Characteristics-based classification research on typical petroleum contaminants of groundwater

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Abstract: Petroleum pollution has become an important factor to threaten the groundwater environment, and the classification of its typical characteristics will contribute to pollution assessment and environmental management. Under the same hydrogeological features condition, the reaction of typical petroleum pollutants in groundwater depends on the characteristics. This paper takes the typical toxicity, oil pollutant migration, degradation, water-soluble *etc.* as evaluation indexes, and with AHP method the typical petroleum pollutants in groundwater are divided into four classifications according to comprehensive calculated values: comprehensive value≥2.5, Class I hazardous pollutant; 2.0≤comprehensive value< 2.5, Class II hazardous pollutant; 1.5≤comprehensive value<2.0, Class III hazardous pollutant; comprehensive value<1.5, Class IV hazardous pollutant. The pollutant group shall be managed according to the classification, and obtained classification list will provide technical support for priority monitoring and priority repair of groundwater environmental management.

Keywords: Groundwater; Petroleum; Pollutants; AHP; Classification

The water pollution caused in petrochemical industry is increasingly pressing. The contamination accidents occurred repeatedly in recent years have brought great challenges to the groundwater environment protection and environmental management. Additionally, the decentralized distribution of the petroleum resources and the scattered petroleum processing enterprises expand the range of groundwater contamination and increase the difficulty for pollution control.

There are a great variety of petroleum organic pollutants, among which most are toxic and can have physical and chemical reaction with groundwater, doing harm to human health. For example, during the production, storage and utilization of mixed diesel, oil leakage occurs often due to the incorrect storage or misuse. The leaked oil may run into the water environment along the runoff, damaging the function of water body and the aquatic biological resources (YAN Xue *et al*. 2014). However, most of those petroleum organic pollutants are not included in the list of monitoring of Quality Standard for Ground Water (State Bureau of Technical Supervision, 1993) and Water Standard for Drinking Water Sources (Ministry of Health of the People's Republic of China, 1993). In 1990, China made a blacklist of prior-controlled pollutants (including 68 types of pollutants) (ZHOU Wen-Min *et al*. 1990) for prior control and monitoring (ZHU Fei-fei *et al*. 2013), part of which involve the specific pollutants of petrochemical industry. Due to the particularity of the groundwater environment, the petroleum specific pollutants present great variety. Definitely, a uni-

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versal pattern for environmental management will lag behind relatively. Therefore, the classifycation and grading of petrochemical organics can optimize and complete the prior-control list and thus realize a more scientific groundwater environmental protection.

Based on the assumption of a uniform groundwater aquifer medium, the authors of the paper select the physical property, chemical property, toxicity and the migratory direction of typical petrochemical pollutants in groundwater as the evaluation indexes to grade the hazard, which may facilitate the environment protection and improvement.

1 Determination of classification method

The typical specific pollutants in groundwater usually vary in terms of toxicity, migration, degradability and water solubility. The weighted values of multiple factors shall be considered for the comprehensive evaluation. In this paper for the study, the commonly used Analytic Hierarchy Process with strong adaptability is employed.

The Analytic Hierarchy Process (YANG Bao-an and ZHANG Ke-jing, 2008) (herein after referred to as AHP) is a systematic and hierarchical method for decision-making analysis developed in 1970s, combining qualitative analysis with quantification. Due to its practicability and effectiveness, it has also been used for selecting and ranking of decision objectives scientifically and systematically. The AHP as a comprehensive evaluation method now has been widely used in risk assessment, particularly in safety and environment risk assessment (GUO Jin-yu *et al*. 2008).

The details of the basic principle of AHP are stated in References (LU Zhong-da and ZHANG Jiang-shan, 2007). Modeling based on the single hierarchical arrangement can be carried out following 4 procedures:

(1) To determine the environmental influencing factors and set up a hierarchical model and a weighted judgment matrix:

$$p = \begin{bmatrix} b11 & b12 & b13 & b14 \\ b21 & b22 & b23 & b24 \\ b31 & b32 & b33 & b34 \\ b41 & b42 & b43 & b44 \end{bmatrix} \quad (1)$$

(2) To calculate the weight coefficient under a single criterion: calculating the geometric mean of the factors in each line of the judgment matrix p:

$$\overline{w_i} = \sqrt[n]{\prod_{i=1}^{n} b_{ij}}$$ （i=1,2,3,4; j=1,2,3,4; n — the order of a matrix） (2)

