ISSN: 2790-5209 Vol 2, No.2, 2024

A review of the effects of typical biogeochemical and hydrogeological features on the natural attenuation of soil petroleum contaminants

Xinyu Shi [1], Xiujun Guo [1,*]

[1] Ocean University of China College of Environmental Science and Engineering,Qingdao 266000,China)

* guojunqd@163.com

Abstract

Oil spills in soil can form source areas of contamination that are ecologically hazardous in the long term. The natural process by which the concentration, toxicity and mobility of petroleum contaminants in soil decrease under the combined effects of biochemistry and other aspects without human interference is called natural attenuation. This paper provides a systematic review of the natural attenuation characteristics of petroleum contaminants in soil and its research tools, focusing on the typical biogeochemical and hydrogeological characteristics of the site, and describes the influence of both on the natural attenuation process of contaminants in soil and its mechanism. It also clarifies the influence of petroleum properties, sediment types, organic matter changes, photo-oxidation reactions and microorganisms on the natural attenuation of the source area, and summarises the relevant indicators that can characterise the natural attenuation of petroleum contamination in the source area; at the same time, it outlines the various types of prediction methods of natural attenuation processes, and points out the focus and difficulties of the multidisciplinary fusion of the research directions and the multi-data drive, and finally puts forward a proposal for the study of natural attenuation of petroleum in soils. Finally, the research on the natural attenuation of soil oil pollution source area is proposed. Overall, due to the complexity of organic matter, mineral and microbial components, and the inhomogeneity of hydrogeological conditions, the study of the influence of the intrinsic properties of the site on the natural attenuation of pollutants needs to be further strengthened, and this paper focuses on the identification of the spatial and temporal dynamics of the natural attenuation of pollutants, and the deepening of the understanding of the interaction mechanisms between typical biogeochemical and hydrogeological conditions of the site and the pollutants.

Keywords

Petrochemical, Hydrogeology, Biogeochemical characteristics, Natural attenuation, Contaminated area.

1. Introduction

The quality of soil determines a society's ability to develop, and biomass grown on soil will become an increasingly important feedstock for fuel and manufacturing. Pipeline corrosion, natural disasters and other causes may cause oil storage facilities and pipeline leaks. Once oil enters the soil, it will cause serious damage to the soil ecosystem. Oil pollutants infiltration in the soil for a long time after retention, the formation of a pollution reservoir and lead to long-term emission of harmful substances, causing serious harm to the ecological environment. The corresponding treatment measures are also difficult, and artificial in situ soil remediation is not only expensive, but also may bring secondary pollution[1].Natural attenuation refers to the process of reducing the concentration and total amount of pollutants in soil or groundwater, and the toxicity and mobility of pollutants under the involvement of multiple effects (e.g., dilution, volatilization, biochemical effects, etc.)[2],which has been widely used to assess the feasibility of treatment and remediation programs and the cost-effectiveness of remediation programs, as a technology relying on the full capacity of natural purification[3].For this reason a large number of studies have focused on assessing the natural attenuation capacity and exploring the main factors influencing the rate of natural attenuation. In the past, there is a scarcity of studies on the natural attenuation process of petroleum contaminants in soils, and the mechanisms by which the natural degradation process of petroleum contaminants in soil systems is affected by the intrinsic characteristics of the site are not well defined.

This paper reviews the relevant methods for studying the natural attenuation of petroleum contaminated source areas in soil and the key role of site intrinsic features in the natural attenuation process, summarizes the characteristics of the changes in relevant geophysical and geochemical, and biological indicators caused by this process, and provides different methods for multi-perspective and more comprehensive assessment of the future environment affected by the natural attenuation process in order to ensure that a foundation is laid for the next step of the study and provide useful guidance for the field of soil contamination remediation and assessment fields.

