



Contamination and natural attenuation characteristics of petroleum hydrocarbons in a fractured karst aquifer, North China

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Abstract

A rare super-large fractured karst aquifer located in Zibo city, Shandong Province of Northern China was polluted by petroleum hydrocarbons from a petrochemical company. Over the last 30 years, it has been the focus of several remediation efforts. In this study, the contamination and natural attenuation characteristics of the petroleum hydrocarbons were elucidated using hydrogeochemical indicators (DO, DOC, Cl^- , HCO_3^- , pH, NO_3^- , and SO_4^{2-}), petroleum hydrocarbons elements and environmental isotopes ($\delta^{15}\text{N}_{\text{NO}_3}$, $\delta^{18}\text{O}_{\text{NO}_3}$, $\delta^{13}\text{C}_{\text{DIC}}$, and $\delta^{13}\text{C}_{\text{DOC}}$). With the aid of GIS, statistical analyses, as well as first-order decay model and electron-acceptor-limited kinetic model, the spatio-temporal evolution characteristics of the petroleum hydrocarbons were modeled. Results showed a positive natural attenuation trend over the last 3 decades where intrinsic biodegradation mechanism was found to be the most important factor driving the degradation of hydrocarbons in the aquifer system. The hydrogeochemical association between the indicators and petroleum hydrocarbons provided the evidences of biodegradation and also served as markers, highlighting the occurrence of anaerobic respiration without methanogenic activities within the heterogeneous karst media. Furthermore, the mean natural attenuation rate of petroleum hydrocarbons was calculated to be $3.76 \times 10^{-3}/\text{day}$ whereby the current highest petroleum hydrocarbons concentration ($361.13 \mu\text{g/L}$) is estimated to be degraded completely in 6 years under the present hydrogeological and environmental conditions.

Keywords Petroleum hydrocarbons · Fractured karst aquifer · Natural attenuation · Hydrogeochemical indicators · Environmental isotopes

Highlights

- Spatio-temporal concentrations of petroleum hydrocarbons had an obvious decreasing trend over the last 30 years with a mean natural attenuation rate of $3.76 \times 10^{-3}/\text{day}$.
- The occurrences of aerobic and anaerobic respiration without methanogenic activities were demonstrated by analyzing hydrogeochemical indicators, petroleum hydrocarbons and environmental isotopes.
- The current highest petroleum hydrocarbons concentration ($361.13 \mu\text{g/L}$) in the contaminant sources area could be degraded completely in 6 years based on the present biodegradation capacity and mean natural attenuation rate.

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Introduction

Petroleum hydrocarbons have become the most common groundwater contaminants because of their extensive use by humans (Marić et al. 2018) and are reported to be a serious environmental problem globally (Lv et al. 2019). Hydrocarbons are persistent organic contaminants in the environment (Lang et al. 2016; Marić et al. 2018) with most of their compounds being carcinogenic, teratogenic, and mutagenic, as such, have severe impact on ecological biodiversity (Lv et al. 2019). In groundwater, petroleum hydrocarbons pose significant risks to human health, especially in areas where groundwater resources are the main water sources (Qian et al. 2018; Lee et al. 2019; van der Waals et al. 2018). Consequently, several studies have focused on not only the cost but also the effectiveness of groundwater remediation methods (Lv et al. 2018).

Natural attenuation is one of the bio-remediation methods gaining attention in numerous remediation strategies (Lv et al. 2018; Marić et al. 2018). It is a passive remedial approach which might combine a variety of physical, chemical or biological mechanisms in order to reduce the toxicity, mobility, mass, or concentration of contaminants in the environment (Chiu et al. 2017). The non-destructive physical processes of natural attenuation are dissolution, advection, dispersion, diffusion, and sorption, whereas biodegradation is the main destructive mechanism that drives natural attenuation (Marić et al. 2018). It is the only process that breaks down the hydrocarbon bonds (thereby eliminating toxicity) where the by-products have no negative impact on the surrounding environment (Declercq et al. 2012; Kim et al. 2013; Chiu et al. 2017; Müller et al. 2017; Lv et al. 2018; Sperfeld et al. 2018). Consequently, bioremediation is a more field-applicable, economical, energy saving, and environmentally sustainable technology for treating petroleum hydrocarbon polluted sites. It has become an attractive alternative remedial approach in numerous remediation strategies (Varjani and Upasani 2017; Chiu et al. 2017; Marić et al. 2018; Lee et al. 2019). Natural biodegradation meets the criteria of the green remediation concept (being an in situ, passive, and biological method) and is also a sustainable technology that is not expected to cause secondary pollution problems (USEPA 2010; Lee et al. 2019).

For petroleum hydrocarbons, the intrinsic biodegradation mechanism occurs as a sequence of oxidation and reduction reactions where the hydrocarbons become the electron donors and dissolved oxygen (DO) the acceptor under aerobic biodegradation conditions and processes. However, under anoxic or anaerobic biodegradation conditions, NO_3^- , Mn^{4+} , Fe^{3+} , SO_4^{2-} , and HCO_3^- are the priority order of electron acceptors (McMahon and Chapelle 2008; Cassidy et al. 2015). Long-term exposure of groundwater to petroleum hydrocarbons would have great influences on the chemical and isotopic

compositions of the water. Spatial and temporal variation of hydrochemical indicators (DO, NO_3^- , Mn^{4+} , Fe^{3+} , SO_4^{2-} , and HCO_3^-) would demonstrate the corresponding mechanisms of biodegradation (Lv et al. 2018). Spatial and temporal evolution of hydrochemical indicators would also reveal the occurrence and main mechanism of biodegradation (Lv et al. 2018). Physical processes, water-rock interaction and other non-biological processes also have great influences on the concentrations of geochemical indicators (Lv et al. 2019). The isotope ratios of degradation products and electron acceptors could be used to evaluate petroleum hydrocarbons degradation (Lv et al. 2019). Intrinsic degradation of ^{13}C -depleted organic matter without methanogenic process would decrease the $\delta^{13}\text{C}_{\text{DIC}}$ in groundwater (Lv et al. 2018). However, there would be a distinct fractionation of stable C isotope between CO_2 and CH_4 during the methanogenesis process (Jones et al. 2008; Amos et al. 2011). Influences of methanogenic microorganisms could produce ^{13}C -depleted CH_4 and ^{13}C -enriched CO_2 , the dissolution of ^{13}C -enriched CO_2 would increase the $\delta^{13}\text{C}_{\text{DIC}}$ in groundwater (Lv et al. 2018). Oxide ions in groundwater would have enriched isotopes because of the preferential utilization of the lighter isotopes by microorganism (Lv et al. 2018).

Karst aquifers play a key role in supplying drinking water to about one quarter of the world's population (Hillebrand et al. 2015). However, they are vulnerable to contamination due to their high hydraulic conductivities and short residence times (Hillebrand et al. 2015). Therefore, it is vital to understand the mass transport and attenuation processes of contaminants in order to protect and manage karst groundwater resources.

In this study, a very-large fractured karst aquifer that was contaminated by petroleum hydrocarbons was selected for investigation. The site is located in Zibo city, Shandong Province where karst aquifers are the main water source for the inhabitants (Guo et al. 2016). The contamination occurred in 1980s due to production activities by a local petrochemical company (Li et al. 2001). The petrochemical company (comprising alkene plants, alkali-chlorine plant, plastic plants, and others) was built in the 1980s (Zhu et al. 2000). More than 60 species of organic compounds were found in monitoring wells sited in the location in 1990s (Chen et al. 2000). The highest detected contamination level was 78.23 mg/L in July, 1994, which is about 261 times more than the drinking water standard value of 0.30 mg/L in the GB 5749–2006 (2006) of China.

Over the past few decades, several researchers have studied the hydrogeochemical changes induced by oil sewage leakage into the water source (Liu et al. 1996; Chen et al. 1998; Chen and Zhu 1999; Zhu et al. 2000; Liu 2013). Others evaluated the karst groundwater quality and environment based on qualitative or semiquantitative methods (Li et al. 2001; Xing et al. 2008; Guo et al. 2016; Guo et al. 2018). However, the evolution processes, natural attenuation and intrinsic

biodegradation mechanisms of the contaminants at the site have not been described in detail. The migration mechanisms of petroleum hydrocarbons are important in predicting, controlling and remediating organic contaminations in the fractured karst aquifer. Hence, in this paper, data describing hydrogeochemical indicators, petroleum hydrocarbons, and environmental isotopes were collected and analyzed to elucidate the contamination and natural attenuation characteristics in the groundwater system over the last three decades. Overall, the objectives of the research were to (1) determine the evolution characteristics of petroleum hydrocarbons contamination in the last three decades, (2) evaluate and elucidate the biodegradation processes of petroleum hydrocarbons based on important hydrogeochemical indicators (DO , DOC , Cl^- , HCO_3^- , pH , NO_3^- , and SO_4^{2-}), (3) identify the intrinsic biodegradation mechanisms of petroleum hydrocarbons, and (4) calculate the petroleum hydrocarbons decay rate and predict the biodegradation trend of petroleum hydrocarbons.

Materials and methods

Description of the contamination site and groundwater characteristics

The contamination site, with a spatial coverage of $\sim 115 \text{ km}^2$, is a karst water source located in the Linzi district of Zibo City, Shandong Province, China. The area is characterized by a warm temperate continental monsoon climate with an average annual temperature of 13.1°C and rainfall of 630 mm, occurring between July and September (Guo et al. 2016).

It is a rare super-large fracture-karst water source that supplies water to the inhabitants of the city. All faults mapped in Fig. 1 can transport water from one side to the other (Zhu et al. 2000; Guo et al. 2016). Recharging sources of groundwater are mainly from lateral runoff and precipitation infiltration, while losses are mainly through human abstraction, lateral/baseflow discharge to rivers or evaporation from shallow aquifer (Guo et al. 2016). There are two aquifer groups. The first is the upper aquifer group located at the piedmont tending north mainly comprise of Quaternary, the lithology of which is loose rock mass (Sandy conglomerate) (Fig. 1). The second group comprises Ordovician limestone, leopard limestone, dolomitic limestone, and dolomite, which are thick-bedded (Fig. 1). The formations fractured, karstified and form a uniform aquifer system (Guo et al. 2018). The thickness of the Quaternary aquifer is between 20 and 160 m as shown in the hydrogeological section along the main groundwater flow path (Fig. 1). Groundwater samples for this work were collected from the carbonate aquifers with the sampling well depth greater than 200 m. The major groundwater flow direction is northeast-east (NEE), while the coefficients of transmissivity in the carbonate aquifers were reported to be high,

between 35,000 and 50,000 m^2/day (Zhu et al. 2000). Similarly, tracer tests showed very high groundwater flow velocities, between 5352 and 14,400 m/day (Zhu et al. 2000).