(3) To normalize the vector quantity $\overline{w} = (\overline{w_1}, \overline{w_2}, \overline{w_3}, \overline{w_4})^T$, take w_i in the equation $w_i = \frac{\overline{w_i}}{\sum_{j=1}^{n} \overline{w_i}} (j = 1,2...,n)$ as the weight coefficient of the index to be calculated, then the weight vector can be figured out:

$$w = (w_1, w_2, w_3, w_4)^T \quad (3)$$

(4) Check the uniformity of the judgment matrix

Calculate the maximum value of the judgment matrix and the maximum eigen-value：

$$\lambda_{max} = \frac{1}{n} \sum_{i=1}^{n} \frac{(pw)_i}{w_i} \quad (4)$$

Check the uniformity of the matrix and define

$$CI = \frac{\lambda_{max} - n}{n-1} \quad (5)$$

When the order ≤ 2, the matrix is of full uniformity; when the order > 2, $CI = \frac{CI}{RI}$ is called the random uniformity ratio; when CI < 0.1, or when CI is at around 0.1, the matrix is of satisfactory uniformity; otherwise, the matrix shall be readjusted (HU Qun and LIU Wen-yun, 2009).

2 Determination of index quantification

By consulting copious literatures and referring to the blacklist of prior-controlled pollutants in water and the data from International Agency for Research on Cancer (IARC) (DI Xue-yun, 1999), the authors of this paper select 22 kinds of common organic pollutants as the research objects, including the methyl ethyl ketone, acetic ether, butyl acetate, methanol, ethyl alcohol, dichloromethane, trichloromethane, carbon tetrachloride, benzene, methylbenzene, dimethylbenzene, acetone, isopropanol, ethylbenzene, tetrachloroethylene, dichlorobenzene, phenol, N-nitrosodiethylamine, naphthaline, nitrobenzene, *etc*.

2.1 Toxicity index

The more toxic the pollutant is, the severer harm it may do to groundwater. And the toxicity of the organic pollutants is higher than that of the inorganic ones. Median Lethal Dose (LD_{50}) means the minimum quantity of bacteria or toxin required to make half of the animals of a certain weight and a certain age die through a specified infection route within a limited time span.

According to toxicology, Median Lethal Dose, referred to as LD_{50} (Lethal Dose, 50%, Unit: mg/kg) is a commonly used index to describe the toxicity of toxic substance or the degree of radiation. The smaller the value of LD_{50} is, the stronger the toxicity of the substance is. Conversely, the larger the value is, the weaker the toxicity is. According to Book of Chemical Substances Toxicity (Philip H H *et al*. 1991), based on LD_{50}, toxicity can be rated to 5 classes: $LD_{50}>5\ 000$, $500\leqslant LD_{50}\leqslant 5\ 000$, $50<LD_{50}\leqslant 500$, $1<LD_{50}\leqslant 50$, $LD_{50}\leqslant 1$. The pollutants of each grade are as shown in Table 1.

2.2 Degradability index

The degradability of pollutants is determined by their half-life period in soil. The degradation rates of the pollutants in nature vary largely due to their own molecule structural differences. The specific numerical values of half-life can be found in Handbook of Environmental Degradation rates (Philip H H *et al*. 1991). The pollutants with longer half-life period are more difficult to be degraded, may cause greater harm and be rated in higher degradation rate. In Handbook of Environmental Degradation Rates, the half-life period is divided into 4 levels as per degradation time: T<1 day, 1 day≤T≤7 days, 7 days≤T≤4 weeks, 4 weeks≤T≤6 months. The pollutants of each level are as shown in Table 2.

Table 1 Petroleum pollutants toxicity grading

Grade	Oral test with rats	Name of pollutant
1	Slight toxicity	methyl ethyl ketone, acetidin, butyl acetate, methyl alcohol, ethyl alcohol
2	Low toxicity	dichloromethane, trichloromethane, carbon tetrachloride, benzene, methylbenzene, dimethylbenzene, acetone, isopropanol, ethylbenzene, etrachloroethylene
3	Moderate toxicity	dichlorobenzene, phenol, N-Nitrosodiethylamine, naphthaline, nitrobenzene
4	High toxicity	N/A
5	Lethal toxicity	N/A

Table 2 Pollutant degradation classification

Grade	Degradability level (Time: t)	Name of pollutant
1	Fast	ethyl alcohol
2	Moderately fast	phenol, methyl alcohol, isopropanol, methyl ethyl ketone, acetidin, acetone, butyl acetate
3	Slow	Methylbenzene
4	Resistant	dichloromethane, tetrachloromethane, ethylbenzene, naphthaline, dichlorobenzene dimethylbenzene, nitrobenzene, N-nitrosodiethylamine, benzene, tetrachloroethylene, trichloromethane

2.3 Migration index

Migration is a property that can indicate the diffusion condition of the pollutants. The degree of migration may affect the perniciousness of the pollutant directly. The stronger the migration is, the greater harm it may do. Assuming that the pollutants migrate in the same aquifer, then the migration of pollutants in groundwater will be only affected by the density and coefficient of kinematic viscosity, without considering the hydrodynamic condition.

