollution episodes, and the soil in these areas has high concentrations of NAs (Gheorghe et al., 2025). Huang retrieved 55 soil samples from several Chinese oilfields, including Karamay, Korla, Daqing and Shengli in Xinjiang. The concentrations of NAs in contaminated soil are 2.3-132.9 mg $kg^{-1}$, which is over ten times higher than the PAHs at the same sampling locations (Jie et al., 2015). The quantity of oil contaminated soil in China, a significant oil producer and consumer of the world, has reached nearly 100,000 tons since 1978. This oil-contaminated soil issue in China affects an estimated area of 80 million $m^2$ of land. Soil contaminated with NAs in China is estimated to amount to 100 million tons (Jie et al., 2015; Aguelmous et al., 2019).

### 3.2 Adsorption/desorption of NAs in soil

Adsorption–desorption processes play a crucial role in controlling the mobility, transformation, and bioavailability of NAs in soil environments. NAs exhibit selective adsorption behavior, with components in the C13–C17 carbon number range showing a higher affinity for soil particles. Notably, this carbon number range also corresponds to a transition in biodegradability, as NAs with more than 13 carbon atoms tend to degrade more slowly. The combined effect of stronger adsorption and reduced biodegradation can enhance the persistence of these compounds in soil systems by limiting their mobility and microbial accessibility. Research shows that after adsorption for more than 30 days, the concentrations of eight typical NAs decrease significantly in soil, with more pronounced effects observed for $Z = 0$, $Z = -12$, and $Z = -14$ (Medeiros et al., 2023). In addition, organic-rich soils exhibit greater adsorption capacity (Janfada et al., 2006).

Soil adsorption capacity and organic matter content usually correlate linearly and strongly, with maximum adsorption sites predominantly located in the aggregates with a regular arrangement of hydrophobic interaction and hydrogen bonds. Studies on the adsorption of NAs using syllites reveal that hydrophobic actions, hydrogen bonds and π-π interactions are involved (Medeiros et al., 2023). Carbon and petcoke were found to remove a substantial quantity of dissolved NAs from Oil Sands Process-Affected Water (OSPW), with efficacy being a function of petcoke content, pH, and temperature (Niasar et al., 2016). As a result, the efficiency of adsorption through hydrophobic interaction, hydrogen bonding, π-π interaction, acid-base interaction and functional groups characteristics in respect of pH and temperature (Figure 4), depends on both the chemical structure of NAs and organic matter content of soil.

The adsorption model for NAs generally fits the Freundlich isotherm. The Langmuir model is also used for describing adsorption of NAs on soil (Xiang et al., 2019). Nonetheless, linear isotherms rather than Langmuir or Freundlich models best represent NAs in certain studies (Peng et al., 2002). Adsorption behavior of NAs under different conditions or of NAs of different changes (anions, cations and zwitterionic ions) with soil components is not defined by these classical models and may therefore miss the accurate adsorption mechanism of NAs in soil. Developing a new adsorption model may be needed to promote accurate prediction of NAs adsorption behaviour in soil, which may effectively depict NAs adsorption under various influencing factors.

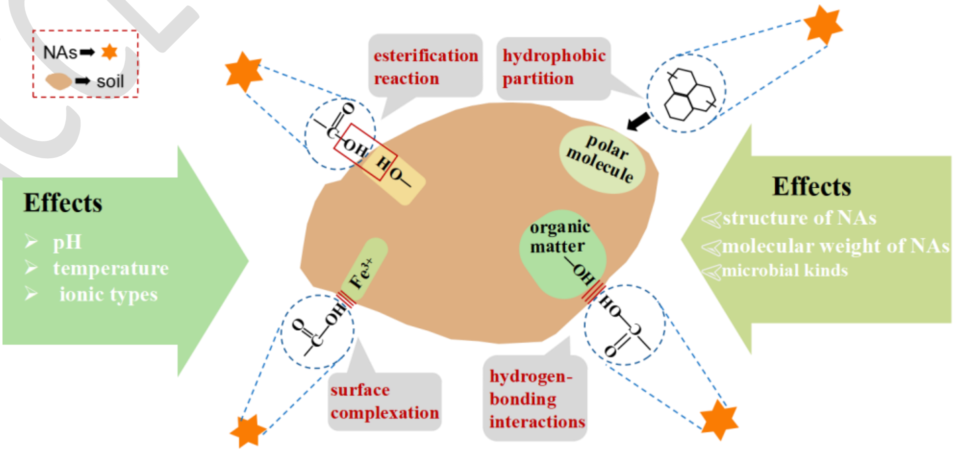

Figure 4 Adsorption mechanism of NAs in soil

### 3.3 Volatilization and percolation of NAs

Because of their viscous character, NAs are not easily volatilized and most of them can be absorbed in the soil. Nonetheless, soil particles can be transported alongside the still retained lower molecular-weight NAs. Under certain rainfall and irrigation leaching conditions, residual soil oil pollutants may release and desorb, thereby stimulating the movement of pollutants towards the saturation zone. When oil pollutants move forward to the capillary zone due to infiltration or leaching, the gravity and capillary forces will cause vertical as well as lateral migration. This allows a rapid infiltration. The pollution interface is generated in capillary zone by lateral migration and expansion (Wang et al., 2026). A portion of the oil pollutants goes to the saturated zone and pollutes groundwater while others remain at the capillary zone. Larger oil pollutants in the vadose and capillary regions get washed down and contaminate the underground water sources with rains (Schroth et al., 1998).

## 4. Remediation of NAs in soil

NAs are considered a new type of pollutant and require a variety of remediation methods ranging from physical, chemical and biological (Zhang et al. 2024; Woo et al. 2009). The cost of the geochemical remediation is cheap but residual toxicity, climate and productivity impact are major limitations. Moreover, physical remediation (heat treatment, isolation, concentration and drying and stripping) mainly achieves treatment through pollutant migration. In addition, it is expensive in cost. Also, it may cause secondary pollution. As a result, their application is limited. In chemical remediation (solvent extraction, surfactant leaching, chemical oxidation and photocatalysis), the use of oxidants to achieve the degradation of NAs into harmless substances is a widely employed technology (Xu et al, 2011). Notable challenges have plagued non-degradable technologies like the complex operation of catalytic oxidation, the expensive nature of ozonation, and inefficient photodegradation. On the contrary, bioremediation which involves phytoremediation, microbial remediation and combined plant-microbial remediation is more eco-friendly. It takes in, breaks down and alters NAs through biosynergistic action and lowers its toxicity (Huang et al., 2010; Hoang et al., 2021). According to Rio et al. (2006), this technology has many advantages such as low energy consumption, high efficiency, and less secondary pollution. However, its effectiveness can be significantly compromised in extremely polluted soils where NAs concentrations exceed microbial tolerance levels. In such cases, bioremediation needs to be integrated with other remediation technologies. According to Table 1, the concentration and composition of NAs vary significantly across different environmental matrices and analytical methods, which directly influence the selection and effectiveness of remediation strategies. Therefore, remediation strategies should be selected based on site-specific conditions, particularly NAs concentration levels, compositional characteristics, and soil matrix effects as revealed by analytical assessments.

### 4.1 Photodegradation

Photocatalysis is a fast photoreaction that mainly uses photocatalysts to generate reactive oxygen species (ROS) like •OH to oxidise, which degrades pollutants (Woo et al., 2009). A study by McMartin et al. (2004) indicated that exposure to UV light has the potential to change the structure and toxicity of NAs. Titanium dioxide was used as the catalyst to study the degradation of NAs and its analogue 4-methylcyclohexanoacetic acid (Livera et al., 2018) by sunlight. The results showed that about 75% of the NAs degraded after 8 hours of light exposure when 4-methylcyclohexanoacetic acid was fully degraded. The dark control group showed no significant increase in degradation, indicating that light plays a critical role in NAs removal. Furthermore, the different components of NAs result in photodegradation at different rates and extents. NAs bearing three or fewer rings are more prone to photodegradation than those bearing more than three rings where the steric effects of spatial structure increasingly emerge as decisive factors in determining photodegradation rates

(Burdová et al., 2025) Importantly, the natural photolysis of NAs in soil is limited since high-energy radiation wavelengths penetrate only the top soil layer. Thus, photolysis cannot completely and effectively degrade NAs in soil. The future study of Fenton oxidation and other light-assisted catalytic processes may enhance photodegradation efficacy and bioavailability (Headley et al., 2004; Zeng et al., 2024).

