Environmental Behavior of Petroleum in Soil and its Harmfulness Analysis

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Abstract. The environmental behavior of rock and oil pollutants in soil has always been the focus of environmental protection research. In this paper, the sources, hazards and existing states of the stone oil pollutants in the soil are briefly introduced, and their migration, adsorption and degradation behaviors in the soil, as well as their behavior characteristics and influencing factors are also introduced. It is of great significance to protect the ecological environment and promote the sustainable development of petroleum industry to fully understand the environmental behavior of stone and oil pollutants in soil.

1. Introduction

Oil is called economic and even the society as a whole "black gold", "economic blood", as a kind of important energy, its application scope continues to expand, consumption is increasing, in oil exploitation, refining and stored, in use process, because of the limitation of technological level and the processing technology of waste water, waste residue containing petroleum matter inevitably discharged into the soil, followed by the problem of environmental pollution is becoming more and more serious, abounds in oil in the soil environment seriously affect the whole soil ecosystem.

It is estimated that about 100 billion kg of oil and petroleum products enter groundwater, surface water and soil by various means worldwide every year, including 600 million kg in China [1]. In the heavily polluted area of LiaoHe oilfield in China, the content of crude oil in the soil is as high as 10,000 mg/kg, more than 20 times of the critical value (500 mg/kg), with 100 million kg of newly polluted soil per year [2]. In recent years, soil oil pollution and its treatment have attracted widespread attention at home and abroad [3].

Some special cases about the environmental behavior and harmfulness of petroleum pollutants in soil have been involved to varying degrees in relevant literatures, but it is still rare to systematically summarize and study them. A comprehensive understanding of the environmental behavior and harmfulness of petroleum pollutants in soil is of great theoretical significance for the prevention and control of petroleum pollutants.

2. Environmental behavior of petroleum pollutants in soil

Soil is an important part of human environment. It is a multi-medium complex system composed of solid-liquid-gas-biology. The environmental behaviors of oil in soil mainly include migration, adsorption and degradation. The environmental behavior of petroleum in the soil and its harmfulness analysis pollutants will infiltrate into the soil and remain in the soil. Because there are a large number
of organic and inorganic colloids, soil plants, animals and microorganisms in the soil, the pollutants entering the soil are continuously adsorbed, decomposed, migrated and transformed through the physical, chemical and biological processes of the soil. Generally, the migration ability of oil in the soil is very weak, and it is mostly absorbed and concentrated in the surface soil. The oil on the soil surface can be self-purified by volatilization. When the pollution intensity is high and the content of small molecules of hydrocarbons is high, they can migrate into the groundwater aquifer.

2.1. Oil pollutants migrate through the soil

With the flow of water, the petroleum pollutants can migrate to the deep soil layer relatively freely or have planar diffusion motion, while the part adsorbed on the particles basically does not migrate significantly under the condition that the soil layer is not destroyed. The migration of petroleum pollutants along the direction of soil depth is mainly affected by gravity and the plane diffusion movement occurs mainly under the action of capillary force. Adsorption quantity of soil particles is limited, a large number of of petroleum pollutants are not exist in the soil, in the event of rain, some will accelerate under the action of infiltration water deep penetration to the soil, after a long time, under the influence of factors such as hydraulic, gravity, the diffusion and mixing, will gradually form a more stable state [4].

If the water table is buried shallower, the amount of surface oil pollutants is larger, and the hydrodynamic drive is larger. Under certain conditions, the oil pollutants will penetrate deeper into the soil, and the infiltration front can reach the water table. Petroleum pollutants will migrate and expand quite significantly transversely in the capillary zone near the groundwater level, and these expansions will be larger than those along the groundwater level, and transversely along the direction of groundwater flow [5].

2.2. Adsorption of petroleum pollutants on soil

The adsorption of soil to petroleum pollutants is one of the important factors affecting the environmental behavior of pollutants in soil. The oil molecules are easy to reach the soil surface and adhere to the soil particle surface, while the oil pollutants adhering to the soil particle surface tend to adhere to more oil pollutants. The adsorption of oil on soil particles is mainly physical adsorption, but there is also a small amount of chemical adsorption. Because petroleum is a hydrophobic substance with high viscosity, its solubility in water is very small, and it mostly exists in the state of fine particles. The force between it and the surface of solid particles mainly comes from intermolecular force and electrostatic attraction. However, some organic matter in the soil can promote the dissolution of pollutants, so it also plays a distributive role [6].