If the density of pollutants is greater than that of water, the pollutants will mainly migrate vertically in the aquifer; if the density of pollutants is less than that of water, the pollutants will mainly migrate laterally in the aquifer. Based on the density of pollutant relative to that of water, we classify the migration of pollutants into two types, namely, lateral migration and vertical migration, as shown in Table 3.

Table 3 Contaminant migration classification

Migration	Name of pollutant
Lateral migration	acetidin, butyl acetate, N-nitrosodiethylamine, benzene, methylbenzene, dimethylbenzene, methyl ethyl ketone, methyl alcohol, isopropanol, acetone, ethyl alcohol, ethylbenzene
Vertical migration	carbon tetrachloride, tetrachloroethylene, trichloromethane, dichloromethane, dichlorobenzene, phenol, naphthaline, nitrobenzene

According to the equation $K = \frac{\rho . g}{\mu} .k$ (*K* - permeability coefficient, *p* - density, *g* - gravity coefficient, *k* - permeability rate, μ - coefficient of kinematic viscosity) (WANG Da-chun *et al.* 1980), in the same aquifer, the factors that affect the migration is the ratio between the relative density and coefficient of kinematic viscosity. The higher the ratio is, the stronger the migration are and conversely, the lower the ratio is, the weaker the migration is. In a condition that the coefficient of kinematic viscosity is unavailable, it can be considered as 1. The vertical migration and lateral migration can be divided into 4 levels based on the relative density, as shown in Table 4 and Table 5.

Table 4 Lateral migration of pollutants based grading

Grade	Migration level (density relative to water)	Name of pollutant
1	<0.79	acetone, ethyl alcohol, ethylbenzene
2	0.79-0.84	methyl ethyl ketone, methyl alcohol, isopropanol
3	0.84-0.89	benzene, methylbenzene, dimethylbenzene
4	0.89-1.00	acetidin, butyl acetate, N-nitrosodiethylamine

Table 5 Contaminants to migrate vertically oriented classification

Grade	Migration level (density relative to water)	Name of pollutant
1	1.00-1.30	dichlorobenzene, phenol, naphthaline, nitrobenzene
2	1.30-1.50	dichloromethane
3	1.50-1.60	trichloromethane
4	>1.60	carbon tetrachloride, tetrachloroethylene

2.4 Water solubility index

Water solubility is an index indicating the water solubility of the pollutant. The more soluble the pollutant is, the larger harm it may cause. According to the chemicals database, the water solubility of organics is classified into 3 levels: soluble, slightly soluble and indissoluble. The research pollutants in this paper, based on the description of their water solubility, are classified into 3 levels, as shown in Table 6.

3 Discussion on classification of typical petroleum pollutants

3.1 Determination of index weight

The toxicity may cause a more direct influence on groundwater environment than the migration, degradability and water solubility do in terms of the water quality of water supply and the influence range and influence degree. The migration and degradability have similar influence on the groundwater environment in terms of time and space. Preceding research results show that most organic pollutants are dissoluble in water. So, the water solubility may have the lowest influence on the groundwater environment. The migration of the pollutants in the same aquifer can be determined based on the empirical value, the lateral migration being about 10 times of the vertical migration.

According to the grades by experts, we set up a judgment matrix of the evaluation indexes (as shown in Table 7), calculate the initial weight of each evaluation index, then normalize these initial weights and finally figure out the weight coefficient of each index.

Through the calculations as per equation (1)-(5), we get the results that CI =0.0341＜0.1 and the matrix can satisfy the uniformity. Thus we can preliminarily determine the weight of each evaluation index of the pollutants: toxicity - 0.4110, migration - 0.2460, degradability - 0.2460 and water solubility - 0.0969.

Table 6 Classification of water-soluble contaminants

Grade	Water solubility level	Name of pollutant
1	Indissoluble	naphthaline, tetrachloroethylene, nitrobenzene, ethylbenzene, dimethylbenzene, methylbenzene, benzene, dichlorobenzene, trichloromethane
2	Slightly soluble	dichloromethane, carbon tetrachloride, acetidin, butyl acetate, phenol
3	Soluble	acetone, methyl ethyl ketone, methyl alcohol, ethyl alcohol, isopropanol, N-nitrosodiethylamine

Table 7 Evaluation of the judgment matrix

Judgment matrix (P)	Toxicity (W_1)	Migration (W_2)	Degradability (W_3)	Water solubility (W_4)
Toxicity (W_1)	1	9/5	9/5	4
Migration (W_2)	5/9	1	1	3
Degradability(W_3)	5/9	1	1	3
Water(W_4)	1/4	2/5	2/5	1

