Analysis of the Control Factors of Groundwater Petroleum Hydrocarbons Contamination in a City’s West Part

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Abstract. Based on study of the hydrogeological condition and the characteristics of petroleum hydrocarbons pollution in karst groundwater, an oil refinery located in western part of a certain city is chosen as the study site to have an analysis on the control factors of groundwater petroleum hydrocarbons contamination. The study result shows that the control factors of groundwater petroleum hydrocarbons contamination are hydrogeological condition and biodegradation. The soil layer of Quaternary is very thin, the limestone is exposed in the surface, which makes the petroleum hydrocarbons easy to permeate into the water bearing layer. Karst-fractured zone in aquifer determines the migration way of petroleum hydrocarbons to be convection, but the magmatic rock in northern part has certain blocking effect on the migration of petroleum hydrocarbons. Biodegradation makes both the contamination plume area of petroleum hydrocarbons and the content of petroleum hydrocarbons decreased.

1. Introduction
With the rapid development of China’s petroleum industry, the contamination of soil and petroleum hydrocarbons in groundwater system becomes even more serious day by day, and its sphere of affection expands wildly\cite{1}. A great amount of petroleum hydrocarbons inevitably enter the environment as a result of accidents and improper handling in the exploitation, transport, and refinery of crude oil. Petroleum pollutants can not only permeate into surface water body, causing surface water contamination, but also can permeate into deep soil and groundwater, causing groundwater contamination\cite{2}. Among a large number of pollutants, the contamination caused by petroleum components in underground environment arouses the most attention. In 2000, Favara had a research on the spatial evolution of hydro-chemical field of groundwater and the process of groundwater pollution there in Salso River Basin, finding that the primary pollutant in the region was urban waste water. It indicated that the hydrochemical field of groundwater had close connection with the formation and distribution of groundwater pollutants\cite{3} . Xiaoli Lv had a detection on the VOCs (volatile organic compounds) existing in groundwater of a petrochemical site in a northwest capital city. The results showed that BTEX had a higher detection rate, as high as 60%. The source of petroleum hydrocarbons contamination in groundwater there mainly came from the crude oil storage tanks in petrochemical site, the leakage of grease trap, and the unreasonable industrial sewage discharge in the process of oil refining and machining operation\cite{4}. When petroleum hydrocarbons are released into the environment, microbial transformation and degradation can be chosen as the main way to remove them. Thus, more and more research interests are turning to the biodegradation. On the basis of distribution
characteristics of petroleum hydrocarbons contamination in groundwater, a western oil refinery in a city is chosen as the research site, in which it has a study about the control function on petroleum hydrocarbons contamination by analyzing hydrogeology condition, biological degradation and other factors.

2. Overview of the study area
The study area is located in western part of a certain city, whose southern part is mountainous area with higher ground and northern part is plain with low-lying.

The aquifer in groundwater system is the Paleozoic Ordovician limestone and Quaternary loose rock mass. Ordovician limestone forms in karst-fissure, which has strong permeability and hydraulic conductivity, and it is the main water-bearing formation in the area. Water-bearing layer plays a great important role in the research on groundwater contamination, whose karst-fissure provides necessary conditions for the infiltration of surface water and the migration of groundwater. The water in the study area flows from southeast to northwest in karst-fissure.

3. The distribution characteristics of petroleum hydrocarbons contamination
On the basis of environmental geological survey in the study area, combining with cluster analysis method it had a qualitative analysis on the sources of petroleum hydrocarbons contamination in the study area. A quantitative calculation was adopted to calculate the contribution rate of pollution sources by using of multivariate linear regression model, which showed that the petroleum pollution sources had contribution rate of 68.62%. Therefore, the petroleum pollutants is the main source of petroleum hydrocarbons in karst-fissure groundwater in the study area.

In the case of the presence of pollution, in 1991 petroleum hydrocarbons contamination in groundwater had the largest area (Figure 1), take 0.05mg/L as limit, the contamination area covered approximately 3km². The monitoring hole (J20) nearby the oil refinery had the highest concentration of petroleum hydrocarbons, up to 1.77mg/L, exceeding the standard by 35.4 times. J20 as center, petroleum hydrocarbons spread out all around with concentration decreasing gradually, it moved fast along with groundwater flowing direction, forming an oval contamination plume that distributed long-narrowly and its long axis barely had same direction with the groundwater flowing.