## 4.2 Fenton oxidation

Efforts on Fenton-based remediation of petroleum pollution have focused on optimization of catalyst systems and process parameters. Much attention has not been paid to complex heterocyclic compounds (Zhu et al., 2023; Mansour et al., 2024). The Fenton mechanism is based on the $Fe^{2+}$ catalyzed formation of hydroxyl radicals •OH (Eq(1)), which are more powerful oxidants than ozone or $H_2O_2$ and can oxidize recalcitrant NAs. The efficiency of chemical reactions is affected by several factors including the dosage of the reagent, pH (optimum range of 3.0-4.0), temperature and time of contact (Neyens et al., 2003). Under conditions of optimized Fenton, Lu et al. (2010) was able to achieve 80% removal of NAs in the soil. However, the acidic conditions required for Fenton reactions may negatively impact soil health by inhibiting microbial activity and disrupting ecological functions. Organic chelators (e.g., catechol, EDTA) can help buffer the system, maintaining pH within a range of 6.0-9.0 while preserving degradation efficiency. In this context, high-efficiency electro-assisted catalytic Fenton-like reactions have been investigated for the degradation of refractory NAs (Chen, et al., 2022). The researchers developed an electrochemical/peroxymonosulfate/iron (III) (EC/PMS/Fe (III)) system for the effective degradation of NAs compounds like CHA. The existence of the electric field intensifies the redox cycling of Fe (III)/Fe (II) and activates PMS for NA degradation (Song et al., 2025). Within 30 minutes, total degradation of NAs compounds (5 mg $L^{-1}$) was achieved in the EC/PMS/Fe (III) system (Figure 5). Studies show that $\bullet OH^-$, $SO_4^{\bullet -}$, and $^1O_2$ are the main reactive oxygen species (ROS) in the EC/PMS/Fe (III) system. (Chen et al., 2022; Mora et al., 2020). The simultaneous action of the electric field and Fe (III)/Fe (II) redox cycle activates PMS Eq (2–4).

$$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+\bullet OH+OH^- \quad Eq(1)$$

$$Fe^{3+}+e^- \rightarrow Fe^{2+} \quad Eq(2)$$

$$Fe^{2+}+HSO_5^- \rightarrow Fe^{3+} + SO_4^{\bullet -}+OH^- \quad Eq(3)$$

$$Fe^{2+}+HSO_5^- \rightarrow Fe^{3+} + \bullet OH+SO_4^{2-} \quad Eq(4)$$

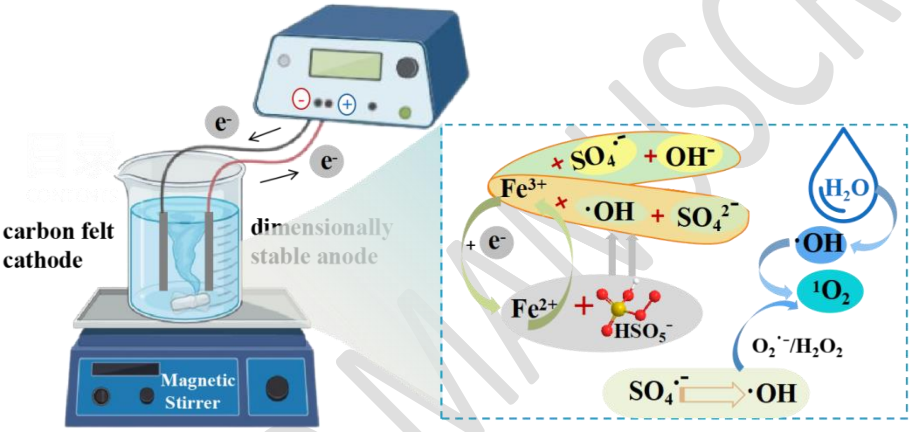

Figure 5 Mechanism diagram of the EC/PMS/Fe (III) system for NAs removal.

Photodegradation and Fenton oxidation differ in efficiency, limitations, and applicability. Fenton processes typically achieve higher and faster degradation due to strong oxidative radicals, but are constrained by acidic conditions and potential impacts on soil microorganisms. In contrast, photodegradation is more environmentally benign but limited by light penetration and is mainly effective in surface soils. From a practical perspective, Fenton oxidation is more suitable for rapid treatment of heavily contaminated soils, whereas photodegradation serves better as a supplementary approach. Therefore, remediation strategies should be selected based on contamination level, soil depth, and environmental conditions, with combined approaches offering improved effectiveness.

### 4.3 Other oxidation methods

Ozone oxidation is a novel advanced oxidation process among several techniques that are used to treat the recalcitrant NAs (Mansas et al., 2020; Kou et al., 2023). Ozone is a strong oxidant with fast reaction rates. Upon being infused into water, ozone generates two powerful free radicals, $HO_2$• and OH•. These species have been effectively used for organic wastewater pollution. However, they have not been used for soil remediation (Ye et al., 2021). In oil sands tailings wastewater having 59 mg $L^{-1}$ NAs, the degradation rate of NAs was about 70% with ozone treatment, while 96.6% was reached after 130 min (Scott et al. 2008b). The GC/MS analysis demonstrated a decrease in the ratio of high molecular weight NAs components. The overall ozone oxidation has been proved better than the biodegradation in reducing concentration of high molecular weight alkyl branched NAs, which causes increase in biodegradation to produce more volatile intermediates Kannel et al. (2012) However, anions compete with free radicals for catalytic adsorption sites, which could give rise to new pollutants and lower the efficacy of ozone oxidation.

In addition, studies show that ozonation can effectively reduce high molecular weight alkyl branched NAs so that biodegradation is expedited to form less stable intermediates (Kannel et al., 2012). However, in the presence of anions, the efficiency of ozonation may reduce as anions compete with free radicals to occupy free radical adsorption sites on the surface of the catalyst. The above may lead to the formation of new pollutants. Recent studies have examined the removal of NAs with ozone-activated persulfate (How et al., 2023). Significantly 2:1 ozone/PMS ratio treatment of model adamantane NA compound (1-adamantane carboxylic acid; ACA) removed 85% of the compound after 45 seconds of reaction time. The role of hydroxyl radicals and sulfate radicals is crucial in the removal of ACA. The role of ozone, however, is not much. ACA decomposition pathways are primarily hydroxylation, carboxylation, and polymerization under ozone/PMS conditions. The ozone molecules and the radicals •OH and $SO_4^{\bullet-}$ produced from the ozone/PMS process follow the equations below (Eqs. 5-10) (Mao et al., 2020; Yang et al., 2015).

$$SO_5^{-}+O_3 \rightarrow SO_8^{2-} \qquad k=(2.12\pm0.03)\times10^{4}\ M^{-1}\ s^{-1} \qquad \text{Eq(5)}$$

$$SO_8^{2-} \rightarrow SO_5^{\bullet-}+O_3^{\bullet-} \qquad \text{Eq(6)}$$

$$SO_5^{\bullet-}+O_3 \rightarrow SO_4^{\bullet-}+2O_2 \qquad k=1.6\times10^{5}\ M^{-1}\ s^{-1} \qquad \text{Eq(7)}$$

$$SO_5^{\bullet-}+SO_5^{\bullet-} \rightarrow 2SO_4^{\bullet-}+O_2 \qquad k=2.1\ \times10^{8}\ M^{-1}\ s^{-1} \qquad \text{Eq(8)}$$

$$O_3^{\bullet-} \rightarrow O^{\bullet-}+O_2 \qquad \text{Eq(9)}$$

$$O^{\bullet-}+H_2O \rightarrow \bullet OH+OH \qquad \text{Eq(10)}$$

The method of using microwave irradiation technology for the degradation of NAs is based on the interaction of microwave and radiation, and consequently, with the ionization or excitation of activated atoms and molecules. It leads to physical and chemical reaction of the NAs and other organic refractory material for the degradation process. In the investigation performed by Huang et al. (2006), microwave irradiation was used for degrading NAs under optimal reaction conditions, which were constant reaction pressure of 0.11 MPa, the volume ratio of reaction solvent to crude oil of 0.23:1, irradiation power of 375 W and irradiation time of 5 minutes. Following the reaction time of 25 minutes, the NAs content of the crude oil reduced greatly from 0.6300 to 0.0478 mg $g^{-1}$ (KOH) which shows 92.4% removal efficiency. Furthermore, 99.3% of crude oil was recovered in the experimental assessment. Using microwave irradiation technology for the treatment of wastewater has many advantages such as high removal rate, low cost and less secondary pollution. Nonetheless, the use of this on a larger scale faces challenges which are due to some complexities and limitations (Niasar et al., 2018).