2.3. Degradation of petroleum pollutants in soil

After entering the soil environment, petroleum pollutants can be transformed and degraded through three natural pathways, namely volatilization into the atmosphere, self-oxidation and Degradation, which mainly includes biodegradation, photolysis and mechanical degradation, is a very slow process. The final destination of oil in the environment is basically microbial degradation. When petroleum hydrocarbons enter the environment, various microorganisms will participate in their biodegradation. Microorganisms absorb petroleum as a nutrient and convert it into organic components or multiply it into new microorganisms. The rest is oxidized and decomposed into simple organic or inorganic substances, such as methane, carbon dioxide and water.

When petroleum substances enter the cells of degrading microorganisms, they are degraded through three assimilation processes: aerobic respiration, anaerobic respiration and fermentation. This is a very complex process. In aerobic conditions, molecular oxygen is combined into the matrix under the catalysis of oxygenase to form oxygen-containing intermediates, which are then converted into other substances. During the degradation of alkanes, an atom in O₂ is bound; In the process of aromatic hydrocarbon degradation, the two atoms of O₂ are combined into the aromatic ring. Since oil is a mixture of various hydrocarbons, its degradation can only be accomplished through the joint action of a variety
of microorganisms, which have different metabolic pathways and mechanisms for different hydrocarbon compounds in petroleum.

3. The harm of petroleum pollutants to soil ecological environment

Petroleum pollutants are the most important pollutants in the process of oilfield development and petroleum processing. Every link of petroleum industry may produce petroleum pollutants and pollute the soil environment. Investigation shows that the oil content of soil collected within 100m of oil Wells in Shengli and Daqing oil fields is mostly higher than the national standard threshold (500mg/kg)[7]. The area of land contaminated by oil is expanding and the pollution level is becoming increasingly serious. In the seriously polluted area of Liaohe oilfield, the oil content in the soil has reached 10000mg/kg. The land cannot be cultivated and it usually takes 50 years to recover. As an important place for various material circulation and energy exchange, soil is usually the destination of pollutant migration, detention and deposition in the environment, and the ultimate recipient of environmental pollution. The large amount of petroleum substances in soil will cause harm to it.

3.1. Degradation of petroleum pollutants in soil

Oil contamination of the soil is concentrated at the surface of about 20cm. When oil is discharged into soil, it can damage soil structure, affect soil permeability, change soil organic matter composition and structure, and reduce soil quality. Because the water-solubility of petroleum substances is generally very small, soil particles can not easily be infiltrated by water after adsorbing petroleum substances, thus forming no effective water passage, reducing soil permeability and water permeability. Persistent, cumulative petroleum substances in soil, the stronger, can significantly affect the soil environment of matter and energy exchange with the outside world, the oil into the soil in the process of infiltration to the underground along the surface diffusion and erosion of soil, salinization, asphalt, harden, under the action of gravity along the migration of deep soil, because of heavy oil viscosity, viscosity, form small range of high concentration of pollution in a short time, change the physical and chemical properties of soil, the changing nature of the soil will directly influence the behavior of the compounds in the soil, destroying soil production function. In addition, under certain environmental conditions, the part of petroleum hydrocarbon that is not easily absorbed by soil can seep into the ground and pollute the groundwater, and its potential harm to the groundwater cannot be ignored.

When petroleum pollutants enter the soil, the content of fresh organic carbon in the soil increases greatly, while the available nitrogen and available phosphorus do not change correspondingly, resulting in the serious imbalance of carbon, nitrogen and phosphorus in the soil. The massive introduction of available carbon into the soil stimulates the growth of autotrophic microorganisms in the soil, while the massive propagation of hydrophilic microorganisms fixes the nutrient elements in the soil (such as nitrate nitrogen), resulting in the lack of nutrient supply, which leads to the competition between microorganisms and plants for soil nutrient elements, thus hinders the development of both sides. In addition, the oil in the soil interferes with the passage of nutrients from the soil particles into the soil solution.

3.2. Effects of petroleum pollutants on plants

When the content of oil in the soil is less than 1mg/kg, oil can promote the growth of plants, because plants can convert carbon, hydrogen, oxygen, nitrogen and other substances in the oil into substances needed for plant growth through lignification. Only when the oil content in the soil is relatively high, can it inhibit the growth of plants. Different plant species have different inhibitory effects on oil pollutants. The oil pollutants in the soil form a layer of mucous membrane on the root system of the plant, which impedes the respiration and absorption of the root system. The oil absorbed by the root system from the soil can move to the leaves and fruits, and accumulate and amplify. The different fractions in petroleum have different effects on plants. The petroleum fractions with the boiling point within 150°C~275°C are more toxic to plants, because they can penetrate the plant interior, operate in
the intercellular space and vascular bundle system, and destroy the normal physiological functions of plants.

In addition, due to the oil pollution to the soil, can lead to some oil pollutants into food, cause the biological accumulation of pollutants, amplification, not only affects the quality of the food, making the quality of some vegetables change bad, taste astringent, more important is to make oil pollutants enter the food chain, harm to human health, a vicious cycle in the environment.