Based on the occurrence of groundwater, water types can be classified into porous water, carbonate rock fracture water, clastic, and carbonate rock fracture water (Fig. 1a). As shown in Fig. 1a, water abundance represents the amount a well can yield as the groundwater level in it decreases by one unit length (Guo et al. 2016). Their spatial distributions of different groundwater types are shown in Fig. 1a. The Ordovician carbonate rock fracture water, with over 5000 m^3/day , is the most abundant water type in the study area (Fig. 1). Groundwater volume increases along the karstified aquifer section suggesting karst development intensity (Guo et al. 2016). There are approximately 37 monitoring wells sited at the contamination site for sampling and hydrogeological parameter estimation. Groundwater samples parallel to and perpendicular to the migration of petroleum hydrocarbons were collected over different periods.

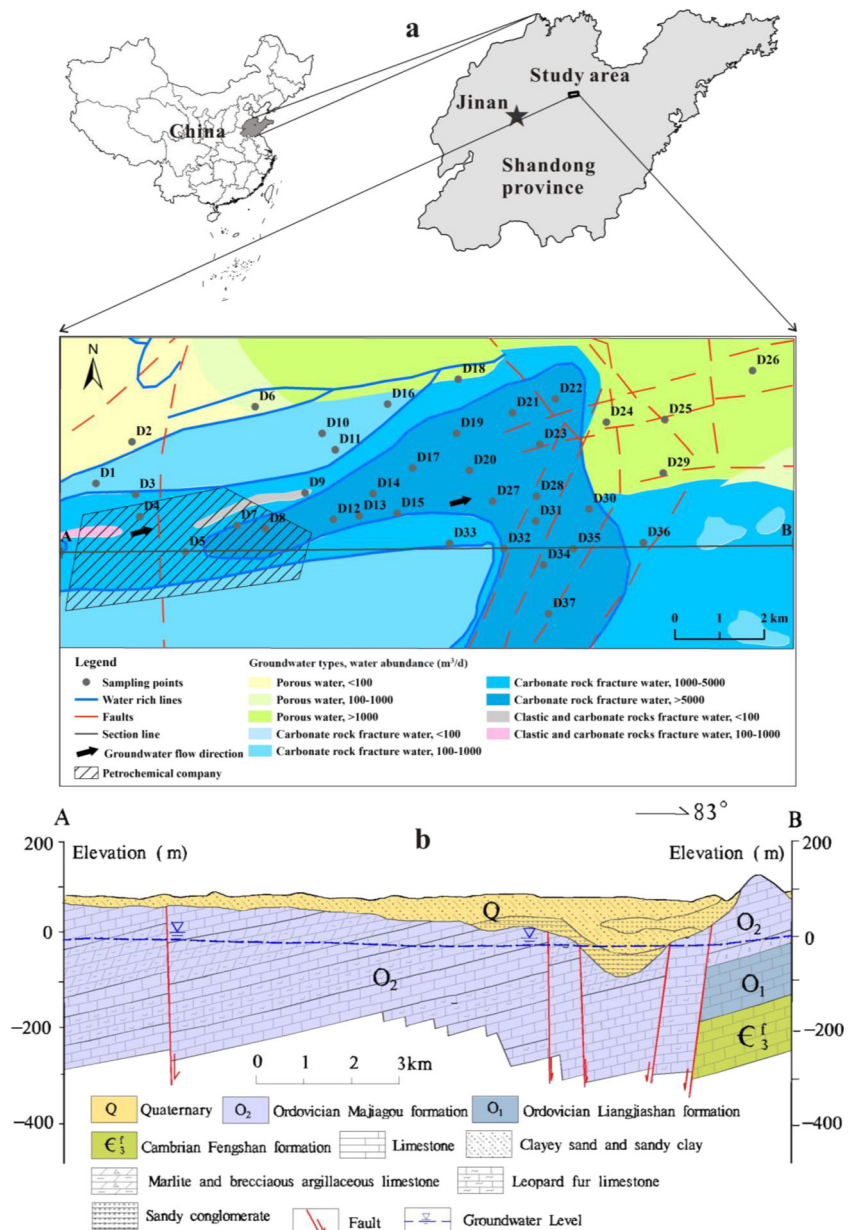
The thickness of the Quaternary structure at the contamination site is thin, making it easy for leaked oil wastewater to percolate into the aquifers (Zhu et al. 2000). In 1994, the detected concentration of total petroleum hydrocarbons was 78.23 mg/L at the leakage points (Zhu et al. 2000). Meanwhile, groundwater levels fell severely due to the high intensity of groundwater exploration by the petrochemical company (Zhu et al. 1999; Shang 2013; Guo et al. 2016). The contamination had harmful impacts on the local inhabitants (Liu et al. 1996; Chen et al. 2000). Since then, numerous remediation strategies were deployed (Liu and Dai 1996; Zhu et al. 1997; Chen and Zhu 1999; Li et al. 2001), however, the volume remediated by natural attenuation (biodegradation) has not been estimated.

Sample analyses

Hydrochemical analyses

Groundwater samples were collected by pumping water from the monitoring wells where physical and chemical properties were measured in the field. Temperature (T , $^\circ\text{C}$), pH, total dissolved solids (TDS, mg/L), oxidation-reduction potential or electric potential (ORP or Eh, mv), and dissolved oxygen (DO , mg/L) were analyzed using a multiparameter probe (PONSEL, France) with the resolutions of 0.01°C , 0.01 pH unit, 0.1 mg/L, 0.1 mv and 0.01 mg/L, respectively. Concentrations of HCO_3^- (mmol/L) in groundwater samples were titrated in the field using a portable alkalinity meter (Merck KGaA Co., Germany) with a precision of 0.05 mmol/L. Groundwater samples for analyzing ions were collected in 500 mL high-density polyethylene (HDPE) bottles; while samples for cations were acidified to $\text{pH} < 2$ with 1:1 HNO_3 . Each petroleum hydrocarbons analysis sample was

Fig. 1 The study area. **a** The hydrogeological map and sampling points of the contamination site. **b** The hydrogeological section map along the groundwater flow path



collected in a 1000-mL brown glass bottle and two 40-mL brown glass bottles with polytetrafluoroethylene (PTFE) caps to avoid the influence of light.

Hydrogeochemical compositions of cations and anions, chemical oxygen demand (COD), and metal elements were analyzed by Seven multi pH/EC/ions integrated testing instrument, IRIS Intrepid II XSP ionomer spectrometer, visible spectrophotometer, and iCAPQ ionomer mass spectrometer. Petroleum hydrocarbons (including volatile and semi-volatile organic components) in groundwater samples were analyzed by LC-20A Liquid chromatography and Agilent 7890A-5975C Gas Chromatograph/Mass Spectrometer. They were measured at the Key Laboratory of Karst Dynamics/Institute of Karst Geology, CAGS, MNR&GZAR.

Isotopic analyses

Groundwater samples for stable nitrogen and oxygen ($\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$) analyses were collected in 50-mL HDPE bottles. They were measured using Gas-Bench-Mat 253 stable isotopes mass spectrometry (America, Therm corporation) with a precision of $\pm 0.3\text{‰}$ in Third Institute of Oceanography, Ministry of Natural Resources. $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ were calibrated by the N_2 in atmosphere and Vienna Standard Mean Ocean Water (VSMOW), respectively.

Groundwater samples used for the stable carbon isotopes of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) and dissolved organic carbon ($\delta^{13}\text{C}_{\text{DOC}}$) analyses were collected in 50-mL HDPE bottles added with two drops of a saturated solution of HgCl_2 .

Values of $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{DOC}}$ were measured using MAT-253 mass spectrometer (America, Thermo Fisher company) with a precision of $\pm 0.15\%$ at Third Institute of Oceanography, Ministry of Natural Resources. The stable carbon isotopic values were calibrated using the international standard Vienna Pee Dee Belemnite (VPDB).

Methods of analysis

Geospatial analysis has been widely used in analyzing spatio-temporal patterns successfully (Chien et al. 2013; Yu et al. 2015). Geographic Information System (ArcGIS 10.2) was used to analyze the spatial characteristics of petroleum hydrocarbons using inverse distance weighted (IDW) interpolation technique to describe the spatial distribution patterns of the concentration levels.

Statistical analyses often elucidate obscured relationships among hydrogeochemical indicators (pH, DO, TDS, and others) (Lv et al. 2019). Furthermore, graphical methods are employed along to describe the intrinsic biodegradation processes during remediation.

The first-order decay model is the most appropriate model for describing chemical mass of transformation reactions (Newell et al. 2014; Chiu et al. 2017; Lv et al. 2018). It is used here to calculate the natural attenuation or intrinsic biodegradation rate for individual wells and also to predict the biodegradation processes over time. The model equation is given as:

$$C_{t2} = C_{t1}e^{(-k\Delta t)} \quad (1)$$

where C_{t1} is the concentration of contaminant in the monitoring well at time t_1 ; C_{t2} is the concentration of contaminant in the same monitoring well at time t_2 ; k is the first-order decay rate constant; $\Delta t = t_2 - t_1$ ($t_2 > t_1$).