### 4.4 Phytoremediation

Phytoremediation refers to the use of plants to absorb, change, and detoxify environmental pollutants (Jia et al., 2023). Mechanisms of phytoremediation include volatilization, plant fixation, plant extraction, and plant degradation. Volatilization is a process that leads to the upward movement of pollutants that are absorbed by the roots of plants. Thus these pollutants are released in the atmosphere through transpiration. Plant fixation is when plants tightly bind pollutants to soil aggregates; it prevents non-availability and dissipation to the environments (Rong et al., 2021; Yousaf et al., 2022). In the plant extraction a plant takes up a pollutant by its roots which is then sequestered in plant tissue and converted into a non-toxic intermediates through the process of lignification. This type of plant degradation takes place through the related enzymes and root secretions which plant roots release, as well as, the plants and rhizosphere microbe synergism (Hoang et al., 2021).

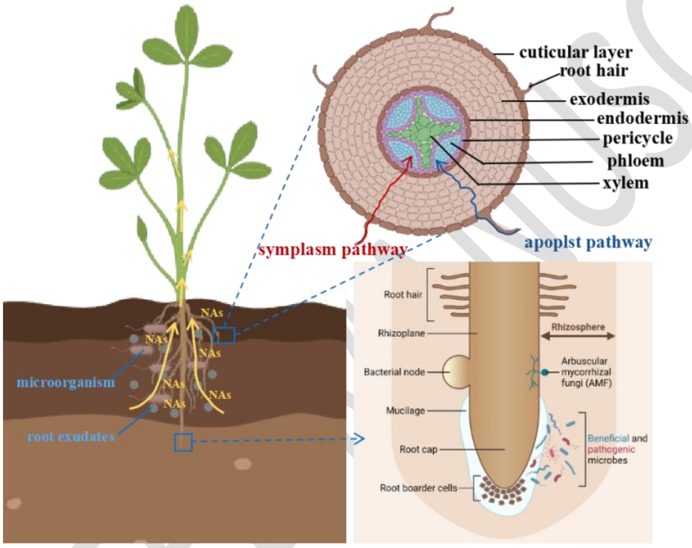

Figure 6 Pathways of uptake and transport of NAs by plants

Usually, the plant absorption of petroleum pollutants takes place through two pathways, as shown in Figure 6. Accordingly, the symplastic pathway refers to the movement of pollutants through the desmotubules into the cytoplasms of cells. On the other hand, the apoplastic pathway refers to the movement of pollutants into the cell walls, cell spaces, and duct cavities. Research suggests that organic pollutants first adsorb on the outer surface of the root cell membranes (exocytosome) and subsequently diffuse inside the root moving through the hydrophobic Casparian strip into the endodermis and then into the xylem vessels for further transport by the plant (Schreiber 2010). The physical and chemical characteristics of NAs (water solubility, molecular weight, vapor pressure), environmental characteristics (temperature, pH, organic matter, soil water content) and attributes of plant species (root types, enzyme types) are mainly the factors governing phytoremediation (Li et al., 2017). In addition, when a plant is under stress during growth an inorganic ion or an organic compound (like organic and amino acids) is secreted which activates insoluble substances in the soil. It also provides energy for the rhizosphere microorganisms. Furthermore, it changes the solubility and migration of toxic substances by modifying pH and REDOX condition. When dealing with NAs phytoremediation, it is crucial to take into account the adsorption and desorption of NAs in the soil and work along with other treatments for an enhanced NAs degradation and removal from the soil.

### 4.5 Microbial Remediation

Microbial remediation is a method where microbes use NAs as a carbon source for growth and respiration, and, thus, decompose NAs into $CO_2$, $H_2O$ or low-toxicity organic matter, thanks to various REDOX enzymes and release energy to supply normal metabolic functions (Wang et al., 2017; Li et al 2025b). Microorganisms that can survive at a high concentration of NAs and use NAs as their sole source of carbon for degradation include *Nocardia, Burkholderia, Pseudomonas, Comamonas*, and Bacillus, as well as Mycobacterium, Acinetobacter and Arthrobacter. Other bacteria include Flavobacteria bacteria and methanogens. Mainly aerobic microorganisms like Pseudomonas, Alcaligenes and Acinetobacter are involved in the NAs degradation (Clothier et al., 2016; Zan et al., 2022; Arslan et al., 2022). The microbial remediation process which consists of various factors like temperature, pH, dissolved oxygen and phosphate affect the microbial remediation process. Temperature is the dominating factor which influence the rate of any reaction as temperature levels affect the activity of the enzyme system. The temperature level controls or restrict the microbial NAs degradation within a specific range of temperature. molecular weight is a key factor influencing NA biodegradability. Low-molecular-weight NAs are generally more readily degraded, whereas NAs with more than 13 carbon atoms degrade more slowly, and those exceeding 22 carbon atoms are considered highly recalcitrant (Zan et al., 2022). This further supports the role of molecular structure in controlling the persistence of NAs in soil. Molecular weight is a key factor influencing NAs biodegradability. Low-molecular-weight NAs are generally more readily degraded, whereas NAs with more than 13 carbon atoms degrade more slowly, and those exceeding 22 carbon atoms are considered highly recalcitrant (Zan et al., 2022). This further supports the role of molecular structure in controlling the persistence of NAs in soil. The biodegradation performance is also directly affected by NAs chemical structure. NAs that have extensive branched alkyl and polycyclic structures will be sterically hindered from degrading resulting in the accumulation of persistent NAs in the environment. The arrangement of the alkyl and carboxyl groups is essential. Cis-isomers are generally more resistant to microbial degradation as they participate in hydrogen bonding with the molecules. One example is that the trans-isomer of 4-methylcyclohexanic acid (MCHA) biodegrades three times faster than the corresponding cis-isomer (Li et al. 2025a; Chauhan 2025).

The degradation pathways of NAs include processes like β-oxidation (Quesnel et al., 2011), α and β co-oxidation, and aromatization (Johnson et al., 2011). As stated by Johnson et al. (2012) under aerobic conditions, NAs mainly get degraded from β-oxidation. Special or refractory NAs, on the other hand, may require α and β co-oxidation or aromatization. For example, as shown in Figure 7(a), Alcaligenes PHY12 initiates degradation by oxidizing even C-atom side chains into odd C-atom side chains via alpha oxidation followed by beta oxidation (Rontani et al., 1992). Additionally, Taylo′s research (Reis et al., 2023) revealed *Alcaligenes* sp. The microorganism strain w1 deteriorates the cyclohexanecarboxylic acid (CHCA) by cyclohexene benzoylation which gives the intermediate p-hydroxybenzoic acid. However, side chain substitutions and adjacent ring substitution that is not possible, as shown in Figure 7(b). The second breakdown pathway of CHCA by *Pseudomonas putida*, which results in the formation of hydroxybenzoic acid, is another pathway designated as aromatization (Figure 7(c)). In this pathway, the alicyclic ring experiences an attack, followed by para-hydroxylation and subsequent dehydrogenation of the molecule to form ketones (Gunawan et al., 2014).

The anaerobic microorganisms might need other electron acceptors like nitrates, nitrites, or sulfates to oxidize the organic compounds (Ghattas et al., 2017). However, under strict anaerobic conditions, some methanogens can use acetic acid produced by β oxidation of NAs to produce methane. Using cyclohexylpropionic acid as an example, its biodegradation pathway is as follows (Eqs. 11–13):

$$C_6H_{11}CH_2CH_2COOH+H_2O \rightarrow C_6H_{11}COOH+CH_3COOH+H_2 \quad Eq(11)$$