2. Influence of site hydrogeologic characteristics on natural attenuation of pollution source areas

Petroleum properties, the characteristic hydrogeological conditions of different contaminated areas, and biochemical processes determine the pattern of retention and persistence of petroleum in soil horizons. Usually, petroleum penetrates into the soil in various ways, and the physical and chemical properties of the soil change, a process known as weathering. Subsequently, the contaminated area begins to undergo natural attenuation, and the source area of petroleum contamination is in a dynamic state of change due to the coupling of various factors such as biodegradation. Hydrogeological features play a key role in the natural attenuation process, and in this section, a comprehensive consideration of petroleum properties, geotechnical lithology, and permeability factors in the contaminated area affects the migration and transformation process of pollutants.

2.1. Physical and Chemical Properties and Forms of Petroleum

Petroleum components are more complex, the main components are saturated hydrocarbons and aromatic hydrocarbons, composed of carbon and hydrogen elements. Saturated hydrocarbons usually include aliphatic hydrocarbons (alkanes), naphthenic hydrocarbons (cycloalkanes), etc., which have a high content in crude oil, and are also an important part of light oil[4].Evaporation is an effective way in which petroleum content can be reduced. Studies have shown that most of the low-density oil can escape through evaporation, thereby significantly reducing the oil content in the source area. The community effect associated with

ISSN: 2790-5209 Vol 2, No.2, 2024
the photo-oxidation process during oil evaporation refers to the exposure of crude oil to air and sunlight in natural environments while multiple microbial strains in the microbial community act synergistically to accelerate the degradation and natural attenuation of the oil[5]. The other main way in which the oil content is reduced is through dissolution. The vast majority of hydrocarbons with carbon atoms between 1 and 3 and their water-soluble aromatic compounds can be dissolved in water, and the rate of dissolution is affected by the evaporation process, as the water-soluble substances mentioned above are rapidly evaporated within a few days at the longest.

2.2. Geotechnical properties

Differences in rock and soil lithology are mainly expressed in particle size. This section deals with the effect of lithologic material properties on natural attenuation in areas of soil oil contamination. Oil-sediment interactions and the composition, size, and content of the resulting particle sizes affect the ability of natural attenuation. Oil-sediment interactions result in the formation of a variety of aggregates, including microaggregates and macroaggregates, and the formation of aggregates usually involves the interaction of hydrophobic components of crude oil with the surface of sediment particles. The microaggregates, which are usually formed by the adsorption of hydrophobic components of crude oil with the surface of sediment particles, are called oil-particulate aggregates (OPAs), and the macroaggregates, which are formed by physical and chemical adsorption between crude oil and sediment particles, are called sediment-oil aggregates (SOAs) or sediment-oil-like aggregates (SOMs)[6].Oil-Particulate Aggregates (OPAs) are aggregates formed when oil interacts with fine sediment particles, typically less than 10 μm in size[7], Fine sediment particles may match the particle size of the tiny hydrophobic constituents in the newly spilled oil, making it easier for them to adhere and form OPAs[8].It was experimentally demonstrated that there is an inverse relationship between the particle size of the sediment and the total amount of oil-particulate aggregates (OPAs) formed. This finding suggests that smaller sediment particles are more likely to adsorb and interact with hydrophobic components of oil, resulting in the formation of more OPAs[9].Different types of sediments have different physicochemical properties that further affect the morphology of the aggregates. For example, sediments containing highly adsorbent minerals may be more likely to form flaky aggregates[10]. Compared with other minerals such as quartz, clay minerals have a larger specific surface area and more adsorption sites, which makes it easier for clay minerals to adsorb with hydrophobic components in petroleum, promoting the formation of OPAs and accelerating the formation of oil and gas enrichment areas. Hydrophobic minerals usually have high lipophilicity, which is easy to be attracted to the hydrophobic components in the petroleum and promote the formation of particle agglomerates[11].