Table 8 Results of each evaluation pollutants

Pollutants of evaluation index	Toxicity	Migration	Degradability	Water solubility	Comprehensive
Methyl ethyl ketone	0.411	0.221	0.246	0.291	1.169
Methyl alcohol	0.411	0.443	0.492	0.097	1.443
Isopropanol	0.411	0.443	0.492	0.291	1.637
Ethyl alcohol	0.822	0.443	0.246	0.291	1.802
Acetone	0.822	0.221	0.492	0.291	1.826
Phenol*	1.233	0.025	0.492	0.194	1.943
Trichloromethane*	0.822	0.074	0.984	0.097	1.977
Acetidin	0.411	0.886	0.492	0.194	1.982
Butyl acetate	0.411	0.886	0.492	0.194	1.982
Tetrachloroethylene*	0.822	0.098	0.984	0.097	2.001
Dichlorobenzene*	0.822	0.049	0.984	0.194	2.049
Carbon tetrachloride*	0.822	0.098	0.984	0.194	2.098
Dichloromethane	0.822	0.664	0.492	0.097	2.075
Methylbenzene	0.822	0.664	0.492	0.097	2.075
Ethylbenzene	0.822	0.221	0.984	0.097	2.124
Benzene	0.822	0.664	0.738	0.097	2.321
Dimethylbenzene*	1.233	0.025	0.984	0.097	2.339
Naphthaline*	1.233	0.025	0.984	0.097	2.339
Nitrobenzene*	1.233	0.025	0.984	0.097	2.339
N-nitrosodiethylamine	1.233	0.886	0.984	0.291	3.393

Note: * means vertical migration while others are lateral migration; hereinafter inclusive.

Table 9 Table of pollutants management

Classification	Pollutant managed	Management measures
Level IV	methyl ethyl ketone, methyl alcohol,	Ordinary supervision, routine monitoring
Level III	isopropanol, ethyl alcohol, acetone, phenol*, trichloromethane*, acetidin, butyl acetate	Ordinary supervision, key monitoring
Level II	tetrachloroethylene*, dichlorobenzene*, carbon tetrachloride *, dichloromethane, methylbenzene, ethylbenzene, benzene, dimethylbenzene*, naphthaline*, nitrobenzene*	Key supervision, key monitoring
Level I	N-nitrosodiethylamine	Strict confinement, key monitoring

3.2 Characteristics classification of pollutants

By calculating the comprehensive value of each pollutant, we get the results as shown in Table 8, which ranges from 1.0-3.5. The pollutant with higher comprehensive value may do more harm, while the one with lower comprehensive value may do less harm relatively. The classification of hazardous pollutants is determined as following: Level I (comprehensive value$\geqslant$2.5), Level II (2.0$\leqslant$comprehensive value$<$2.5), Level III (1.5$\leqslant$comprehensive value$<$2.0), Level IV (comprehensive value$<$1.5).

According to the calculation results, the petroleum pollutants are classified into 4 levels and corresponding management groups for typical petroleum pollutants in groundwater are formulated, as shown in Table 9.

4 Conclusions

(1) Hydrogeological condition has a certain influence on the migration and degradability of the typical petroleum pollutants in groundwater. The research result is reached based on the assumption of a uniform aquifer medium and the characteristics of the pollutants in groundwater may have certain reference significance for the future research. However, when applied in specific region, the vulnerability evaluation index of the groundwater shall also be considered.

(2) Comparing the classification result with the physical and chemical characteristics of each pollutant, we found that the result conforms to the actual effect of pollutants in groundwater in general, which indicates that the classification method for petroleum pollutants in groundwater based on AHP is rational. However, since the gasoline and diesel are mixtures with complicated composition, this classification method is not suitable for them and further study shall be conducted on them to find a suitable classification method.

(3) The classification method employed this time can generally satisfy the requirement of the selected 22 kinds of research objects. However, considering the wide varieties of the petroleum pollutants in groundwater and the complicated and variable influence factors, further studies shall be also carried out with additional evaluation indexes taken into consideration, such as, leaching migration of organic pollutants (Guzzella L, *et al*. 2006; Gustafson D I, 1989), bioaccumulation, octanol-water partition coefficient (Kow) (CHEN Hong-ping *et al*. 2004), sediment-water partition coefficient (Koc), microorganism-water partition coefficient (KB), Henry's constant (Hc), photolysis rate constant (Kox), biotrasformation rate constant (Kh) (QUAN Xie *et al*. 1996) *etc*, thus to set up a complete and accurate classification system for petroleum pollutants in groundwater.

(4) On the basis of the classification result of this research, strict supervision on the organic pollutants generated during the storage, transportation and processing of petrochemical products shall be carried out, corresponding prevention and control measures shall be formulated and intensified monitoring shall be conducted on the existing pollution sources.

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