Also, the electron-acceptor-limited kinetic model is used to determine biodegradation capacity for biological reactions using electron-accepting capacity of groundwater (USEPA 2004; Chiu et al. 2017). An approximate biodegradation capacity for petroleum hydrocarbons can be determined based on the theories, procedures and average values described in (USEPA) 2004, which is expressed as:

$$\begin{aligned} BC = & (B_{\text{DO}} - S_{\text{DO}})/3.10 + (B_{\text{NO}_3^-} - S_{\text{NO}_3^-})/4.81 \\ & + (B_{\text{SO}_4^{2-}} - S_{\text{SO}_4^{2-}})/4.65 + S_{\text{Fe}^{2+}}/21.70 \\ & + S_{\text{CH}_4}/0.77 \end{aligned} \quad (2)$$

where BC is biodegradation capacity for petroleum hydrocarbons (mg/L); B_{DO} , $B_{\text{NO}_3^-}$ and $B_{\text{SO}_4^{2-}}$ are concentrations of DO, NO_3^- , and SO_4^{2-} before contamination (mg/L), respectively; S_{DO} , $S_{\text{NO}_3^-}$, $S_{\text{SO}_4^{2-}}$, $S_{\text{Fe}^{2+}}$, and S_{CH_4} were concentrations of DO, NO_3^- , SO_4^{2-} , Fe^{2+} , and CH_4 in contamination sources area (mg/L), respectively.

Results and discussions

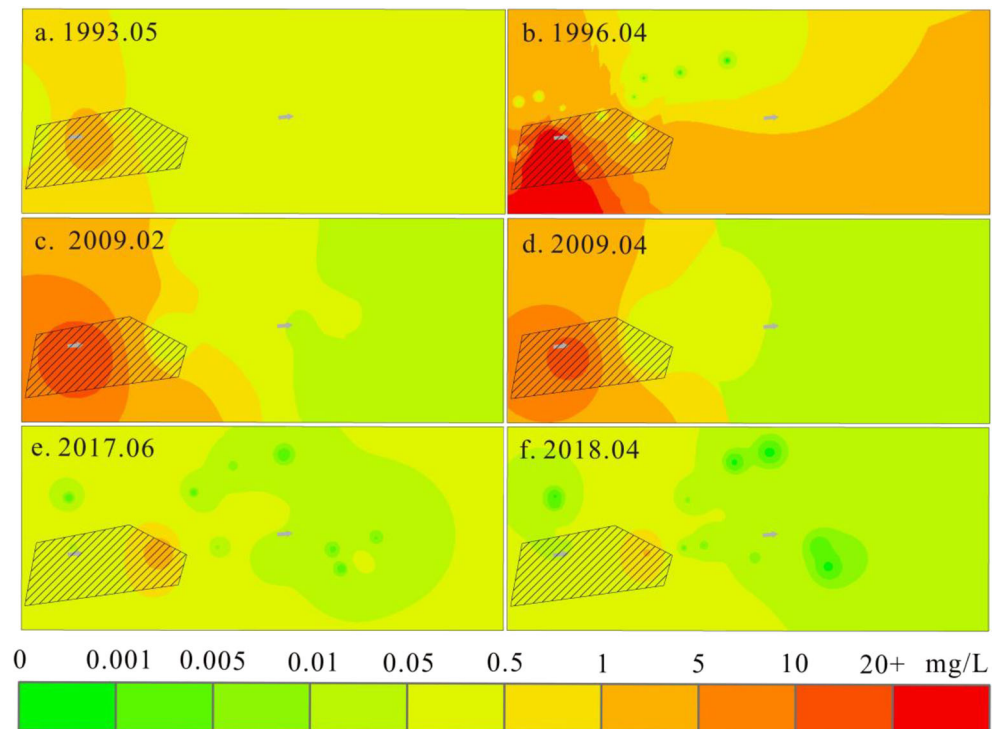
Contamination characteristics of petroleum hydrocarbons

Spatio-temporal distribution of petroleum hydrocarbons

Spatial distributions of the concentration levels of petroleum hydrocarbons in the carbonate aquifers during the last three decades (1990s, 2000s, 2010s) were mapped in Fig. 2 using ArcGIS 10.2. The spatial interpolation method (inverse distance weighted) did not perfectly depict the reality in the field due to uneven distribution of monitoring wells. This highlights the intrinsic limitation of spatial interpolation methods (Yu et al. 2015) especially when describing a non-homogeneous karst aquifer media (Guo et al. 2016). Despite this limitation, the overall trend was captured adequately as the decreasing trend in concentration levels over the last three decades is clearly demonstrated in Fig. 2. The transportation rate of dissolved contaminants has a linear relationship with groundwater velocity (USEPA 2004; Alvarez and Illman 2005), and for our study area implies strong hydrodynamics advection and dispersion due to very high groundwater velocities (Zhu et al. 2000; USEPA 2004). Evidently, the spatial distribution characteristics are controlled by the hydrodynamic conditions in the karstified aquifer. Figure 2 shows that the spatial distribution of petroleum hydrocarbons for each respective decade maintains a similar pattern where the concentration values of pollutants decrease around the contamination sources area, especially along the groundwater flow direction. Therefore, the different spatial distribution of contaminant concentration for each period was mainly defined by the varying amount of petroleum hydrocarbons recharged into the groundwater system from contamination sources.

It is important to note that the petrochemical company from which the contamination originated started production in 1987, and by 1988, oil components were detected in groundwater wells near the company site (Li et al. 2001). The wide range of petroleum hydrocarbons contamination was caused by dissolved components in the study area (Zhu et al. 2000). Concentrations of total petroleum hydrocarbons in contamination sources increased rapidly at the early stage, and then began to decrease slowly (Fig. 2). The detected concentration was not severe from 1988 to 1993 (Fig. 2a) because the oil leakage was not serious in this initial period. The concentration level in the center of the contaminant plume was highest (> 20 mg/L) in 1996, which was also reported by Chen et al. (2000) and Zhu et al. (2000). In 1996, many of the drainage pipelines placed around Ordovician limestones were damaged by corrosive wastewater; consequently, leaked oil contaminants percolated into the karst aquifer. The efficiency of remediation efforts that followed were not obvious during the early stages, as such higher levels were recorded in 1996 (Fig. 2b).

Fig. 2 The spatial and temporal concentrations of petroleum hydrocarbons in carbonate aquifers at different periods



Therefore, it became necessary to evaluate the contaminant fate, in order to improve the remediation process. It is noteworthy that large volume of groundwater in the area had very strong dilution and advection effects on the contaminant (Guo et al. 2016), as such, the lowest concentrations zones were found in areas with abundant water compared to the downstream areas as shown in Fig. 2b–f. Numerous remediation strategies were deployed in 1990s (Liu and Dai 1996; Zhu et al. 1997; Chen and Zhu 1999; Li et al. 2001), but it was not until the 2000s that the quality of karst groundwater started improving (Shang 2013). As shown in Fig. 2, the cores of contaminant plumes moved with the groundwater flow direction due to high velocity rate in the karst aquifer groundwater which transmits groundwater at maybe hundreds or thousands of times as usually observed in typical equal porous media (Zhu et al. 2000). From 1996 to 2018, concentration levels decreased from > 20 mg/L in 1996 to 10–20 mg/L in 2009, 1–5 mg/L in 2017 and 2018 establishing a strong correlation with natural attenuation. The observed spatial and temporal variation patterns of pollutants affirmed the efficacy of natural attenuation mechanism in controlling the impact of petroleum hydrocarbons in the fractured karst aquifer.

Evolution characteristics of petroleum hydrocarbons at the contamination site over time

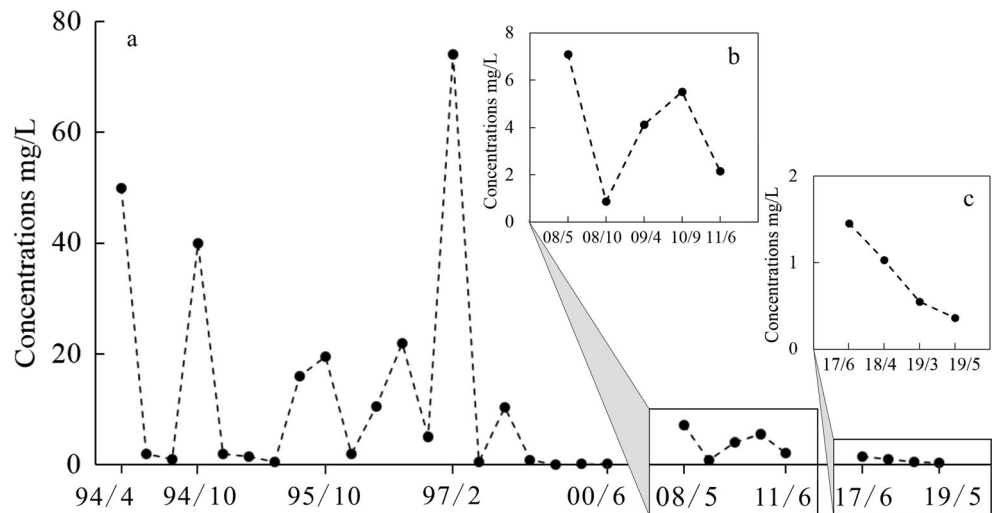
The long-term monitoring concentrations of petroleum hydrocarbons in the contamination sources area (D5) are plotted in Fig. 3, and factors influencing variation characteristics of

contaminants in the fractured karst aquifer at different monitoring periods are discussed in the following sections.

Joint actions of advection and dispersion are characteristics of petroleum hydrocarbons plume in porous media. Nevertheless, each water abundant area (Fig. 1) has unique hydraulic conductivity; hence, the transport of petroleum hydrocarbons is not uniform especially in karst media. Due to the quantity and flow velocity within the aquifer matrix, small changes in the contamination source would have a strong and immediate impact on petroleum hydrocarbons concentrations in monitoring wells. The curve of petroleum hydrocarbons versus time was plotted based on the long-time monitoring data in the contamination sources area (Fig. 3). Even though great changes existed in the variation curve, the decreasing trend of petroleum hydrocarbons concentrations is obvious over the last three decades.

The range in variation of contaminant concentrations was much and rapid in 1990s (Fig. 3a). Leakage points of oil wastewater were not controlled efficiently due to the obscurity of their locations and surrounding hydrogeological environment at the time. The leakage amount of wastewater was also not clear; meanwhile, the contaminated soil polluted by wastewater became a secondary source of petroleum hydrocarbons (Guo et al. 2016). Consequently, there was a large quantity of residual petroleum hydrocarbons in the vadose zone, the uneven precipitation in different seasons and unscheduled pumping of groundwater resulted in wider fluctuation of groundwater levels. Also, the variational hydrodynamic field carried more variable amount of petroleum hydrocarbons into the fractured karst aquifers at

Fig. 3 Variation curve of petroleum hydrocarbons over time of D5 located in contamination sources area



different periods, hence, the detected concentrations of petroleum hydrocarbons in D5 had greater changes. The fractured karst aquifer media is characterized by pores, fissures, cavities and other dual porosity matrixes, this ultimately makes for a discontinuous hydrodynamic field. Water velocity and quantity in each continuum were also various due to the nonhomogeneous aquifer media, the spatial hydrodynamic advection and dispersion of fractured karst aquifer system for the petroleum hydrocarbons were heterogeneous, and the arriving petroleum hydrocarbons to D5 had great fluctuation in different time.