2.3. Influence between permeability and mass transfer processes

Differences in the size of rock particles in porous media affect the flow of fluid mass transfer (both liquid and gas phases) in porous media. Smaller particles have a relatively larger surface area, which can provide more reaction sites and increase the rate of reactions such as adsorption, precipitation, and dissolution of solutes in the groundwater, which affects the water quality and the physicochemical properties of the subsurface environment. Microorganisms live on the surface and in the pores of rock particles in porous media, and their distribution and activity can also be affected by particle size. Rocks and soils with low

ISSN: 2790-5209 Vol 2, No.2, 2024

permeability usually have limited pore space, which restricts the conditions for microorganisms to survive. Microorganisms require moisture and oxygen for their metabolic processes. If moisture cannot be transported efficiently through the geotechnical soil, the survival and activity of microorganisms will be limited[12-14].Coarse-grained sediments have large and interconnected pore spaces that facilitate the free flow of water and diffusion of nutrients. Due to the limited permeability in fine-grained sediments, oxygen delivery to microorganisms is restricted, and high matrix blocking factors can limit microbial activity[15-17]. Therefore, the high porosity, high oxygen content and strong dilution effect of sandy soils are favorable to the metabolic activities of microorganisms[18-20],Therefore, the biodegradability of hydrocarbon contaminants under this lithological condition is high[21]. Clay is characterized by its tiny pores and a high degree of adsorption between the particles, has a low hydraulic conductivity, water moves more slowly in the clay, so the filtration and interception of pollutants in the water, coupled with a large number of microbial activities available in the pore space can provide more biodegradation sites to support the growth of microorganisms and metabolic activities, which contributes to the halogenated hydrocarbon pollutants in the reduction of dehalogenated[22-24].

3. Characterization of natural attenuation indicators for oil contaminated source areas

The first task in the remediation of petroleum-contaminated soils is to determine whether active natural attenuation processes are occurring in the source area of the contamination..." Monitored Natural Attenuation (MNA) is a subsurface remediation approach that relies on natural processes to reduce the concentration of contaminants in the subsurface without the introduction of external interventions[25].The key to the application of this method is the accurate monitoring of the natural attenuation of pollutants in the source area, which requires less investment and is easier to implement than traditional treatment programs. Geophysical, chemical and biological indicators provide information on the natural decay processes in the contaminated area, and by monitoring these indicators, the extent of the contamination plume and the stage of degradation in the source area can be determined.

3.1. Geophysical indicators

The involvement of microorganisms in the natural attenuation of petroleum in contaminated source areas is an important and indispensable factor. With the participation of microorganisms, natural attenuation can occur in both aerobic and anaerobic environments. It has been demonstrated that the presence and activity of microorganisms affects the electrical characteristics of the contaminated area[26], At the same time, chemical changes in pore fluids, alteration of solid phases and increase in biodegradation by-products change the electrical characteristics of the degradation zone. Microbial activity can break down petroleum compounds and produce products such as organic acids, carbonic acids and surfactants, the growth of which can cause changes in porosity and thus affect the water-holding capacity of the aquifer[27].

3.2. Geochemical indicators

Degradation of petroleum hydrocarbons by microorganisms, the main common products are: CO_2, water, organic acids, extracellular polymers, etc[28]. The pH of pore fluids decreases with

ISSN: 2790-5209 Vol 2, No.2, 2024
the formation of carbonic acid from dissolved carbon dioxide and the production of organic acids, which are usually monitored below background values. If bicarbonates are detected in the soil, they enhance the buffering properties of the sediment layer, resulting in a neutral pore water pH. During aerobic biodegradation, where microorganisms are involved and oxygen is more abundant, oxygen is preferentially consumed as the most efficient final electron acceptor, and the reaction proceeds progressively with a lower concentration of dissolved oxygen to be consumed, which is an indicator of active biodegradation. In some studies, changes in bicarbonate concentration can provide information on the progress of biodegradation because bicarbonate (HCO_3^-) is often one of the degradation by-products in redox reactions involving microorganisms[29]. Changes in the concentration of numerous ions can be used to reflect the extent to which biodegradation is taking place, e.g., to demonstrate that biodegradation is taking place under anoxic conditions, which can be known from changes in nitrate concentration, as well as to Mn^{4+}、Fe^{3+} 、SO_4^{2-},all of them can be used as parameter indicators to characterize the biodegradation process.