$$CH_3COOH \rightarrow CH_4+CO_2 \quad Eq(12)$$

$$CO_2+4H_2 \rightarrow CH_4+2H_2O \quad Eq(13)$$

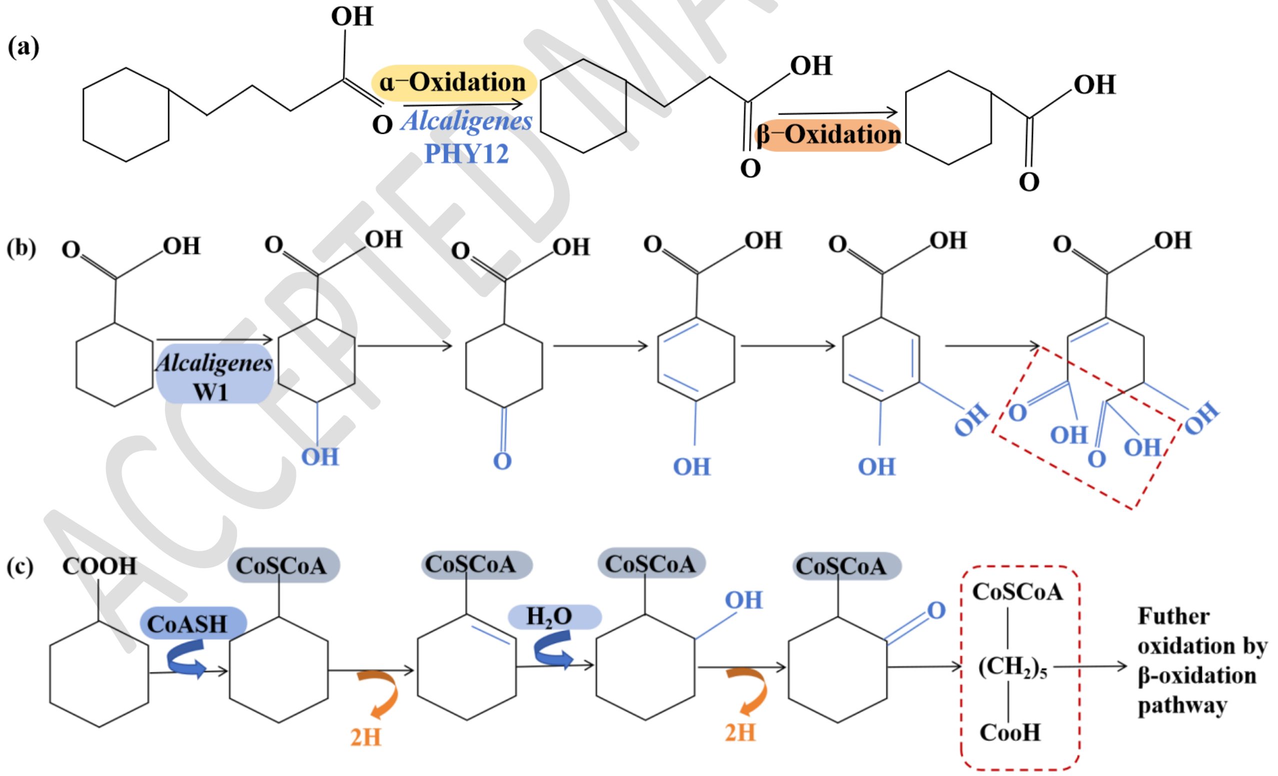

Figure 7 Aerobic degradation pathway of NAs. (a) *Alcaligenes* PHY12 degrades cyclohexanebutyric acid ; (b) Degradation of CHCA by *Alcaligenes* W1; (c) Degradation of CHCA by *Pseudomonas.* (Gunawan et al., 2014; Blakley et al., 1982).

## 4.6 Combined plant-microbial remediation

Plant-microbial joint remediation refers to an approach to soil remediation involving the use of microorganisms in the rhizosphere of plants which can degrade organic pollutants and reduce or eliminate their biological toxicity in order to carry out soil remediation. In order to stimulate soil components that are, in essence, insoluble and serve as a source of energy for rhizosphere microorganisms, Plant roots secrete not only inorganic ions but also organic compounds like amino acids, organic acids, sugars, vitamins, nucleoside, etc. Apart from these, there are also many allelopathic substances that are produced by the roots and includes flavonoids and phenolic acid (Liu et al., 2009). The fast-growing microorganisms facilitate degradation of NAs and favourable environment for plant growth (McMartin et al., 2004). Bacteria in the rhizosphere first ameliorate the NAs. Gradually, with increased adsorption and transpiration, NAs migrate from the root region to the aerial parts. Finally, the plant absorbs them, which are metabolized, volatilized, or accumulated (Arslan et al., 2022). Microorganisms with strong capabilities of NAs degradation were isolated from the rhizosphere of Alberta paper birch and other plants. After a culture period of ten days, NAs concentrations were reduced from 135 mg $L^{-1}$ to 10 mg $L^{-1}$, resulting in significant accumulation of naphthenate ions on the cell membrane. The microbial biomass increased from $2\times10^4$ $mL^{-1}$ to $2\times10^6$ $mL^{-1}$ on the second day. Study indicates that a diverse plant rhizosphere bacteria community is essential for efficient degradation of NAs and reduction of toxicity (Li et al., 2025b). Additionally, the efficacy of the plant-microorganism collaborative effort to degrade organic pollutants is higher than that of a single microorganism (Xie et al., 2018). Xu et al. (2014) used the *Kocuria* sp. Using the P10 strain of Burkella and ryegrass to clean up soil polluted with PAHs. Combined techniques allowed for an overall better performance than individual microbial and phytoremediation strategies, thus enhancing PAH removal rates, and improvement of the soil microbial community diversity and structure. According to Liu et al. (2009), plant-microorganism combinations achieved a 30% increase in degradation before 30 days in comparison to single treatments. Additionally, root exudates note the solubility and mobility of nutrients and pollutants in the rhizosphere by changing pH, the REDOX situation, chelating and lowering actions which control plant pollutant uptake and utilization. It plays a key role in mitigating and overcoming stresses.

## 5. Summary and Future Research Directions

This review synthesizes the current understanding of NAs in soil systems, highlighting critical knowledge gaps in their analysis, environmental behavior, and remediation methods. Addressing the persistent challenge of soil NAs contamination demands a paradigm shift from generic approaches to an integrated, trans-scale (molecular → microdomain → field) and interdisciplinary (chemistry → ecology → engineering → policy) framework. The following is a targeted research agenda to drive innovation:

### 5.1 Analytical Foundations: Toward Soil-Specific Standardization and Predictive Analytics

Although GC-MS is feasible for first screening in complicated soil matrices, insights at molecular levels require advanced techniques like HPLC-HRMS and GC×GC-TOF/MS. The highest priority should be the development of standardized protocols for soil specifically: (i) harmonized extraction methods for free/bound/complexed NAs, with matrix interference removal (e.g., SOM dispersion/mineral release); and ii) soil-relevant internal standards and calibration curves for congener‒specific quantification. In addition to standardization, research should focus on linking high-resolution analytical data with algorithms of choice. For instance, Random Forest can utilize extracted spectral features (e.g., peak intensities, heteroatom class distributions, and carbon numbers) to classify NAs congeners. Meanwhile, Convolutional Neural Networks (CNNs) can directly process raw, high-dimensional mass spectra or 2D-FTIR maps as images to recognize complex molecular patterns and predict bioavailability based on soil properties. This shift toward predictive modeling offers a robust alternative to descriptive fingerprinting.

### 5.2 Environmental Fate: Mechanistic Modeling Across Scales

The adsorption-desorption processes at the soil-water interface are a key but poorly quantified control on the mobility and bioavailability of NAs. Future research should focus on (i) microdomain-scale mechanisms, which include using synchrotron-based X-ray absorption spectroscopy and microfluidic devices to dissect NAs-SOM-mineral ternary interactions and aggregate-scale migration, (ii) trans-scale modeling through process-based models (e.g. HYDRUS-1D)-molecular dynamics coupling for predictions of NAs transport under climate change (e.g. alteration of precipitation and temperature rise) and (iii) soil-groundwater, which involves the quantification of NAs leaching thresholds and the modelling development of linked soil-groundwater models to predict the risk of cross-media contamination. These developments will provide key tools to assess risk accurately.

### 5.3 Remediation Strategies: Precision Engineering and Lab-to-Field Translation

The joint use of plants and microbes for remediation is the most promising sustainable option; nevertheless, current applications are non-specific. We propose that future innovations could focus on: (i) precision bioremediation such as designing congener-specific plant-microbe consortia based on high-resolution NAs profiling (e.g. aromatic NAs → Mycobacterium + Miscanthus; ox-NAs → Bacillus + Phragmites); (ii) synergistic technology integration such as rhizosphere engineering with nanocatalysts (e.g. $TiO_2$ nanoparticles for photodegradation enhancement) or microwave activation (for enhancing bound NAs bioavailability); and (iii) field scale validation like long-term trials to optimise parameters (plant density, microbial inoculant dosage) and evaluate life-cycle sustainability (environmental, economic, social). The gap from lab to field on the application of engineered organisms (e.g., Clustered Regularly Interspaced Short Palindromic Repeats （CRISPR) edited microbial with enhanced NAs degradation), and soil amendment synergy (e.g., biochar as microbial carriers).

### 5.4 Policy and Regulatory Innovation: Soil-Specific Risk Governance

At present, neither the global nor national levels have any standards for the concentration of NAs in soils. The succeeding steps should entail the establishment of soil quality criteria based on congener specific toxicity data (e.g. predicted no-effect concentration (PNEC) values for terrestrial organisms and food chain bioaccumulation thresholds), development of land-use-specific remediation targets (agricultural vs industrial soils) and integration of NAs monitoring in existing regulations regarding petroleum pollution, i.e. mandatory reporting by oil extraction/refining facilities. Further, the smart monitoring) tools (eg biosensors and hyperspectral imaging) for real-time tracking of NAs will improve compliance.

### 5.5 Concluding Synthesis: Toward a Soil-Centric Paradigm

To tackle soil NAs pollution, an ongoing multi-disciplinary effort is essential to bring together innovative analytics, mechanistic fate modelling, engineered remediation technologies and policy governance. Through trans-scaling and inter-disciplinarity, the fragmentation of research can be turned into integrated solutions to expedite restoration of NAs-impacted soils, protecting ecosystem and human health in the long run.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Data availability

Data will be made available on request.