After cutting off pollution sources, according to the monitoring data from 1998, 2007 and 2016, it showed that the concentration of petroleum hydrocarbons nearby oil refinery were all below the detection limit (0.05mg/L), the contamination plume moved towards the lower reaches due to the influence of the groundwater hydrodynamic field. Monitoring hole J11 as contamination center, the highest contamination was respectively 0.34mg/L, 0.24mg/L and 0.18mg/L. It could be seen from the figures (Figure 2, Figure 3, Figure 4) that the petroleum hydrocarbons contamination plume in the lower reaches had relatively stable spatial distribution, but the pollution gradually reduced, which can show as the contamination plume area reducing and the petroleum hydrocarbons concentration decreasing in monitoring hole. The area of contamination plume has decreased from 1.24km² in 1998 to be 0.96km² in 2007 and 0.85km² in 2016. The concentration of pollution center decreased from 0.34mg/L in 1998 to be 0.24mg/L in 2007 and 0.18mg/L in 2016.
4. Controlling factor analysis

4.1. Hydrogeological condition

The oil refinery in the study area is located at the joint zone between the bare limestone and Quaternary, partial limestone is exposed in ground, the lithology of aeration zone is limestone. The soil layer of Quaternary is very thin, the limestone is exposed in the surface, which makes the petroleum hydrocarbons easy to permeate into the water bearing layer.

The medium property in aquifer determines pollutions transport pathways and migration distance. The groundwater flow rate can affect the distribution and accumulation of organic pollutants in groundwater environment, and it affects mostly the transport of organic pollutants\[5\]. The oil refinery locates in the recharge runoff area of aquifer, whose lithology is Ordovician limestone. Karst-fractured
zone in aquifer has good property of permeability and has strong runoff zone, through which petroleum hydrocarbons seeping into underground will migrate fast towards the lower reaches along with the groundwater flow, thus the groundwater in the lower reaches get contaminated. Therefore, the distribution of contamination area shows long-narrow shape. Pollutants in the stationary groundwater, only the molecular migration and diffusion, and in the moving groundwater, the pollutants can migrate faster with the flow, which is the convective migration of the pollutants. The quantity of polluted convective migration is related to the pollutant concentration and the velocity of groundwater. The characteristics of aqueous medium in the study area determines that the main migration of petroleum hydrocarbons in groundwater is convection. Calculation of migrate mass of petroleum hydrocarbons in convection: the velocity of groundwater is 12.96m/d; calculating it with the highest concentration 1.77mg/L in monitoring hall near the oil refinery, we can get the highest convective migrated mass in groundwater nearby the oil refinery 23g/(m²·d). Calculation result shows that the groundwater velocity is the main control factor in groundwater migration of petroleum hydrocarbons. The calculation formulas of pollutants convective migrated mass is like following:

\[ C_k = C \times V \]  \hspace{1cm} (1)

\( C_k \) is the migrated pollutants mass caused by convection. \( C \) is the concentration of pollutants in groundwater. \( V \) is the velocity of groundwater flow.

According to the distribution isgrams of petroleum hydrocarbons contamination, it can be seen that the northern edge part of contamination plume keeps relatively stable. The contamination center also keeps relatively stable after cutting off the pollution source, and the migration speed gradually slows down. That is also closely connected with the hydrogeology conditions. Northern part of the study area distributes magmatic rocks, their occurrence usually shows as laccolith and sill, and their lithology shows mainly as gabbro and diorite that are buried under Quaternary. Because gabbro and diorite has poor permeability property, they can be used as water-blocking rock mass. These natural water-blocking barriers distributing in the northern part of the study area obstruct the groundwater flow, making the groundwater flow slow down; meanwhile it controls the migration of petroleum hydrocarbons. Hence, the contamination plume of petroleum hydrocarbons in northern part has a relatively stable distribution, and its migration towards the lower reaches keeps slow.