3.3. Geo-biological indicators

Hundreds of oil-degrading microorganisms are present in soil. Microbial populations show large variability across time scales and in different types of oil-contaminated soils. Their composition and abundance change over time. In the early stages of oil contamination, some fast-growing microorganisms predominate using petroleum hydrocarbons as a carbon source, and other microorganisms gradually emerge as the concentration of pollutants decreases. For example, some strains of Gammaproteobacteria and Alphaproteobacteria have specific metabolic pathways that allow them to efficiently degrade low molecular weight n-alkanes and aromatic hydrocarbons.This group of bacteria grows rapidly in the early stages of contamination, and as the biodegradation process proceeds, some other strains become dominant and abundant, resulting in a reduction in the diversity of other bacteria,and ultimately a decline in bacterial diversity of about 50 percent[30].

4. Modeling predictions of natural decay processes

The international community has provided instructive programs, standards and technical guidelines on MNA aimed at regulating and guiding the treatment and assessment of organic pollutants[31]. MNA as a remediation technology has great advantages in the remediation of contaminated sites at home and abroad, and its role is not a useless remediation means, as mentioned above, after the assessment of the contamination characteristics of the source area of contamination in various aspects of the long-term monitoring work, and combined with the interdisciplinary mathematical, physical, chemical, biological and other assessment of its impact on the future of the environment. Consideration of multiple chains of evidence and the development of mathematical frameworks can help to ensure the comprehensiveness and scientific validity of the assessment. Interdisciplinary collaboration is required, and multiple chains of evidence are mainly[32]:(i) Inferences based on stratigraphic information: historical sequence data from contaminated sites. This chain of evidence usually involves the analysis of geological and hydrogeological information to infer the state of contaminant transport. Monitoring of groundwater levels, groundwater flow rates, and the distribution of contaminants in groundwater can provide a preliminary indication of whether natural attenuation is occurring. However, this information usually does not provide information on

ISSN: 2790-5209 Vol 2, No.2, 2024

the relationship between specific losses and attenuation. Biodegradation chain of evidence: This chain of evidence involves monitoring changes in geochemical indicators associated with biodegradation, such as metabolic by-products and final electron acceptor concentrations. By analyzing changes in these indicators, it is possible to quantify more accurately the extent of natural petroleum degradation and to infer the mechanisms of natural degradation. Biodegradation is an important process in natural attenuation, so this chain of evidence can provide important information on the rate and mechanism of natural attenuation. Laboratory experiments: Laboratory microbiological experiments can provide more concrete evidence that bacteria play a key role in the biodegradation of oil contaminants. By simulating biodegradation processes in natural environments under controlled conditions, it is possible to measure natural attenuation rates and predict their application in the field.

5. Conclusions and outlook

In order to deepen and improve the study of soil oil pollution, research can be carried out in the following aspects, so as to better understand the impact of the natural decay process on the future ecological environment, and to provide a more reliable scientific basis for the formulation of effective environmental protection policies and management strategies.

(1) Strengthen the integration of MNA processes and complex hydrogeological conditions in soils. This is critical for effective management of soil contamination and prediction of natural attenuation effects. Consideration of hydrogeological features at different scales can help to model remediation in specific areas of the source region, and to better understand and deal with complex hydrogeological features and multifactorial influences on soil oil contamination events.

(2) Extend collaborative and cross-disciplinary research in natural attenuation-related disciplines. Various disciplines, such as soil science, geophysics, biochemistry, data science, etc., play different roles in natural attenuation research, which can provide a more comprehensive understanding of the natural attenuation process, and thus improve the accuracy of modeling and prediction of future ecological evolution. Collaboration and cross-study of these disciplines can provide a better understanding of the natural attenuation process, and predict the trend of the evolution of the future ecological environment.