## References

Aguelmous, A., Elfels, L., Souabi, S., Zamama, M., & Hafidi, M. (2019). The fate of total petroleum hydrocarbons during oily sludge composting: a critical review. Reviews in Environmental Science and Biotechnology, 18(3), 473-493. https://doi.org/10.1007/s11157-019-09509-w

Arslan, M., Müller, J.A., & El-Din, M.G. (2022). Aerobic naphthenic acid-degrading bacteria in petroleum-coke improve oil sands process water remediation in biofilters: DNA-stable isotope probing reveals methylotrophy in Schmutzdecke. Science of the Total Environment, 815, 151961. https://doi.org/10.1016/j.scitotenv.2021.151961

Barros, E.V., Filgueiras, P.R., Lacerda, V., Rodgers, R.P., & Romão, W. (2022). Characterization of naphthenic acids in crude oil samples-A literature review. Fuel, 319, 123775. https://doi.org/10.1016/j.fuel.2022.123775

Bartlett, A.J., Frank, R.A., Gillis, P.L., Parrott, J.L., Marentette, J.R., McInnis, R., & Shang, D. (2017). Toxicity of naphthenic acids to invertebrates: Extracts from oil sands process-affected water versus commercial mixtures. Environmental pollution, 227, 271-279. https://doi.org/10.1016/j.envpol.2017.04.056

Blakley, E.R., & Papish, B. (1982). The metabolism of cyclohexanecarboxylic acid and 3-cyclohexenecarboxylic acid by Pseudomonas putida. Canadian Journal of Microbiology, 28, 1324-1329. https://doi.org/10.1139/m82-198

Bowman, D.T., Warren, L.A., & Slater, G.F. (2020). Isomer-specific monitoring of naphthenic acids at an oil sands pit lake by comprehensive two-dimensional gas chromatography-mass spectrometry. Science of the Total Environment, 746, 140985. https://doi.org/10.1016/scitotenv.2020.140985

Burdová, H., Nebeská, D.P., Marková, K., Říha, J., Trubač, J., Kříženecká, S., & Trögl, J. (2025). Rhizodegradation of diesel and PAH contaminated soils with miscanthus× giganteus: soil, plants, microbes and pollutants interactions after two seasons. Journal of Environmental Management, 381, 125208. https://doi.org/10.1016/j.jenvman.2025.125208

Cancelli, A.M., & Gobas, F.A.P.C. (2022). Treatment of naphthenic acids in oil sands process-affected waters with a surface flow treatment wetland: mass removal, half-life, and toxicity-reduction. Environmental Research, 213, 113755. https://doi.org/10.1016/j.scitotenv.2023.16963

Chauhan, P., Kanaujia, P.K. & Suman, S.K. (2025). Bioremediation of naphthenic acid by bacillus subtilis: degradation kinetics and pathway elucidation. Environmental Pollution, 376, 126383. https://doi.org/10.1016/j.envpol.2025.126383

Chen, Y., Long, X., Huang, R., Zhang, I.Y., Yao, G., Lai, B., & Xiong, Z. (2022). Highly efficient electro-cocatalytic Fenton-like reactions for the degradation of recalcitrant naphthenic acids: Exploring reaction mechanisms and environmental implications. Chemical Engineering Journal, 450(P4), 138331. https://doi.org/10.1016/j.cej.2022.138331

Chen, Y., Wang, Y., Headley, J.V., & Huang, R. (2024). Sample preparation, analytical characterization, monitoring, risk assessment and treatment of naphthenic acids in industrial wastewater and surrounding water impacted by unconventional petroleum production. Science of the Total Environment, 913, 169636. https://doi.org/10.1016/j.scitotenv.2023.169636

Clemente, J.S., & Fedorak, P.M. (2005). A review of the occurrence, analyses, toxicity, and biodegradation of naphthenic acids. Chemosphere, 60(5), 585-600. https://doi.org/10.1016/j.chemosphere.2005.02.065

Clothier, L.N., & Gieg, L.M. (2016). Anaerobic biodegradation of surrogate naphthenic acids. Water Research, 90, 156-166. https://doi.org/10.1016/j.watres.2015.12.019

Frank, R., Fischer, K., Kavanagh, R., Burnison, B.K., Arsenault, G., & Headley, J.V. (2009). Effect of carboxylic acid content on the acute toxicity of oil sands naphthenic acids. Environmental Science & Technology, 43(2), 266-271. https://doi.org/10.1021/es8021057.

Ghattas, A.K., Fischer, F., Wick, A., & Ternes, T.A. (2017). Anaerobic biodegradation of (emerging) organic contaminants in the aquatic environment. Water Research, 116, 268-295. https://doi.org/10.1016/j.watres.2017.02.001

Gheorghe, C.G., Dusescu-Vasile, C.M., Popovici, D.R., Bombos, D., Dragomir, R.E., Dima, F. M., & Vasilievici, G. (2025). Monitoring the biodegradation progress of naphthenic acids in the presence of spirulina platensis algae. Toxics, 13(5), 368. https://doi.org/10.3390/toxics13050368

Grewer, D.M., Young, R.F., Whittal, R.M., & Fedorak, P.M. (2010). Naphthenic acids and other acid-extractables in water samples from Alberta: What is being measured? Science of the Total Environment, 408(23), 5997-6010. https://doi.org/10.1016/j.scitotenv.2010.08.013

Gunawan, Y., Nemati, M., Dalai, A. (2014). Biodegradation of a surrogate naphthenic acid under denitrifying conditions. Water Research, 51, 11-24. https://doi.org/10.1016/j.watres.2013.12.016

Han, X., MacKinnon, M.D., Martin, J.W. (2009). Estimating the in situ biodegradation of naphthenic acids in oil sands process waters by HPLC/HRMS. Chemosphere, 76(1), 63-70. https://doi.org/10.1016/j.chemosphere.2009.02.026

Headley, J.V., Peru, K.M., Mohamed, M.H., Frank, R.A., Martin, J.W., & Hazewinkel, R.R.O. (2013). Chemical fingerprinting of naphthenic acids and oil sands process waters-a review of analytical methods for environmental samples. Journal of Environmental Science and Health, Part A, 48(10), 1145-63. https://doi.org/10.1080/10934529.2013.776332.

Headley, John V., & McMartin, D.W. (2004). A review of the occurrence and fate of naphthenic acids in aquatic environments. Journal of Environmental Science and Health, Part A, 39(8), 1989-2010. https://doi.org/10.1081/ESE-120039370

Hoang, S.A., Lamb, D., Seshadri, B., Sarkar, B., Choppala, G., Kirkham, M.B., & Bolan, N.S. (2021). Rhizoremediation as a green technology for the remediation of petroleum hydrocarbon-contaminated soils.

Journal of Hazardous Materials, 401, 123282. https://doi.org/10.1016/j.jhazmat.2020.123282

How, Z.T., Fang, Z., Chelme-Ayala, P., Ganiyu, S.O., Zhang, X., Xu, B., Chen, C., Gamal El-Din, M. (2023). Ozone-activated peroxymonosulfate ($O_3$/PMS) process for the removal of model naphthenic acids compounds: Kinetics, reactivity, and contribution of oxidative species. Journal of Environmental Chemical Engineering, 11(3), 109935. https://doi.org/10.1016/j.jece.2023.109935

Huang, H., Zhang, S., Christie, P., Wang, S., Xie, M. (2010). Behavior of Decabromodiphenyl Ether (BDE-209) in the soil-plant system: Uptake, translocation, and metabolism in plants and dissipation in soil. Environmental Science & Technology, 44(2), 663-667. https://doi.org/10.1021/es901860r

Huang, M., Zhao, S., Li, P., & Huisingh, D. (2006). Removal of naphthenic acid by microwave. Journal of Cleaner Production, 14(8), 736-739. https://doi.org/10.1016/j.jclepro.2005.04.004

Huang, R.F., Yang, L., How, Z.T., Fang, Z., Bekele, A., & Letinski, D.J. (2021). Characterization of raw and ozonated oil sands process water utilizing atmospheric pressure gas chromatography time-of-flight mass spectrometry combined with solid phase microextractionun. Chemosphere, 266, 129017. https://doi.org/10.1016/j.chemosphere.2020.129017

Islam, M. S., Zhang, Y., McPhedran, K. N., Liu, Y., & El-Din, M.G. (2015). Granular activated carbon for simultaneous adsorption and biodegradation of toxic oil sands process-affected water organic compounds. Journal of Environmental Management, 152, 49-57. https://doi.org/10.1016/j.jenvman.2015.01.020