To sum up, the groundwater petroleum hydrocarbons contamination gets obviously controlled by the hydrogeology condition. Because the soil layer of Quaternary in oil refinery is very thin and its limestone aeration zone has good permeability property, pollutants are easy to permeate into the aquifer. The lithology of aquifer is Ordovician limestone and Karst-fractured zone in aquifer has strong runoff area, where groundwater flows fast and the pollutants can migrate quickly towards the lower reaches, the migration being mainly the convection. The magmatic rock distributing in northern part can plays a blocking role to slow down the migration speed of petroleum hydrocarbons.

4.2. Biodegradation

It can be seen from the distribution characteristics of groundwater petroleum hydrocarbons that the contamination degree of groundwater petroleum hydrocarbons keeps decreasing to be lighter, contamination area keeps reducing, and the contamination concentration also keeps decreasing. All of these are mainly the result of biodegradation of petroleum hydrocarbons. Biodegradation of groundwater petroleum hydrocarbons can change the groundwater chemical composition, thus through analyzing the electron acceptors in contamination plume, the metabolite of biodegradation and quantity change of important geochemical parameters it can acquire the geochemical evidence of biodegradation[6],[7]. The occurrence of petroleum hydrocarbons biodegradation needs microbes, carbon source, energy as well as electron acceptor that can degrade petroleum hydrocarbons. Microbes exists widely around underground environment, which can take petroleum hydrocarbons as their carbon source and energy, and electron acceptor is the main factor of petroleum hydrocarbons biodegradation. Electron acceptor mainly includes \( O_2 \), \( NO^3- \), \( Fe^{3+} \), \( SO_4^{2-} \), \( CO_2 \), and etc. Groundwater in
the study area contains $O_2$, $NO_3^-$, $Fe^{3+}$, $SO_4^{2-}$. $O_2$ and $Fe^{3+}$ does not contribute a lot to the biodegradation of petroleum hydrocarbons because their content in groundwater is very small, hence it mainly considers $NO_3^-$, $SO_4^{2-}$ as the biodegradation of electron acceptor. The connecting line among monitoring hole J01, J05 and J09 basically keeps same direction with the long axis of petroleum hydrocarbons contamination plume. The change situation of hydrochemical field in monitoring hole can be considered as changes of hydrochemical field along with water flow. A line chart (Figure 5) can be drawn according to the change situations of electron acceptor concentration and bicarbonate concentration in monitoring hole. It can be seen from the figure that along with the groundwater flow direction the petroleum hydrocarbon concentration gradually decreases, electron acceptor concentration gradually increases, and bicarbonate concentration also gradually decreases. It can proves that petroleum hydrocarbons in groundwater has biodegradation process. It is the groundwater hydrochemical field that provides favorable condition for biodegradation that the petroleum hydrocarbon biodegradation is able to happen. In the condition of cutting off the pollutants, the amount of groundwater petroleum hydrocarbons keeps decreasing, and the contamination situation is able to get controlled.

![Figure 5. Electron acceptor and bicarbonate concentration.](image)

5. Conclusion

Characteristics of petroleum hydrocarbons in the study area: petroleum hydrocarbons contamination plume is close to oval shape, its long axis is nearly same with groundwater flowing direction. In the condition of cutting off pollutants, the contamination plume will migrate towards the lower reaches along with groundwater flowing, its area and concentration will both gradually reduce.

Groundwater petroleum hydrocarbons contamination is controlled obviously by hydrogeology condition. Pollutants are easily to permeate into the aquifer because the soil layer of Quaternary in oil refinery is very thin and its limestone aeration zone has good permeability property. The lithology of aquifer is Ordovician limestone, Karst-fractured zone in aquifer has strong runoff area, where groundwater flows fast and the pollutants can migrate quickly towards the lower reaches, with the migration as the main convection. Magmatic rock distributing in north part will slow down the migration speed of petroleum hydrocarbons.

The electron acceptor concentration along with groundwater flow in study area shows that the petroleum hydrocarbons has biodegradation. Influenced by the control function from biodegradation, the content of groundwater petroleum hydrocarbons keeps decreased, the contamination plume is also under control and its area gradually reduces.

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