Conversely, the concentrations and variation ranges were lower than the former decade (Figs. 2 and 3a, b). Particularly, from 2017 to 2019, there is drastic improvement due to the long-term effects of natural attenuation (Fig. 3c). In May 2019, only 0.36 mg/L was detected, the lowest value in decades and closer to the drinking water standard value of 0.30 mg/L based on the GB 5749–2006 (2006) of China. Meanwhile, the leaking pipes and tanks have been replaced following the excavation of the contaminated soil and the wastewater discharge treated to meet the standard. Since then, all contamination sources have been controlled, and groundwater resources are now pumped for agricultural and industrial activities. Consequently, the entire aquifer system is expected to improve significantly with time. From the foregoing analysis, we can conclude that petroleum hydrocarbons contamination levels were influenced by groundwater hydrodynamic conditions, human activities, and natural attenuation.

Groundwater chemical analyses and evidences of intrinsic biodegradation processes of petroleum hydrocarbons

Hydrogeochemical indicators are affected by various hydrobiogeochemical processes, whereby correlations among these parameters can be used to identify the dominant processes within a given groundwater system in both space and time

(Lv et al. 2019). Intrinsic biodegradation processes of petroleum hydrocarbons would decrease electron acceptors ($\text{DO} \rightarrow \text{NO}_3^- \rightarrow \text{Mn}^{4+} \rightarrow \text{Fe}^{3+} \rightarrow \text{SO}_4^{2-} \rightarrow \text{HCO}_3^-$) and electron donors (organic contamination concentrations), whereas reduction products of degradation would increase alkalinity and decrease pH through the dissolution of CO_2 .

The lithologies of the karst aquifer media are simple, i.e., calcite, dolomite, and a small amount of gypsum (Lan 1996). Elements of Ca, Mg, and C were reaction components of water-rock interaction in the aquifer in the background conditions (Lan 1996). Therefore, oxidation and reduction reactions of iron and manganese in the intrinsic biodegradation processes can be ignored in the study area.

Relationships between petroleum hydrocarbons and comprehensive indicators

$\text{D5} \rightarrow \text{D8} \rightarrow \text{D14} \rightarrow \text{D27} \rightarrow \text{D23}$, $\text{D5} \rightarrow \text{D7} \rightarrow \text{D8} \rightarrow \text{D12} \rightarrow \text{D13}$ and $\text{D8} \rightarrow \text{D13} \rightarrow \text{D17} \rightarrow \text{D28}$ are horizontal sections of the petroleum hydrocarbons plume from contamination sources area to downgradient in 1999, 2009, and 2019, respectively. Curves of petroleum hydrocarbons versus COD, TDS, or DOC of these horizontal sections were mapped and illustrated in Fig. 4. COD can represent total organic compounds in groundwater, since they had a positive relationship with petroleum hydrocarbons concentrations (Fig. 4a, b). Leakage of oil wastewater would also increase the inorganic and organic components of groundwater, as well as TDS with petroleum hydrocarbons in high concentrations (Fig. 4b, c). Therefore, TDS can be used to infer pollution levels in contamination areas. Dissolved components of petroleum hydrocarbons were found to be the main contaminants in the karst aquifer, where the pollution levels were associated with DOC (Fig. 4c). From section D8 to D17, DOC decreased with the decreasing petroleum hydrocarbons, which imply that petroleum hydrocarbons were the main organic components in the

aquifer system. For example, the sudden increment of DOC and TDS at D28 suggested that other organic contaminant sources infiltrated into D28 (Fig. 4c) due to the uniform transport channel in the karst aquifer and external factors. Since the intrinsic biodegradation processes is expected to decrease the DOC levels in the fractured karst aquifer, the ratios of petroleum hydrocarbons to DOC had an obvious decreasing trend from contamination sources area (D8) to the downstream area (D28) (Fig. 4c). The downgradient point (D28) had low contamination level and relatively high DOC, suggesting that petroleum hydrocarbons formed part of the DOC and degraded in the groundwater system (Fig. 4c) (Chiu et al. 2017).

Hydrogeochemical evidences of intrinsic biodegradation processes

The background groundwater chemistry of the study area was well established in the early 1970s before operation began at the petrochemical company. The mean values of pH, SO_4^{2-} , NO_3^- , HCO_3^- , and Cl^- were reported as 7.4, 149.96 mg/L, 11.55 mg/L, 266.85 mg/L, and 36.54 mg/L, respectively (Liu 2013). Figure 5 illustrates the spatial and temporal variation of the main indicators (pH, SO_4^{2-} , NO_3^- , HCO_3^- , and Cl^-) relative to their background (baseline) mean values along the horizontal sections (D5–D28) at different periods (1999 to 2019). In the last 30 years, petroleum hydrocarbon concentrations had a continuous decreasing trend from the contamination sources area (D8) to the downgradient locations (D28) due to the natural attenuation (Figs. 1 and 5a–c).

Suppose there was no external sources of NO_3^- recharging the karst groundwater, as the most preferred electron acceptor in the anoxic or anaerobic biodegradation of hydrocarbons compounds, its concentration would have decreased with decreasing hydrocarbons over time (National Research Council 2000; Marić et al. 2018). However, NO_3^- was observed to have increased in the monitoring wells as petroleum hydrocarbons concentrations decreased along the groundwater flow path throughout the decades (Fig. 5d–f). Similarly, SO_4^{2-} had the same phenomenon in 1999 (Fig. 5g). Additionally, with a dense population where agriculture is the dominant land use type (Guo et al. 2016), the discharge of domestic sewage water and fertilizer are presumed to be the main sources of NO_3^- and SO_4^{2-} recharging the groundwater under the driven of precipitation (Wang et al. 2016; Guo et al. 2019). Perhaps, these sources of NO_3^- and SO_4^{2-} recharging the groundwater might have caused the abnormal values during the monitoring periods. Again, in 2009 and 2019 (Fig. 5h, i), SO_4^{2-} had the same trend with contaminations. Although NO_3^- was consumed during biodegradation, it remained above the mean baseline value (possibly from other sources) increasing from 1999 to 2019. Conversely, measured SO_4^{2-} levels were consistently below the baseline values (Fig. 5g–i). Oxidation and reduction reactions from intrinsic biodegradation processes use NO_3^- and SO_4^{2-} as electron acceptors. Also, NO_3^- has priority over SO_4^{2-} , as such it was selected as the main electron acceptor in this work.

The biodegradation of petroleum hydrocarbons generates CO_2 , while the dissolution of CO_2 increases HCO_3^- and decreases pH in the groundwater system. Thus, HCO_3^- had

Fig. 4 Variation characteristics of petroleum hydrocarbons, COD, TDS, DOC, and ratios of petroleum hydrocarbons/DOC along the flow path at different monitoring periods