Janfada, A., Headley, J., Peru, K., & Barbour, S. (2006). A laboratory evaluation of the sorption of oil sands naphthenic acids on organic rich soils. Journal of Environmental Science and Health-Part A, 41(6), 985-997. https://doi.org/10.1080/10934520600620105

Jia, H., Zhang, G., Wu, Y., Dai, W., Xu, Q., Gan, S., Ju, X., Feng, Z., Li, R., & Yuan, B. (2023). Evaluation of negative effect of naphthenic acids (NAs) on physiological metabolism and polycyclic aromatic hydrocarbons adsorption of Phragmites australis. Chemosphere, 318, 137909.

https://doi.org/10.1016/j.chemosphere.2023.137909

Jie, W., Cao, X., Chai, L., Liao, J., Huang, Y., & Tang, X. (2015). Quantification and characterization of naphthenic acids in soils from oil exploration areas in China by GC/MS. Analytical Methods, 7(5), 2149-2154. https://doi.org/10.1039/c4ay02658f

Johnson, R.J., Smith, B.E., Rowland, S.J., & Whitby, C. (2013). Biodegradation of alkyl branched aromatic alkanoic naphthenic acids by *Pseudomonas putida* KT2440. International Biodeterioration and Biodegradation, 81, 3-8. https://doi.org/10.1016/j.ibiod.2011.11.008

Johnson, R.J., Smith, B.E., Sutton, P.A., McGenity, T.J., Rowland, S.J., & Whitby, C. (2011). Microbial biodegradation of aromatic alkanoic naphthenic acids is affected by the degree of alkyl side chain branching. ISME Journal, 5(3), 486-496. https://doi.org/10.1038/ismej.2010.146

Johnson, R.J., West, C.E., Swaih, A.M., Folwell, B.D., Smith, B.E., Rowland, S.J., & Whitby, C. (2012). Aerobic biotransformation of alkyl branched aromatic alkanoic naphthenic acids via two different pathways by a new isolate of Mycobacterium. Environmental Microbiology, 14(4), 872-882. https://doi.org/10.1111/j.1462-2920.2011.02649.x

Kamaluddin, M., Zwiazek, J.J. (2002). Naphthenic acids inhibit root water transport, gas exchange and leaf growth in aspen (Populus tremuloides) seedlings. Tree Physiology, 22(17), 1265-1270. https://doi.org/10.1093/treephys/22.17.1265

Kannel, P.R., Gan, T.Y. (2012). Naphthenic acids degradation and toxicity mitigation in tailings wastewater systems and aquatic environments: A review. Journal of Environmental Science and Health-Part A, 47(1), 1-21. https://doi.org/10.1080/10934529.2012.629574

Kou, Y., Jiang, J., Yang, B., Sun, H., Wang, L., Wang, Q., & Chen, C. (2023). Transformation of dissolved organic matter at a full-scale petrochemical wastewater treatment plant. Journal of Environmental Management, 329, 117021. https://doi.org/10.1016/j.jenvman.2022.117021

Li, C., Fu, L., Stafford, J., Belosevic, M., & EL-Din, MG. (2017). "The toxicity of oil sands process-affected water (OSPW): A critical review." Science of the Total Environment, 601, 1785-1802. https://doi.org/10.1016/j.scitotenv.2017.06.024

Li, J., Arslan, M., Yang, L., & El-Din, M.G. (2025a). Fate of dissolved organics in oil sands process water during long-term storage: Mechanistic insights into toxicity removal and microbial processes. Journal of Environmental Management, 380, 125050. https://doi.org/10.1016/j.jenvman.2025.125050

Li, J., Liu, S., Li, S., Song, J., Wang, Q., & Chen, C. (2025b). Naphthenic acids (NAs)-tolerant aerobic granular sludge: Removal performance, degradation mechanism, and microbial response. Journal of Environmental Management. 393, 126997. https://doi.org/10.1016/j.jenvman.2025.126997

Lisa, D.Brown., Ania, C.Ulrich. (2015). Oil sands naphthenic acids: A review of properties, measurement, and treatment. Chemosphere. 127, 276-290. https://doi.org/10.1016/j.chemosphere.2015.02.003.

Liu, J.C., Cli, Y.S., & Zhang, Y.P. (2009). Effect of plants and microorganisms on remediation of petroleum contaminated soil. Journal of Ecology & Rural Environment, 25(2),80-83. https://doi.org/10.1002/jps.20548.

Liu, W., Li, Y., Liu, F., Jiang, W., Zhang, D., & Liang, J. (2019). Visible-light-driven photocatalytic degradation of diclofenac by carbon quantum dots modified porous g-C3N4: Mechanisms, degradation pathway and DFT calculation. Water Research, 151, 8-19. https://doi.org/10.1016/j.watres.2018.11.084

Livera, D., Leshuk, T., Peru, K.M., Headley, J.V., & Gu, F. (2018). Structure-reactivity relationship of naphthenic acids in the photocatalytic degradation process. Chemosphere, 200, 180-190. https://doi.org/10.1016/j.chemosphere.2018.02.049

Lu, M., Zhang, Z., Qiao, W., Guan, Y., Xiao, M., & Peng, C. (2010). Removal of residual contaminants in petroleum-contaminated soil by Fenton-like oxidation. Journal of Hazardous Materials, 179(1-3), 604-611. https://doi.org/10.1016/j.jhazmat.2010.03.046

Lu, W., Ewanchuk, A., Perez-Estrada, L., Sego, D., & Ulrich, A. (2013). Limitation of fluorescence spectrophotometry in the measurement of naphthenic acids in oil sands process water. Journal of Environmental Science and Health-Part A, 48(4), 429-436. https://doi.org/10.1080/10934529.2013.729802

Lutnaes, B.F., Brandalm O., Sjoblom, J., & Krane, J. (2006). Archaeal C80 isoprenoid tetraacids responsible for naphthenate deposition. Organic Biomolecular Chemistry, 4(4), 616-620. https://doi.org/10.1039/B516907K.

Mansas, C., Mendret, J., Brosillon, S., & Ayral, A. (2020). Coupling catalytic ozonation and membrane separation: A review. Separation and Purification Technology, 236, 116221. https://doi.org/10.1016/j.seppur.2019.116221

Mansour, M.S., Abdel-Shafy, H.I., & Ibrahim, A.M. (2024). Petroleum wastewater: Environmental protection, treatment, and safe reuse: An overview. Journal of Environmental Management. 351, 119827. https://doi.org/10.1016/j.jenvman.2023.119827

Mao, Y., Dong, H., Liu, S., Zhang, L., & Qiang, Z. (2020). Accelerated oxidation of iopamidol by ozone/peroxymonosulfate ($O_3$/PMS) process: Kinetics, mechanism, and simultaneous reduction of iodinated disinfection by-product formation potential. Water Research, 173, 115615. https://doi.org/10.1016/j.watres.2020.115615

Mapolelo, M.M., Rodgers, R.P., Blakney, G.T., Yen, A.T., Asomaning, S., & Marshall, A.G. (2011). Characterization of naphthenic acids in crude oils and naphthenates by electrospray ionization FT-ICR mass spectrometry. International Journal of Mass Spectrometry, 300, 149-57. https://doi.org/10.1016/j.ijms.2010.06.005

McMartin, D.W., Headley, J.V., Friesen, D.A., Peru, K.M., & Gillies, J.A. (2004). Photolysis of naphthenic acids in natural surface water. Journal of Environmental Science and Health-Part A, 39(6), 1361-1383. https://doi.org/10.1081/ESE-120037839

Medeiros, D.C., Chelme-Ayala, P., & Gamal El-Din, M. (2023). Sorption and desorption of naphthenic acids on reclamation materials: Mechanisms and selectivity of naphthenic acids from oil sands process water. Chemosphere, 326, 138462. https://doi.org/10.1016/j.chemosphere.2023.138462

Merlin, M., Guigard, S.E., & Fedorak, P.M. (2007). Detecting naphthenic acids in waters by gas chromatography-mass spectrometry. Journal of Chromatography A, 1140(1-2), 225-229. https://doi.org/10.1016/j.chroma.2006.11.089

Meulen I.J.V., Headley J.V., & Mcmartin D.W. (2025). Corrigendum to "On the occurrence, behaviour, and fate of naphthenic acid fraction compound in aquatic environments". Science of Total Environment, 178383 963(000). https://doi.org/10.1016/j.scitotenv.2025.178576.