(3) Promote the investigation of the natural attenuation process of soil petroleum pollutants. The geographic environment of soils in some study areas is relatively complex, and the natural attenuation mechanism of petroleum pollutants needs to be further studied and clarified. To gradually improve the understanding of the natural attenuation mechanism in complex soil contaminated areas, the biogeochemical processes in the contaminated areas and the signal response between the processes and geophysical features should be further refined.

References

[1] OSSAI I C, AHMED A, HASSAN A, et al. Remediation of soil and water contaminated with petroleum hydrocarbon: A review [J]. Environmental Technology & Innovation, 2020, 17: 100526.

[2] YANG Z, SHAH K, LAFOREST S, et al. Occurrence and weathering of petroleum hydrocarbons deposited on the shoreline of the North Saskatchewan River from the 2016 Husky oil spill [J]. Environmental Pollution, 2020, 258: 113769.

ISSN: 2790-5209 Vol 2, No.2, 2024
[3] JIA Hui, WU Xiaofeng, HU Liming, et al. Study on the natural attenuation capacity of petroleum-based pollutants based on field tests [J]. Environmental Science, 2011, 32(12): 3699-703..

[4] BOUFADEL M, GENG X, AN C, et al. A review on the factors affecting the deposition, retention, and biodegradation of oil stranded on beaches and guidelines for designing laboratory experiments [J]. Current Pollution Reports, 2019, 5: 407-23.

[5] LEWAN M D, WARDEN A, DIAS R F, et al. Asphaltene content and composition as a measure of Deepwater Horizon oil spill losses within the first 80 days [J]. Organic geochemistry, 2014, 75: 54-60.

[6] GUSTITUS S A, CLEMENT T P. Formation, fate, and impacts of microscopic and macroscopic oil-sediment residues in nearshore marine environments: A critical review [J]. Reviews of Geophysics, 2017, 55(4): 1130-57.

[7] SUN J, ZHENG X. A review of oil-suspended particulate matter aggregation—a natural process of cleansing spilled oil in the aquatic environment [J]. Journal of Environmental Monitoring, 2009, 11(10): 1801-9.

[8] GUSTITUS S A, JOHN G F, CLEMENT T P. Effects of weathering on the dispersion of crude oil through oil-mineral aggregation [J]. Science of the Total Environment, 2017, 587: 36-46.

[9] ZHANG H, KHATIBI M, ZHENG Y, et al. Investigation of OMA formation and the effect of minerals [J]. Marine pollution bulletin, 2010, 60(9): 1433-41.

[10] STOFFYN-EGLI P, LEE K. Formation and characterization of oil–mineral aggregates [J]. Spill Science & Technology Bulletin, 2002, 8(1): 31-44.

[11] XIA W-X, LI J-C, ZHENG X-L, et al. Enhanced biodegradation of diesel oil in seawater supplemented with nutrients [J]. Engineering in Life Sciences, 2006, 6(1): 80-5.

[12] ABBASIAN F, LOCKINGTON R, MALLAVARAPU M, et al. A comprehensive review of aliphatic hydrocarbon biodegradation by bacteria [J]. Applied biochemistry and biotechnology, 2015, 176: 670-99.

[13] LIU Y, HUANG H, LIU Q, et al. A reversed compositional pseudo-gradient in biodegraded oil column from Liaohe Basin, NE China [J]. Marine and Petroleum Geology, 2020, 117: 104378.

[14] KURT Z, SPAIN J C. Biodegradation of chlorobenzene, 1, 2-dichlorobenzene, and 1, 4-dichlorobenzene in the vadose zone [J]. Environmental science & technology, 2013, 47(13): 6846-54.

[15] SERRANO A, GALLEGO M, GONZáLEZ J L, et al. Natural attenuation of diesel aliphatic hydrocarbons in contaminated agricultural soil [J]. Environmental Pollution, 2008, 151(3): 494-502.