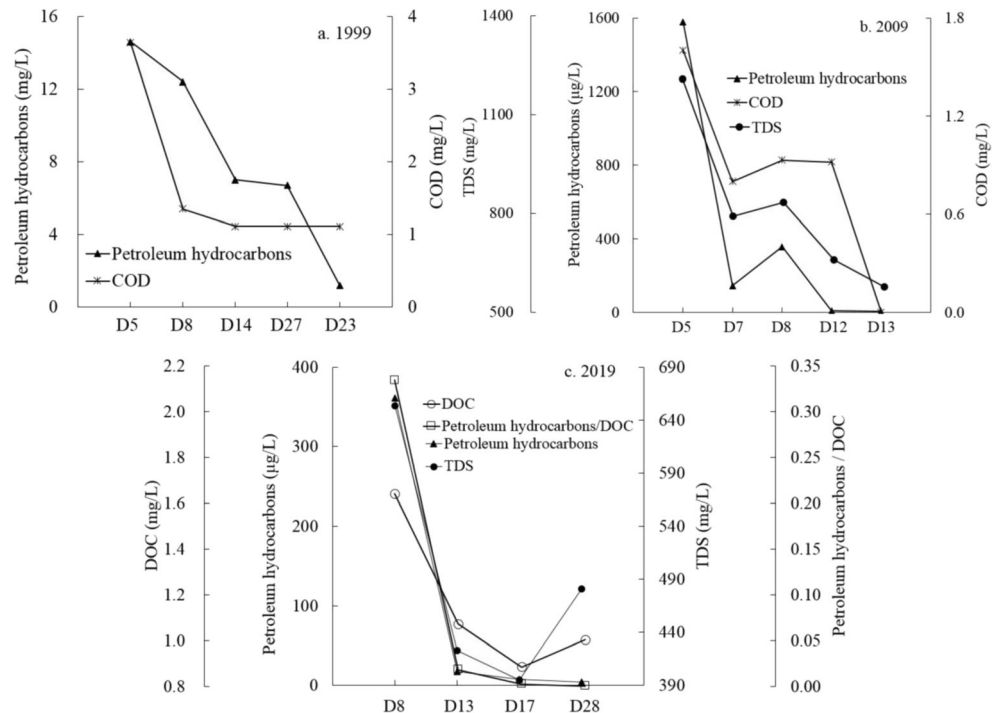
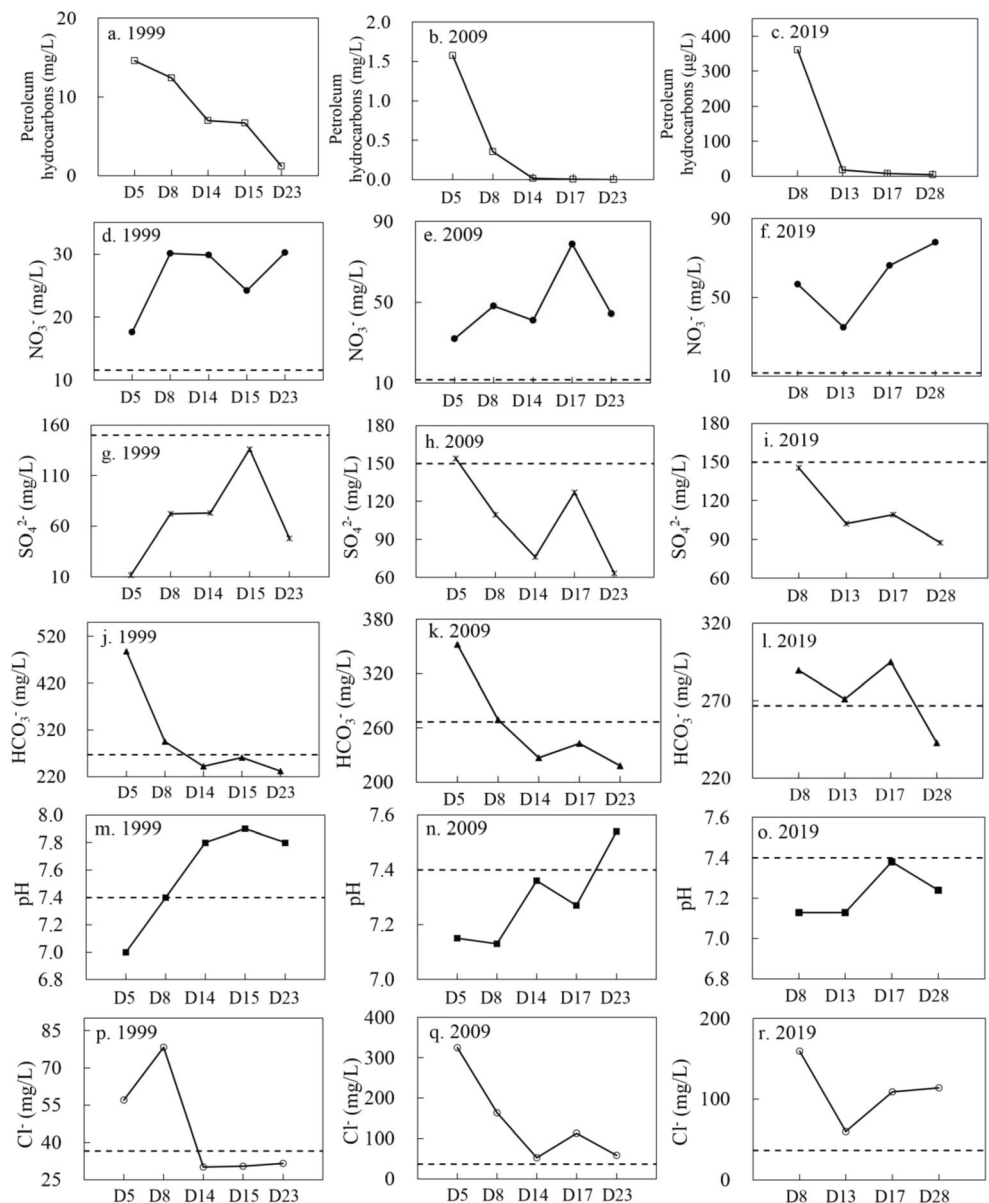


Fig. 5 Variation curves of petroleum hydrocarbons and main chemical indicators along the flow path at different periods (--- mean baseline values of chemical indicators)



the same variation trend with the measured contamination sites (Fig. 5j–l), while pH had the opposite trend (Fig. 5m–o). Along sections D5–D8, petroleum hydrocarbons had higher concentrations, whereas HCO_3^- in the monitoring wells was found to be relatively higher and located above the mean baseline while the pH had the inverse trend. From 1999 to 2019, the pH in the groundwater system shows an apparent decreasing trend which is attributed to the continuous natural biodegradation of petroleum hydrocarbons.

Chlorinated hydrocarbons accounted for 90.51–99.99% of the total organic compounds detected in the polluted karst aquifer. Biodegradation of chlorinated hydrocarbons would increase Cl^- concentration in groundwater. Cl^- is a conservative ion, and high concentrations of Cl^- in groundwater came from wastewater biodegradation products of chlorinated

hydrocarbons (Yang et al. 2019; Wu et al. 2020). From Fig. 5 measured Cl^- levels were mostly above the mean baseline value and had a positive association with petroleum hydrocarbons (Fig. 5p–r) implying that the Cl^- came mainly from biodegradation products of chlorinated hydrocarbons. Consequently, spatial and temporal concentrations of Cl^- could represent the biodegradation stages, in the case of Cl^- measure in monitoring wells located at high contamination areas (D5–D8) (Fig. 5p), where its concentrations were close to the mean baseline downstream (D14–D23) (Fig. 5p). These variation characteristics imply intrinsic biodegradation processes began at an early stage due to dilution and hydrodynamics in the aquifer. It is also important to note that in 2009, concentration levels of Cl^- were relatively higher (Fig. 5q), which was the same period when large amounts of

chlorinated hydrocarbons were degraded. Furthermore, in 2019, biodegradation products of Cl^- decreased due to the very low concentration of petroleum hydrocarbons compared to 2009 (Figs. 1 and 5a–c) when concentration of Cl^- in groundwater also decreased due to advection and dilution from hydrodynamics (Fig. 5q, r).

Biodegradation mechanisms of petroleum hydrocarbons

From the previous sections, it has been established that intrinsic biodegradation processes started since 1980s. In 2019, mean values of DO and Eh were measured at 4.71 mg/L and 181.25 mv, indicating that the total DO in the groundwater has not been consumed as NO_3^- and SO_4^{2-} were also electron acceptors based on the results discussed earlier. It was concluded that both aerobic and anaerobic respiration existed in the biodegradation processes in the noncontinuous karst fractured network media. Mechanisms of petroleum hydrocarbons degradation in 2019 is discussed in this section as the results would be important to predict the degradation trend of the contaminants in the study area.

Recall that NO_3^- was considered the main electron acceptor in the biodegradation processes, and its concentration appears to increase over time as shown in Fig. 5. Therefore, the relationship between $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ was mapped relative to the typical ranges of isotope values from various sources (Kendall 1998) (Fig. 6). $\delta^{15}\text{N}_{\text{NO}_3}$ was in the range of 2.60–7.20‰ with a mean value of 4.79‰, while $\delta^{18}\text{O}_{\text{NO}_3}$ was in the range of 1.01–13.66‰ with a mean value of 6.00‰. Figure 6 shows that NO_3^- in the groundwater came from fertilizer, soil, manure, and septic waste sources. It was worth noting that $\delta^{15}\text{N}_{\text{NO}_3}$ was reported to be higher than 10‰ in animal sources (Spalding et al. 2019), the highest $\delta^{15}\text{N}_{\text{NO}_3}$ value (7.20‰) in the groundwater was lower than 10‰; therefore, the manure source was excluded in the study area. Almost all $\delta^{18}\text{O}_{\text{NO}_3}$ values were in the range of −1.01 to −13.66‰ for the nitrification of ammonia (Spalding et al. 2019). NO_3^- was the most mobile form of N fertilizer for the agricultural activities in the study area, and it could easily percolate through the soil profile driven by rainwater and leaking wastewater. The volatilization and nitrification of N inorganic fertilizer could make $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ within the range of soil-N (Margalef-Martí et al. 2019). Soil-N source was stable for the groundwater system, as such, abnormal variations of NO_3^- in groundwater was most probably caused by human activities. Consequently, NO_3^- has continuous recharging sources in the study area, and its concentration has been increasing over the last three decades (Figs. 5d–f and 6).

Non-biological attenuation processes would not influence the isotopic signature of NO_3^- , such as dilution of non-polluted water or rainwater recharging sources (Margalef-

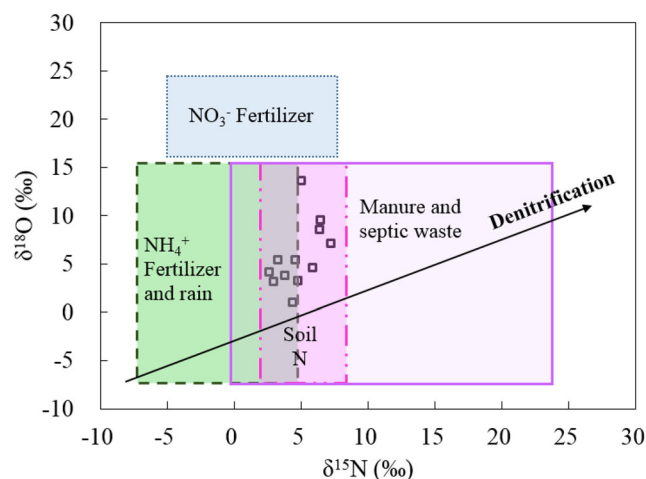


Fig. 6 $\delta^{15}\text{N}_{\text{NO}_3}$ relative to $\delta^{18}\text{O}_{\text{NO}_3}$ of monitoring wells and typical ranges of isotope values from various sources

Martí et al. 2019). Both $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values were positive in all monitoring wells; they were all located above the denitrification line (Fig. 6). Because of the preferential utilization of lighter isotopes by microorganism and the fractionation of nitrogen isotopes in petroleum hydrocarbon biodegradation processes, the heavier isotope values in the residual NO_3^- would be enriched. Hence, as petroleum hydrocarbons concentrations decreased along the groundwater flow path, the NO_3^- concentrations increased and the $\delta^{15}\text{N}_{\text{NO}_3}$ values declined (Figs. 5c and 7). Furthermore, the enriched $\delta^{15}\text{N}$ values in the remaining NO_3^- from the contamination plume areas suggested the occurrence of NO_3^- reduction in biodegradation processes. In addition, NO_2^- (a reduction product of NO_3^-) was detected from D8 to D17, while NH_4^+ being the final reduction product was not found in any of these monitoring wells. From the foregoing we can infer that the biodegradation processes using NO_3^- electron as an acceptor was active from D8 to D17. Both NH_4^+ and NO_2^- were not detected in the downgradient (D28) where petroleum hydrocarbons concentration was as low as 4.14 $\mu\text{g/L}$. This was also due to the groundwater environment being in an oxidation state with Eh value of 163.90 mv and DO value of 2.72 mg/L. Consequently, DO could satisfy biodegradation of petroleum hydrocarbons at D28.