3.3. Effects of petroleum pollutants on animals
Petroleum pollutant mainly through animal feeding, respiration, skin penetration into the animal body, can break the fat soluble organism cell membrane structure, selective damage the body's nervous system, corrosion of the respiratory tract and the toxic effect of biological metabolism of the body, leaving the skin, mouth and nose allergy, inflammation, can't normal feeding; Damage and suppress the immune system, sometimes leading to secondary bacterial or fungal infections; Destroy red blood cells in the blood; Causes liver atrophy, lung, respiratory tract, kidney and other organ failure.

Soil oil pollution has acute and chronic sublethal effects on earthworms. When the oil mass fraction was 1.5%, the survival rate of 7d was less than 40%. When the mass fraction of petroleum in the soil reached 1.0%~2.5%, the number of large earthworms that liked nocturnal activities decreased by half compared with that in untreated soil. Earthworms do not survive for 2 weeks after being treated with 5% crude oil.

3.4. Effects of petroleum pollutants on humans
Oil can generally through breathing, skin contact, the way such as consumption of food containing pollutants into the human body, can affect the normal function of various organs, causing a variety of diseases, causing symptoms include: the skin, lung, bladder, cancer of the scrotum, contact dermatitis, allergic skin, pigmentation, acne, audio and visual illusion, cause depression, gastrointestinal disorders, sensory loss and even a variety of diseases such as memory loss, some components in oil pollutants harm to human health are shown in table 1. Children who were frequently exposed to oil were four times more likely to develop acute leukemia than the average, and seven times more likely to develop acute nonlymphoblastic leukemia. In the adjacent areas polluted by petroleum pollutants, children's skin alkalinity resistance is significantly weakened, white blood cells are decreased, the anemia rate is increased, and lung function is affected. The probability of human hepatoma is significantly higher than that of residents in the control area, and the standardized mortality rate of malignant tumors and malignant tumors of the digestive system is significantly higher than that in the control area. The concentration of petroleum is the key factor to investigate its toxicity, and the toxicity effect of petroleum of different components is also different. With the increase of petroleum concentration and the extension of exposure time, the toxicity is enhanced.
Table 1. Effect of petroleum pollutants on human healthy

| The types of compounds contained in petroleum | Harm to human health |
|---------------------------------------------|----------------------|
| Fat hydrocarbon                             | The saturated lower hydrocarbon mostly has the narcotic effect, the intermediate hydrocarbon has the narcotic stimulation enhancement, and the higher hydrocarbon has the carcinogenic harmful substances thick cyclic aromatic hydrocarbons. |
| Polycyclic aromatic hydrocarbons            | Polycyclic aromatic hydrocarbons (pahs) are carcinogenic and mutagenic substances in the environment. |
| Benzene content                             | Benzene and benzene system have stimulative effect to the skin of the person, mucous membrane, can cause dermatitis, make at hematopoietic organization, induce anaemia, leucocyte reduces wait for each kind of symptom, have cause mutability, have inhibitive to central nervous system, long-term and chronic poison can cause haemorrhagic leukaemia. |
| Phenolic                                    | It is a kind of cell protoplasm poison, with protoplasm protein chemical reaction, and make the cell inactivation. |
| Aniline                                     | It has a strong carcinogenicity, aniline derivatives on the central nervous system has a very obvious impact. |

4. Conclusion

The adsorption, migration and degradation of petroleum pollutants in soil is a complicated process, which depends on the quantity, state and nature of petroleum pollutants and the environmental conditions of soil. The discharge of petroleum pollutants must take into account the environmental capacity of soil and its self-purification capacity, emphasize the fundamental reduction of its direct emissions to the environment, increase the treatment of oil-containing pollutants, shorten the detention time of petroleum pollutants in the environment, and reduce environmental pollution. Predictably, as from different perspectives, different ways of soil pollutants full comprehensive environmental behavioral research, people will be in the soil environment to its behavior have a more clear and comprehensive understanding, at the same time as the deepening research of various processing methods and their application in actual, soil pollutant treatment and prevention of full will achieve satisfactory results.

There is still a big gap between theoretical research and practical application. In the future research, we should choose the research method that is closer to the real soil. At present, most of the research on multiphase flow simulation experiment is conducted in uniform soil, but few studies on undisturbed soil. At the same time, the spatial and temporal scale of the simulated experiment is far from the actual one, which makes it difficult to apply the research results to the actual quantitative and prediction. Therefore, further exploration is needed to bridge the gap between the experiment and the actual one. In addition, the research on multiphase flow model needs to be improved, and it will become a new hotspot to find appropriate methods to verify the predictive power of the model and improve its accuracy and practicability.

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