Miwa, H. (2000). High-performance liquid chromatographic determination of mono-poly and hydroxycarboxylic acids in foods and beverages as their 2-nitrophenylhydrazides. Journal of Chromatography A, 881(1-2), 365-385. https://doi.org/10.1016/S0021-9673(00)00284-3

Mora, V. C., Morelli, I. S., & Rosso, J.A. (2020). Co-treatment of an oily sludge and aged contaminated soil: permanganate oxidation followed by bioremediation. Journal of Environmental Management. 261, 110169. https://doi.org/10.1016/j.jenvman.2020.110169

Negris, L., Brandao, G. P., Flores, E. M., Vicente, M. A., & Santos, M.F. (2024). Micellar solubilization of crude oil acids in oil-in-water nanoemulsions to determine the total acid number of crude oil by potentiometric titration. Fuel, 366, 131379. https://doi.org/10.1016/j.fuel.2024.131379

Neyens, E., Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. Journal of Hazardous Materials, 98(1-3), 33-50. https://doi.org/10.1016/S0304-3894(02)00282-0

Niasar, H.S., Li, H., Kasanneni, T.V., Ray, M.B., & Xu, C.C. (2016). Surface amination of activated carbon and petroleum coke for the removal of naphthenic acids and treatment of oil sands process-affected water (OSPW). Chemical Engineering Journal, 293, 189-199. https://doi.org/10.1016/j.cej.2016.02.062

Niasar, H.S., Li, H., Das, S., Kasanneni, T.V.R., Ray, M.B., & Xu, C.C. (2018). Preparation of activated petroleum coke for removal of naphthenic acids model compounds: Box-Behnken design optimization of KOH activation process. Journal of Environmental Management, 211, 63-72. https://doi.org/10.1016/j.jenvman.2018.01.051

Oetjen, K., Giddings, C.G.S., McLaughlin, M., Nell, M., Blotevogel, J., & Helbling, D.E. (2017). Emerging analytical methods for the characterization and quantification of organic contaminants in flowback and produced water. Trends in Environmental Analytical Chemistry, 15, 12-23. https://doi.org/10.1016/j.teac.2017.07.002

Peng, J., Zhou, P., Zhou, H., Liu, W., Zhang, H., Zhou, C., Lai, L., Ao, Z., Su, S., & Lai, B. (2021). Insights into the electron-transfer mechanism of permanganate activation by graphite for enhanced oxidation of sulfamethoxazole. Environmental Science & Technology, 55(13), 9189-9198. https://doi.org/10.1021/acs.est.1c00020

Peng, J., Headley, J.V., Barbour, S.L. (2002). Adsorption of single-ring model naphthenic acids on soils. Canadian Geotechnical Journal, 39(6), 1419-1426. https://doi.org/10.1139/t02-098

Pérez-Estrada, L.A., Han, X., Drzewicz, P., Gamal, M., Fedorak, P.M., & Martin, J.W. (2011). Structure-reactivity of naphthenic acids in the ozonation process. Environmental Science & Technology, 45(17), 7431-7437. https://doi.org/10.1021/es201575h

Porto, N.A., Crucello, J., Facanali, R., Junior, I.M., Carvalho, R.M., & Hantao, L.W. (2021). Profiling naphthenic acids in produced water using hollow fiber liquid-phase microextraction combined with gas chromatography coupled to Fourier transform Orbitrap mass spectrometry. Journal of Chromatography A, 1655, 462485. https://doi.org/10.1016/j.chroma.2021.462485

Qin, R., How, Z.T., & Gamal El-Din, M. (2019). Photodegradation of naphthenic acids induced by natural photosensitizer in oil sands process water. Water Research, 164, 114913. https://doi.org/10.1016/j.watres.2019.114913

Quesnel, D.M., Bhaskar, I.M., Gieg, L.M., & Chua, G. (2011). Naphthenic acid biodegradation by the unicellular alga Dunaliella tertiolecta. Chemosphere, 84(4), 504-511. https://doi.org/10.1016/j.chemosphere.2011.03.012

Reis, P. C., Correa-Garcia, S., Tremblay, J., Beaulieu-Laliberté, A., Muench, D. G., Ahad, J. M., & Martineau, C. (2023). Microbial degradation of naphthenic acids using constructed wetland treatment systems: metabolic and genomic insights for improved bioremediation of process-affected water. FEMS Microbiology Ecology, 99(12), fiad153. https://doi.org/10.1093/femsec/fiad153

Rio, L.F., Hadwin, A.K., Pinto, L.J., MacKinnon, M.D., & Moore, M.M. (2006). Degradation of naphthenic acids by sediment micro-organisms. Journal of Applied Microbiology, 101(5), 1049-1061. https://doi.org/10.1111/j.1365-2672.2006.03005.x

Rojo, F. (2009). Degradation of alkanes by bacteria. Environmental Microbiology, 11(10): 2477-90. https://doi.org/10.1111/j.1462-2920.2009.01948.x.

Rong, L., Zheng, X., Oba, B. T., Shen, C., Wang, X., Wang, H., Luo, Q., & Sun, L. (2021). Activating soil microbial community using bacillus and rhamnolipid to remove TPH contacted soil. Chemosphere, 275, 130062. https://doi.org/10.1016/j.chemosphere.2021.130062

Rontani, J.F., Bonin, P. (1992). Utilization of n-alkyl-substituted cyclohexanes by a marine Alcaligenes. Chemosphere, 24(10), 1441-1446. https://doi.org/10.1016/0045-6535(92)90266-T

Ross, M.S., Pereira, A.D., Fennell, J., Davies, M., Johnson, J., Sliva, L., & Martin, J.W. (2012). Quantitative and qualitative analysis of naphthenic acids in natural waters surrounding the Canadian oil sands industry. Environmental Science & Technology, 46(23), 12796-12805. https://doi.org/10.1021/es303432u

Rowland, S.J., Scarlett, A.G., Jones, D., West, C.E., & Frank, R.A. (2011). Diamonds in the rough: Identification of individual naphthenic acids in oil sands process water. Environmental Science & Technology, 45(7), 3154-3159. https://doi.org/10.1021/es103721b

Sakin, M. A., Akinci, C., Duzdemir, O., & Donmez, E. (2011). Assessment of genotype x environment interaction on yield and yield components of durum wheat genotypes by multivariate analyses. African Journal Biotechnology, 10(15), 2875-2885. https://doi.org/10.5897/AJB10.2197

Scarlett, A.G., West, C.E., Jones, D., Galloway, T.S., & Rowland, S.J. (2012). Predicted toxicity of naphthenic acids present in oil sands process-affected waters to a range of environmental and human endpoints. Science of the

Total Environment, 425, 119-127. https://doi.org/10.1016/j.scitotenv.2012.02.064

Schramm, L.L., Stasiuk, E.N., & MacKinnon, M. (2010). Surfactants in athabasca oil sands slurry conditioning, flotation recovery, and tailings processes. In Surfactants. https://doi.org/10.1017/cbo9780511524844.011

Schreiber, L. (2010). Transport barriers made of cutin, suberin and associated waxes. Trends in Plant Science, 15(10), 546-553. https://doi.org/10.1016/j.tplants.2010.06.004

Schroth, M.H., Istok, J.D., Selker, J.S., Oostrom, M., & White, M.D. (1998). Multifluid flow in bedded porous media: Laboratory experiments and numerical simulations. Advances in Water Resources, 22(2), 169-183. https://doi.org/10.1016/S0309-1708(97)00043-2

Scott, A.C., MacKinnon, M.D., & Fedorak, P.M. (2005). Naphthenic acids in athabasca oil sands tailings waters are less biodegradable than commercial naphthenic acids. Environmental Science & Technology, 39(21), 8388-8394. https://doi.org/10.1021/es051003k

Scott, A.C., Young, R.F., & Fedorak, P.M. (2008a). Comparison of GC-MS and FTIR methods for quantifying naphthenic acids in water samples. Chemosphere, 73(8), 1258-1264. https://doi.org/10.1016/j.chemosphere.2008.07.024

Scott, A.C., Zubot, W., MacKinnon, M.D., Smith, D.W., & Fedorak, P.M. (2008b). Ozonation of oil sands process water removes naphthenic acids and toxicity. Chemosphere, 71(1), 156-160. https://doi.org/10.1016/j.chemosphere.2007.10.051

Song, F., Xiao, B., Li, Z., Xue, Y., Long, M., & Bai, X. (2025). Silicate chemical weathering disrupts the global patterns of phosphorus limitation. Nature communication, 16(1), 10742. https://doi.org/10.1038/s41467-025-65773-1

Sutton, P.A., Smith, B.E., & Waters, D. (2010). Rowland SJ. Identification of a novel ester obtained during isolation of $C_{80}$ (ARN) tetraprotic acids from an oilfield pipeline deposit. Energy Fuels, 24, 5579-5585. https://doi.org/10.1021/ef1008743.