The reduction occurrence of NO_3^- and SO_4^{2-} in biodegradation processes indicated the occurrence of anaerobic activities (Chiu et al. 2017). Also, organisms prefer ^{12}C for the chemical and biological activities, because the occurrence of methanogenic activities would deplete the ^{13}C values in CH_4 and enrich the ^{13}C values in CO_2 and/or DIC (Lv et al. 2018). Besides, Lv et al. (2015) and Marić et al. (2018) reported the use of $\delta^{13}\text{C}_{\text{DIC}}$ in groundwater to verify petroleum hydrocarbons biodegradation (Lv et al. 2015; Marić et al. 2018). In addition, $\delta^{13}\text{C}$ values in DOC were also considered for evaluating the biodegradation processes. The hydrochemical relationships between DO, HCO_3^- , CO_2 , and $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{13}\text{C}_{\text{DOC}}$

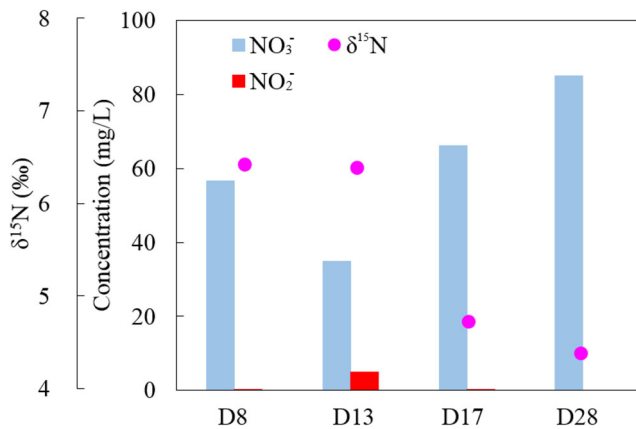


Fig. 7 Relationships among NO_3^- , NO_2^- , and $\delta^{15}\text{N}_{\text{NO}_3}$ along the groundwater flow path

from samples collected along the contamination sources area (D8) to the downgradient (D28) were mapped in Fig. 8.

Petroleum hydrocarbons were found to be the main dissolved organic matters in the karst groundwater system, with $\delta^{13}\text{C}_{\text{DOC}}$ in the groundwater falling into the range of -27.18 to -15.17‰ due to petroleum hydrocarbons along with depleted $\delta^{13}\text{C}$ value of approx. -26‰ (Parker et al. 2012). $\delta^{13}\text{C}$ values of carbonate minerals ranged from -1.50 to -7.80‰ (Garlick and Epstein 1966; Parker et al. 2012). pH in the groundwater system ranged from 7.07 to 7.54; hence, HCO_3^- was the main component of DIC. It was observed that $\delta^{13}\text{C}_{\text{DIC}}$ in groundwater with the range of -12.35 to -7.84‰ fell into the range between petroleum hydrocarbons and carbonate minerals, leading to the conclusion that parts of DIC came from the dissolution of CO_2 generated by degradation of petroleum hydrocarbons.

Microbial respiration consuming petroleum hydrocarbons produced ^{13}C -depleted CO_2 , while the occurrence of methanogenic activity produced ^{13}C -enriched CO_2 . $\delta^{13}\text{C}_{\text{DIC}}$ in the groundwater with the positive Eh values (oxidation state) decreased with increasing CO_2 (Fig. 8a) confirming the assumption that there was no methanogenic activity in the fractured aquifer. The biodegradation processes of ^{13}C -depleted petroleum hydrocarbons produced ^{13}C -depleted CO_2 , with the remaining petroleum hydrocarbons or DOC in the groundwater being ^{13}C -enriched. The dissolution of ^{13}C -depleted CO_2 would increase the DIC but decrease $\delta^{13}\text{C}_{\text{DIC}}$ in the groundwater, consequently, $\delta^{13}\text{C}_{\text{DOC}}$ increased as DIC and CO_2 increased (Fig. 8b, d) while $\delta^{13}\text{C}_{\text{DIC}}$ decreased as DIC increased (Fig. 8c).

Similarly, $\delta^{13}\text{C}_{\text{DIC}}$ increased as DO increased suggesting that microbial respiration influence isotopic values significantly (Parker et al. 2012) (Fig. 8e). The higher the remaining DO in the groundwater, the weaker the microbial respiration, and the less the dissolution of ^{13}C -depleted CO_2 , the higher the $\delta^{13}\text{C}_{\text{DIC}}$ in the groundwater (Fig. 8e). Likewise, the higher the remaining DO in the groundwater, the less the degradation

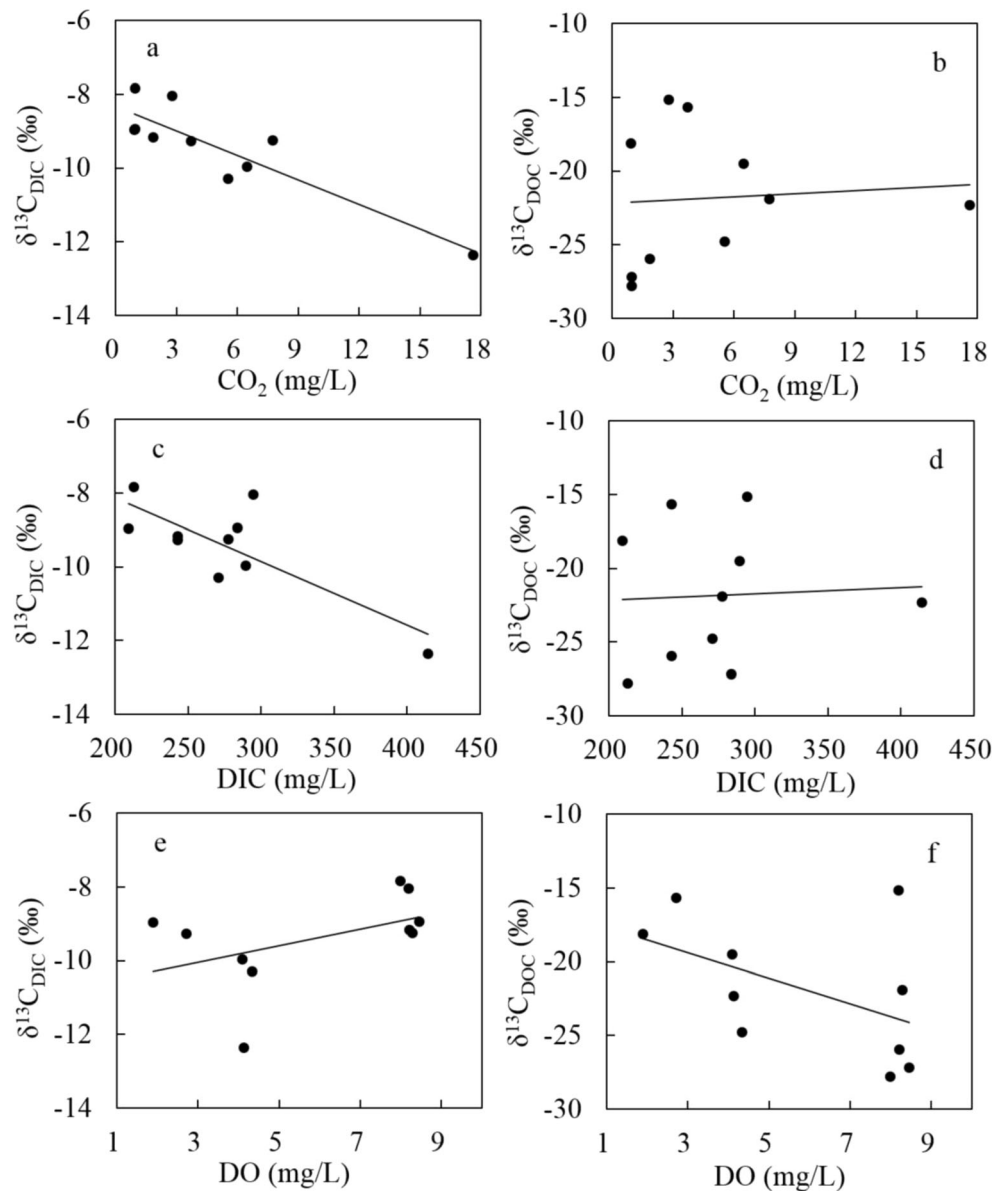
of ^{12}C in petroleum hydrocarbons, and lesser $\delta^{13}\text{C}_{\text{DOC}}$ in the groundwater (Fig. 8f).

Natural attenuation rate of petroleum hydrocarbons

The first-order decay rates of individual wells were calculated for different periods based on first order kinetics and a series of monitoring data (petroleum hydrocarbon concentrations). The natural attenuation rates ranged between 1.30×10^{-3} – $4.10 \times 10^{-3} \text{ day}^{-1}$, 2.57×10^{-3} – $7.66 \times 10^{-3} \text{ day}^{-1}$, and 1.00×10^{-3} – $9.53 \times 10^{-3} \text{ day}^{-1}$ for the 1990s, 2000s, and 2010s, respectively. The mean natural attenuation rates for 1990s, 2000s and 2010s were $2.58 \times 10^{-3} \text{ day}^{-1}$, $4.98 \times 10^{-3} \text{ day}^{-1}$, and $3.70 \times 10^{-3} \text{ day}^{-1}$, respectively. Additionally, over the last three decades, the estimated mean natural attenuation rate of petroleum hydrocarbons in the fractured karst aquifer was about $3.76 \times 10^{-3} \text{ day}^{-1}$. Even though there existed a big fluctuation in the fractured karst aquifer due to the inhomogeneous permeability, different types of natural attenuation rates were still in the same order of magnitude. These calculated decay rates were close to or a little higher than the mean attenuation rate of 49 gas station contaminated sites ($1.26 \times 10^{-3} \text{ day}^{-1}$, Reid et al. 1999) in the USA and research results of other investigations by Choi and Lee (2011), Chiu et al. (2017), and Lv et al. (2018).