[16] PERUJO N, SáNCHEZ-VILA X, PROIA L, et al. Interaction between physical heterogeneity and microbial processes in subsurface sediments: a laboratory-scale column experiment [J]. Environmental Science & Technology, 2017, 51(11): 6110-9.

[17] FUENTES S, MéNDEZ V, AGUILA P, et al. Bioremediation of petroleum hydrocarbons: catabolic genes, microbial communities, and applications [J]. Applied microbiology and biotechnology, 2014, 98: 4781-94.

[18] PUIGSERVER D, CORTéS A, VILADEVALL M, et al. Processes controlling the fate of chloroethenes emanating from DNAPL aged sources in river–aquifer contexts [J]. Journal of contaminant

hydrology, 2014, 168: 25-40.

[19] GIELNIK A, PECHAUD Y, HUGUENOT D, et al. Effect of digestate application on microbial respiration and bacterial communities' diversity during bioremediation of weathered petroleum hydrocarbons contaminated soils [J]. Science of the total environment, 2019, 670: 271-81.

[20] BECKINGHAM L E. Evaluation of macroscopic porosity-permeability relationships in heterogeneous mineral dissolution and precipitation scenarios [J]. Water Resources Research, 2017, 53(12): 10217-30.

[21] TRAN H-T, LIN C, BUI X-T, et al. Aerobic composting remediation of petroleum hydrocarbon-contaminated soil. Current and future perspectives [J]. Science of the Total Environment, 2021, 753: 142250.

[22] TAKEUCHI M, KAWABE Y, WATANABE E, et al. Comparative study of microbial dechlorination of chlorinated ethenes in an aquifer and a clayey aquitard [J]. Journal of contaminant hydrology, 2011, 124(1-4): 14-24.

[23] PUIGSERVER D, HERRERO J, PARKER B L, et al. Natural attenuation of pools and plumes of carbon tetrachloride and chloroform in the transition zone to bottom aquitards and the microorganisms involved in their degradation [J]. Science of The Total Environment, 2020, 712: 135679.

[24] TOBISZEWSKI M, NAMIEŚNIK J. Abiotic degradation of chlorinated ethanes and ethenes in water [J]. Environmental Science and Pollution Research, 2012, 19: 1994-2006.

[25] FORD R G, WILKIN R T, ACREE S. Site characterization to support use of monitored natural attenuation for remediation of inorganic contaminants in ground water [M]. US Environmental Protection Agency, National Risk Management Research Laboratory, 2008.

[26] ABDEL AAL G Z, ATEKWANA E A, SLATER L D, et al. Effects of microbial processes on electrolytic and interfacial electrical properties of unconsolidated sediments [J]. Geophysical research letters, 2004, 31(12).

[27] ALLEN J P, ATEKWANA E A, ATEKWANA E A, et al. The microbial community structure in petroleum-contaminated sediments corresponds to geophysical signatures [J]. Applied and environmental microbiology, 2007, 73(9): 2860-70.

[28] HOREL A, SCHIEWER S. Influence of inocula with prior hydrocarbon exposure on biodegradation rates of diesel, synthetic diesel, and fish-biodiesel in soil [J]. Chemosphere, 2014, 109: 150-6.

[29] COZZARELLI I M, HERMAN J S, BAEDECKER M J. Fate of microbial metabolites of hydrocarbons in a coastal plain aquifer: the role of electron acceptors [J]. Environmental science & technology, 1995, 29(2): 458-69.

[30] HUETTEL M, OVERHOLT W A, KOSTKA J E, et al. Degradation of Deepwater Horizon oil buried in a Florida beach influenced by tidal pumping [J]. Marine Pollution Bulletin, 2018, 126: 488-500.

[31] RIVETT M O, THORNTON S F. Monitored natural attenuation of organic contaminants in groundwater: principles and application, F 2008]. Thomas Telford Ltd.

[32] SINKE A J C. Monitored natural attenuation; moving forward to consensus [J]. Land Contamination and Reclamation, 2001, 9(1): 111-8.