Terra, L.A., Filgueiras, P.R., Pereira, R.C.L., Gomes, A.O., Vasconcelos, G.A., Tose, L.V., Castro, E.V.R., Vaz, B.G., Romão, W., & Poppi, R.J. (2017). Prediction of total acid number in distillation cuts of crude oil by ESI (-) FT-ICR MS coupled with chemometric tools. Journal of the Brazilian Chemical Society, 28(9), 1822-1829. https://doi.org/10.21577/0103-5053.20170073

Valente Roque, J., Rodrigues, M. F., M. Dufrayer, G. H., Medeiros Júnior, I., de Carvalho, R. M., da Silva Lima, G., & Vaz, B.G. (2024). Characterization and quantification of naphthenic acids in produced water by orbitrap MS and a multivariate approach. Journal of American Society for Mass Spectrometry, 35(9), 2128-2135. https://doi.org/10.1021/jasms.4c00172

Vander Meulen, I.J., Schock, D.M., Akhter, F., Mundy, L.J., Eccles, K.M., Soos, C., & Pauli, B.D. (2023). Site-specific spatiotemporal occurrence and molecular congener distributions of naphthenic acids in Athabasca oil sands wetlands of Alberta, Canada. Environmental Pollution, 333, 0269-7491. https://doi.org/10.1016/j.envpol.2023.122061

Volpe, A., Pagano, M., Mascolo, G., Grenni, P., & Rossetti, S. (2017). Biodegradation of UV-filters in marine sediments. Science of the Total Environment, 575, 448-457. https://doi.org/10.1016/j.scitotenv.2016.10.001

Wang, B.L., Cui, H., Liu, H., & Wan, Y. (2019). Derivatization for nontargeted screening of acids in oilfield refinery wastewater: identification and behaviors of recalcitrant chlorinated naphthenic acids. Environmental Science & Technology. 53, 1022-1030. https://doi.org/10.1021/acs.est.8b05310

Wang, R., Diao, P., Chen, Q., Wu, H., Xu, N., & Duan, S. (2017). Identification of novel pathways for biodegradation of bisphenol A by the green alga *Desmodesmus* sp.WR1, combined with mechanistic analysis at the transcriptome level. Chem. Eng. J. 321, 424–431. https://doi.org/10.1016/j.cej.2017.03.121

Wang, Y., Wang, S., & Jin, F. (2026). Hydro-mechanical behaviour of Nanyang expansive soil during the wetting-drying cycles. Canadian Geotechnical Journal, https://doi.org/10.1139/cgj-2025-0775

Whitby, C. (2010). Microbial naphthenic acid degradation. Advances in Applied Microbiology, 70, 93-125.

https://doi.org/10.1016/S0065-2164(10)70003-4

Wild, E., Dent, J., Thomas, G.O., & Jones, K.C. (2005). Direct observation of organic contaminant uptake, storage, and metabolism within plant roots. Environmental Science & Technology, 39(10), 3695-3702. https://doi.org/10.1021/es048136a

Woo, O.T., Chung, W.K., Wong, K.H., Chow, A.T., & Wong, P.K. (2009). Photocatalytic oxidation of polycyclic aromatic hydrocarbons: Intermediates identification and toxicity testing. Journal of Hazardous Materials, 168(2–3), 1192-1199. https://doi.org/10.1016/j.jhazmat.2009.02.170

Wu, C., De Visscher, A., & Gates, I.D. (2019). On naphthenic acids removal from crude oil and oil sands process-affected water. Fuel, 253, 1229–1246. https://doi.org/10.1016/j.fuel.2019.05.091

Xiang, L., Wang, X.D., Chen, X.H., Mo, C.H., Li, Y.W., Li, H., Cai, Q.Y., Zhou, D.M., Wong, M.H., & Li, Q.X. (2019). Sorption mechanism, kinetics, and isotherms of di-n-butyl phthalate to different soil particle-size fractions. Journal of Agricultural and Food Chemistry, 67(17), 4734-4745. https://doi.org/10.1021/acs.jafc.8b06357

Xie, W., Li, R., Li, X., Liu, P., Yang, H., Wu, T., & Zhang, Y. (2018). Different responses to soil petroleum contamination in monocultured and mixed plant systems. Ecotoxicology and Environmental Safety, 161, 763-768. https://doi.org/10.1016/j.ecoenv.2018.06.053

Xu, J., Pancras, T., & Grotenhuis, T. (2011). Chemical oxidation of cable insulating oil contaminated soil. Chemosphere, 84(2), 272-277. https://doi.org/10.1016/j.chemosphere.2011.03.044

Xu, X., Pliego, G., Alonso, C., Liu, S., Nozal, L., & Rodriguez, J.J. (2019). Reaction pathways of heat-activated persulfate oxidation of naphthenic acids in the presence and absence of dissolved oxygen in water. Chemical Engineering Journal, 370(3), 695-705. https://doi.org/10.1016/j.cej.2019.03.213

Xu, Y., Sun, G.D., Jin, J.H., Liu, Y., Luo, M., Zhong, Z.P., & Liu, Z.P. (2014). Successful bioremediation of an aged and heavily contaminated soil using a microbial/plant combination strategy. Journal of Hazardous Materials, 264, 430-438. https://doi.org/10.1016/j.jhazmat.2013.10.071

Yang, Y., Jiang, J., Lu, X., Ma, J., Liu, Y., 2015. Production of sulfate radical and hydroxyl radical by reaction of ozone with peroxymonosulfate: a novel advanced oxidation process. Environmental Science & Technology, 49(12), 73307339. https://doi.org/10.1021/es506362e.

Ye, H., Yang, B., Wang, Q., How, Z. T., Nie, C., Chelme-Ayala, P., & El-Din, M.G. (2021). Influences of integrated coagulation-ozonation pretreatment on the characteristics of dissolved organic pollutants (DOPs) of heavy oil electric desalting wastewaters. Journal of Environmental Management. 300, 113756. https://doi.org/10.1016/j.jenvman.2021.113756

Yen, T.W., Marsh, W.P., MacKinnon, M.D., & Fedorak, P.M. (2004). Measuring naphthenic acids concentrations in aqueous environmental samples by liquid chromatography. Journal of Chromatography A, 1033(1), 83-90. https://doi.org/10.1016/j.chroma.2004.01.030

Yousaf, U., Ali Khan, A.H., Farooqi, A., Muhammad, Y.S., Barros, R., Tamayo-Ramos, J.A., Iqbal, M., & Yousaf, S. (2022). Interactive effect of biochar and compost with Poaceae and Fabaceae plants on remediation of total petroleum hydrocarbons in crude oil contaminated soil. Chemosphere, 286(P2), 131782. https://doi.org/10.1016/j.chemosphere.2021.131782

Yuan, L., Wu, Y., Fan, Q., Li, P., Liang, J., Wang, Z., Li, R., & Shi, L.P. (2022). Spatial distribution, composition, and source analysis of petroleum pollutants in soil from the Changqing Oilfield, Northwest China. Marine Pollution Bulletin, 185(PB), 114338. https://doi.org/10.1016/j.marpolbul.2022.114338

Zan, S., Wang, J., Wang, F., Li, Z., Du, M., & Cai, Y. (2022). A novel degradation mechanism of naphthenic acids by marine *Pseudoalteromonas* sp. Journal of Hazardous Materials, 424, 127534. https://doi.org/10.1016/j.jhazmat.2021.127534

Zan, S., Wang, J., Wang, F., Han, Y., Du, M., & Fan, J. (2019). Variation and distribution of naphthenic acids in Dalian Bay sediment. Marine Pollution Bulletin, 140, 597-602.

https://doi.org/10.1016/j.marpolbul.2019.01.061

Zeng, Y., Wang, H., Hu, J., Zhang, J., Wang, F., Wang, T., & Chen, Z. (2024). Illuminated fulvic acid stimulates denitrification and As (III) immobilization in flooded paddy soils via an enhanced biophotoelectrochemical pathway. Science of Total Environment, 912, 169670. https://doi.org/10.1016/j.scitotenv.2023.169670

Zhan, D., Fenn, J.B. (2000). Electrospray mass spectrometry of fossil fuels. International Journal of Mass Spectrometry, 194(2-3), 197-208. https://doi.org/10.1016/S1387-3806(99)00186-4

Zhang, Y., Song, H., Zanganeh, J., & Moghtaderi, B. (2024). A review on microwave assisted thermal remediation of hydrocarbons contaminated soil: Influential factors, mechanism, and prospective. Journal of Environmental Chemical Engineering, 12(6), 114726. https://doi.org/10.1016/j.jece.2024.114726

Zhu, S., Li, Z., Yu, M., Wang, Q., Chen, C., Ma, J. (2023). Efficient removal of naphthenic acids from real petroleum wastewater by natural pyrite activated persulfate system. Journal of Environmental Management, 348, 119239. https://doi.org/10.1016/j.jenvman.2023.119239