Temperature plays a vital role in the natural attenuation of petroleum hydrocarbons; it affects both the mobility of hydrocarbons as well as biodegradation rate (Varjani and Upasani 2017). The preferred temperature ranges for aerobic and anaerobic biodegradation processes are reported to be 15 – 30°C and 25 – 35°C , respectively (Atlas 1981). The average temperature of the karst groundwater at 22°C falls into the appropriate ranges. What is more, the adequate electron acceptors in the groundwater system could increase bioremediation activity thereby enhancing aerobic biodegradation processes (Abbasian et al. 2015; Varjani and Upasani 2017). The former results indicate that there are adequate electron acceptors of NO_3^- and SO_4^{2-} in the karst aquifers. The transportation rate of dissolved contaminants is usually taken to be equal to the average linear groundwater velocity (USEPA 2004; Alvarez and Illman 2005), which is about 5352 m/day and $14,400 \text{ m/day}$ in our study area as established by the tracer tests conducted by Nanjing University and Geological Environment Monitoring Station of Shandong (Zhu et al. 2000). Therefore, the fractured karst aquifer system can transport large volumes of contaminant relative to the groundwater velocity in a unit time. The aquifer matrix also promotes mechanical mixing and stronger hydrodynamic dispersion of pollutants as groundwater flows through the media, twisting around individual grains and interconnected pore spaces at different velocities (USEPA 2004). The foregoing effectively promotes conditions in the fractured karst aquifers suitable for enhanced natural attenuation of petroleum hydrocarbons.

Fig. 8 **a** CO_2 vs $\delta^{13}\text{C}_{\text{DIC}}$. **b** CO_2 vs $\delta^{13}\text{C}_{\text{DOC}}$. **c** DIC vs $\delta^{13}\text{C}_{\text{DIC}}$. **d** DIC vs $\delta^{13}\text{C}_{\text{DOC}}$. **e** DO vs $\delta^{13}\text{C}_{\text{DIC}}$. **f** DO vs $\delta^{13}\text{C}_{\text{DOC}}$



Prediction of petroleum hydrocarbons biodegradation trend

The minerals of the fractured karst aquifer are mainly carbonate, there was no methanogenic activity in the petroleum hydrocarbons biodegradation processes, and Fe and CH_4 were not detected in the groundwater. Various factors influenced SO_4^{2-} and NO_3^- concentrations over the last three decades, in order to represent the current groundwater environment, background (baseline) conditions of DO, SO_4^{2-} , and NO_3^- were considered to use the uncontaminated or completely degraded monitoring well in 2019. DO, SO_4^{2-} , and NO_3^- in the sources area were 4.09 mg/L, 145.53 mg/L, and 56.71 mg/L, respectively. DO, SO_4^{2-} , and NO_3^- in the background conditions were 4.94 mg/L, 257.2 mg/L, and 75.28 mg/L, respectively. The calculated biodegradation capacity for petroleum

hydrocarbons (mg/L) was about 27.48 mg/L using the Eq. (2) based on the electron-acceptor-limited kinetic model. The highest petroleum hydrocarbons concentration was 361.13 $\mu\text{g/L}$ in the present. It is noteworthy that the formation of hydrogeological structure is a long-term evolutionary process, with little changes over short periods (Teng et al. 2010). The fractured karst aquifer system can be said to be in a dynamic equilibrium state under care and the management of public authority. Therefore, the prevailing hydrogeological and environmental conditions are not expected to change drastically in the short and medium terms. Hence, the biodegradation capacity presently established can effectively degrade the remaining contamination based on the measured biodegradation mechanisms. Consequently, based on the calculated mean natural attenuation rate ($3.76 \times 10^{-3} \text{ day}^{-1}$) of petroleum hydrocarbons, considering all prevailing hydrogeological and

environmental conditions remain steady, it will take approximately 6 years to completely degrade all petroleum hydrocarbons under the detection limit of 0.10 µg/L. Overall, this result suggests that quality of the karst aquifer system will continue to improve driven by natural attenuation. Also, the natural biodegradation processes of petroleum hydrocarbons could consume the inorganic oxidation ions (especially NO_3^- and SO_4^{2-}) in the aquifer. In addition, other remediation strategies can possibly make the biodegradation process even faster. Moving forward, net-environmental benefit and cost should guide decision makers on how to proceed. Continuous monitoring of groundwater hydrodynamics in the area remains essential towards sustainable development of the groundwater resources for the region.

Conclusions

In this study, the contamination and natural attenuation characteristics of petroleum hydrocarbons in a contaminated super-large fractured karst aquifer in Zibo City, Northern China, were elucidated using hydrogeochemical indicators, multiple isotopes, and concentrations of petroleum hydrocarbons. Spatio-temporal variation characteristics of petroleum hydrocarbons and variation curve of petroleum hydrocarbons in contamination sources area were mapped and analyzed from 1990s to 2010s. Concentrations of petroleum hydrocarbons in the groundwater were found to be heavily influenced by hydrodynamic conditions, human activities, and natural attenuation. Natural attenuation due to biodegradation of the contaminant highlighted a 30 years positive trend leading to the conclusion that intrinsic biodegradation is the most important mechanism driving the degradation process. The relationships between hydrogeochemical indicators (DO , DOC , Cl^- , HCO_3^- , pH , NO_3^- , and SO_4^{2-}) and petroleum hydrocarbons presented the evidences of active biodegradation in the area. Environmental isotopes showed that aerobic and anaerobic respiration without methanogenic activities existed in the biodegradation processes within the heterogeneous karst media. Over the past three decades, the mean first-order decay rate of petroleum hydrocarbons in the fractured karst aquifer was calculated to be $3.76 \times 10^{-3} \text{ day}^{-1}$. At the current biodegradation capacity of petroleum hydrocarbons (27.48 mg/L), and considering all prevailing hydrogeological and environmental conditions remain steady, the highest concentration levels at 361.13 µg/L would be completely degraded below the detection limit of 0.10 µg/L in about 6 years. Fractured karst aquifers are complicated heterogeneous systems that are extremely vulnerable to pollution, often requiring specialized methods of investigation. This study establishes a positive outlook towards extensive remediation works in other contaminated karst regions of the world.

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References

- Abbasian F, Lockington R, Mallavarapu M, Naidu R (2015) A comprehensive review of aliphatic hydrocarbon biodegradation by bacteria. *Appl Biochem Biotechnol* 176:670–699. <https://doi.org/10.1007/s12010-015-1603-5>
- Alvarez PJ, Illman WA (2005) Bioremediation and natural attenuation: process fundamentals and mathematical models. John Wiley & Sons
- Amos RT, Bekins BA, Delin GN, Cozzarelli IM, Blowes DW, Kirshtein JD (2011) Methane oxidation in a crude oil contaminated aquifer: delineation of aerobic reactions at the plume fringes. *J Contam Hydrol* 125:13–25. <https://doi.org/10.1016/j.jconhyd.2011.04.003>
- Atlas RM (1981) Microbial degradation of petroleum hydrocarbons: an environmental perspective. *Microbiol Rev* 45(1):180–209
- Cassidy DP, Srivastava VJ, Dombrowski FJ, Lingle JW (2015) Combining in-situ chemical oxidation, stabilization and anaerobic bioremediation in a single application to reduce contaminant mass and leachability in soil. *J Hazard Mater* 297:347–355. <https://doi.org/10.1016/j.jhazmat.2015.05.030>
- Chen YD, Zhu XY (1999) Mechanisms of biodegradation of hydrocarbon contaminants in the groundwater in Dawu well field in Zibo. *Guangxi Geology* 12(2):31–34 (in Chinese)
- Chen YD, Zhu XY, Liu JL (1998) Distribution characteristics and fate of hydrocarbons in Dawu water source in Zibo city. *Chin Sci Bull* 43(1):81–85
- Chen YD, Zhu XY, Zhu YS, Jiang YP, Xie QL (2000) Transformations and hydraulic captures of petrochemical contaminants in a karst-fractured aquifer. *Environ Geol* 39(11):1304–1308
- Chien LC, Yu HL, Schootman M (2013) Efficient mapping and geographic disparities in breast cancer mortality at the county-level by race and age in the U.S. *Spat Spatiotemporal Epidemiol* 5:27–37. <https://doi.org/10.1016/j.sste.2013.03.002>
- Chiu HY, Verpoort F, Liu JK, Chang YM, Kao CM (2017) Using intrinsic bioremediation for petroleum-hydrocarbon contaminated groundwater cleanup and migration containment: effectiveness and mechanism evaluation. *J Taiwan Inst Chem E* 72:53–61. <https://doi.org/10.1016/j.jtice.2017.01.002>
- Choi HY, Lee JY (2011) Groundwater contamination and natural attenuation capacity at a petroleum spilled facility in Korea. *J Environ Sci* 23:1650–1659. [https://doi.org/10.1016/S1001-0742\(10\)60568-2](https://doi.org/10.1016/S1001-0742(10)60568-2)
- Declercq I, Cappuyns V, Duclos Y (2012) Monitored natural attenuation (MNA) of contaminated soils: state of the art in Europe—a critical evaluation. *Sci Total Environ* 426:393–405. <https://doi.org/10.1016/j.scitotenv.2012.03.040>
- Garlick GD, Epstein S (1966) The isotopic composition of oxygen and carbon in hydrothermal minerals at Butte, Montana. *Econ Geol* 61: 1325–1335

- GB 5749–2006 (2006) Quality standard for drinking water, People's Republic of China, Ministry of Environmental Protection
- Guo YL, Zhai YZ, Wu Q, Teng YG, Jiang GH, Wang JS, Guo F, Tang QJ, Liu SH (2016) Proposed APLIE method for groundwater vulnerability assessment in karst-phreatic aquifer, Shandong Province, China: a case study. *Environ Earth Sci* 75:112–114. <https://doi.org/10.1007/s12665-015-4903-8>
- Guo YL, Wu Q, Li CS, Zhao ZH, Sun B, He SY, Jiang GH, Zhai YZ, Guo F (2018) Application of the risk-based early warning method in a fracture-karst water source, North China. *Water Environ Res* 90: 206–219. <https://doi.org/10.2175/106143017X15131012152771>
- Guo YL, Quan XQ, Wang QG, Zhang C, Wu Q (2019) Characteristics of groundwater chemistry in Dawu karst water source. South-to-North Water Transfers and Water Science & Technology (in Chinese). <http://kns.cnki.net/kcms/detail/13.1334.TV.20191031.1138.002.html>. Accessed 31 Oct 2019
- Hillebrand O, Nödler K, Sauter M, Licha T (2015) Multitracer experiment to evaluate the attenuation of selected organic micropollutants in a karst aquifer. *Sci Total Environ* 506:338–343. <https://doi.org/10.1016/j.scitotenv.2014.10.102>
- Jones DM, Head IM, Gray ND, Adams JJ, Rowan AK, Aitken CM, Bennett B, Huang H, Brown A, Bowler BFJ, Oldenburg T, Erdmann M, Larter SR (2008) Crude-oil biodegradation via methanogenesis in subsurface petroleum reservoirs. *Nature* 451: 176–180. <https://doi.org/10.1038/nature06484>
- Kendall C (1998) Tracing nitrogen source and cycling in catchments. In: Kendall C, McDonnell JJ (eds) *Isotope tracers in catchment hydrology*. Elsevier Science B.V., The Netherlands, pp 519–576
- Kim DJ, Park MR, Lim DS, Choi JW (2013) Impact of nitrate dose on toluene degradation under denitrifying condition. *Appl Biochem Biotechnol* 170:248–256. <https://doi.org/10.1007/s12010-013-0176-4>
- Lan JK (1996) Simulation models of water-rock interaction in the aquifer of Linzi area, Zibo city, Shandong. *Journal of Guilin Institute of Technology* 16(4):410–414 (in Chinese)
- Lang FS, Destain J, Delvigne F, Druart P, Ongena M, Thonart P (2016) Characterization and evaluation of the potential of a diesel-degrading bacterial consortium isolated from fresh mangrove sediment. *Water Air Soil Poll* 227:58–20. <https://doi.org/10.1007/s11270-016-2749-7>
- Lee TH, Cao WZ, Tsang DCW, Sheu YT, Shia KF, Kao CM (2019) Emulsified polycolloid substrate biobarrier for benzene and petroleum-hydrocarbon plume containment and migration control—a field-scale study. *Sci Total Environ* 666:839–848. <https://doi.org/10.1016/j.scitotenv.2019.02.160>
- Li D, Song XL, Niu PS (2001) A simulation of the groundwater environment and study on control of the petroleum pollution in water supply source of Dawu. *Beijing Geology* 13(4):20–24 (in Chinese)
- Liu SL (2013) The analysis of water quality evaluation regular pattern and the pollution trend prediction of groundwater in Dawu well field, Zibo City. China University of Geosciences (Beijing), post-graduate thesis
- Liu XH, Dai QL (1996) Remediation programme study on oil pollution in groundwater system. *Journal of South China University of Technology (Natural Science)* 24:188–192 (in Chinese)
- Liu XH, Fu JM, Shen ZL, Zhong ZS (1996) Hydrogeochemical change induced by oil sewage leakage—a case of the groundwater source in Zibo city, Shandong province, China. *Geochimica* 25(4):331–338
- Lv H, Wang Y, Su XS, Zhang YL (2015) Combined ^{14}C and $\delta^{13}\text{C}$ analysis of petroleum biodegradation in a shallow contaminated aquifer. *Environ Earth Sci* 74:431–438. <https://doi.org/10.1007/s12665-015-4049-8>
- Lv H, Su XS, Wang Y, Dai ZX, Liu MY (2018) Effectiveness and mechanism of natural attenuation at a petroleum-hydrocarbon contaminated site. *Chemosphere* 206:293–301. <https://doi.org/10.1016/j.chemosphere.2018.04.171>
- Lv H, Wang Y, Wang H (2019) Determination of major pollutant and biogeochemical processes in an oil-contaminated aquifer using human health risk assessment and multivariate statistical analysis. *Hum Ecol Risk Assess* 25(3):505–526. <https://doi.org/10.1080/10807039.2018.1449099>
- Margalef-Martí R, Carrey R, Viladés M, Jubany I, Vilanova E, Graue R, Soler A, Otero N (2019) Use of nitrogen and oxygen isotopes of dissolved nitrate to trace fieldscale induced denitrification efficiency throughout an in-situ groundwater remediation strategy. *Sci Total Environ* 686:709–718. <https://doi.org/10.1016/j.scitotenv.2019.06.003>
- Marić N, Matić I, Papić P, Beškoski VP, Ilić M, Gojgić-Cvijović G, Miletić S, Nikić Z, Vrvic MM (2018) Natural attenuation of petroleum hydrocarbons—a study of biodegradation effects in groundwater (Vitanovac, Serbia). *Environ Monit Assess* 190:89. <https://doi.org/10.1007/s10661-018-6462-4>
- McMahon PB, Chapelle FH (2008) Redox processes and water quality of selected principal aquifer systems. *Groundwater* 46(2):259–271. <https://doi.org/10.1111/j.1745-6584.2007.00385.x>
- Müller JB, Ramos DT, Larose C, Fernandes M, Lazzarin HS, Vogel TM, Corseuil HX (2017) Combined iron and sulfate reduction biostimulation as a novel approach to enhance BTEX and PAH source-zone biodegradation in biodiesel blend-contaminated groundwater. *J Hazard Mater* 326:229–236. <https://doi.org/10.1016/j.jhazmat.2016.12.005>
- National Research Council (2000) *Natural attenuation for groundwater remediation*. National Academy Press, Washington, DC
- Newell CJ, Kueper BH, Wilson JT (2014) *Natural attenuation of chlorinated solvent source zones*. Chlorinated solvent source zone remediation. Springer, New York, pp 459–508
- Parker SR, Gammons CH, Smith MG, Poulson SR (2012) Behavior of stable isotopes of dissolved oxygen, dissolved inorganic carbon and nitrate in groundwater at a former wood treatment facility containing hydrocarbon contamination. *Appl Geochem* 27:1101–1110. <https://doi.org/10.1016/j.apgeochem.2012.02.035>
- Qian H, Zhang Y, Wang J, Si C, Chen Z (2018) Characteristics of petroleum contaminated groundwater during natural attenuation: a case study in northeast China. *Environ Monit Assess* 190:80. <https://doi.org/10.1007/s10661-017-6449-6>
- Reid JB, Reisinger HJ, Gray JC, Hullman AS (1999) A comparative assessment of the long-term behavior of MTBE and benzene plumes in Florida, USA. *Nat Attenuat Chlorin Solv Petrol Hydrocarbons Other Org Compd* 1:97–102
- Shang YN (2013) Study on karst water level dynamic change for many years of Dawu water resources area in Zibo city. *Land and Resources in Shandong Province* 29:44–47 (in Chinese)
- Spalding RF, Hirshb AJ, Exner ME, Littled NA, Kloppenborg KL (2019) Applicability of the dual isotopes $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ to identify nitrate in groundwater beneath irrigated cropland. *J Contam Hydrol* 220:128–135. <https://doi.org/10.1016/j.jconhyd.2018.12.004>
- Sperfeld M, Rauschenbach C, Diekert G, Studenik S (2018) Microbial community of a gasworks aquifer and identification of nitrate-reducing Azoarcus and Georgfuchsia as key players in BTEX degradation. *Water Res* 132:146–157. <https://doi.org/10.1016/j.watres.2017.12.040>
- Teng YG, Zuo R, Wang JS, Lin XY (2010) Progress in geochemistry of regional groundwater evolution. *Adv Water Sci* 21(1):127–136. <https://doi.org/10.14042/j.cnki.32.1309.2010.01.002>
- United States Environmental Protection Agency (USEPA) (2004) *How to evaluate alternative cleanup technologies for underground storage tank sites: a guide for corrective action plan reviewers*
- United States Environmental Protection Agency (USEPA) (2010) *Green remediation best management practices: clean fuel & emission technologies for site cleanup*. EPA 542-F-10-008, Washington DC
- van der Waals MJ, Pijls C, Sinke AJ, Langenhoff AA, Smidt H, Gerritse J (2018) Anaerobic degradation of a mixture of MtBE, EtBE, TBA,

- and benzene under different redox conditions. *Appl Microbiol Biotechnol* 102:3387–3397. <https://doi.org/10.1007/s00253-018-8853-4>
- Varjani SJ, Upasani VN (2017) A new look on factors affecting microbial degradation of petroleum hydrocarbon pollutants. *Int Biodeterior Biodegrad* 120:71–83. <https://doi.org/10.1016/j.ibiod.2017.02.006>
- Wang JL, Jin MG, Lu GP, Zhang DL, Kang FX, Jia BJ (2016) Investigation of discharge-area groundwaters for recharge source characterization on different scales: the case of Jinan in northern China. *Hydrogeol J* 24(7):1723–1737. <https://doi.org/10.1007/s10040-016-1428-5>
- Wu NJ, Zhang W, Wei WX, Yang SC, Wang HJ, Sun ZP, Song Y, Li PZ, Wang Y (2020) Field study of chlorinated aliphatic hydrocarbon degradation in contaminated groundwater via micron zero-valent iron coupled with biostimulation. *Chem Eng J* 384:123349. <https://doi.org/10.1016/j.cej.2019.123349>
- Xing YQ, Dou M, Zhang Z, Fu B, Zhang YL (2008) Dynamic analysis and water quality evaluation of groundwater in Dawu water source. *Henan Science* 26(1):80–87
- Yang J, Meng L, Guo L (2019) In situ remediation of chlorinated solvent-contaminated groundwater using ZVI/organic carbon amendment in China: field pilot test and full-scale application. *Environ Sci Pollut Res* 25(6):5051–5062. <https://doi.org/10.1007/s11356-017-9903-7>
- Yu X, Ghasemizadeh R, Padilla I, Irizarry C, Kaeli D, Alshawabkeh A (2015) Spatiotemporal changes of CVOC concentrations in karst aquifers: analysis of three decades of data from Puerto Rico. *Sci Total Environ* 511:1–10. <https://doi.org/10.1016/j.scitotenv.2014.12.031>
- Zhu XY, Xu SH, Si JF (1997) Application of tracing test to the remediation of contaminated fracture-karst water in Zibo city. *Carsologica Sinica* 16(2):131–144
- Zhu XY, Liu JL, Qian XX (1999) The influence of Zihé stream on the groundwater resources of the Dawu well field and on the discharge at the Heiwang iron mine, Zibo City area, Shandong Province, China. *Hydrogeol J* 7:477–482
- Zhu XY, Liu JL, Zhu JJ, Chen YD (2000) Characteristics of distribution and transport of petroleum contaminants in fracture-karst water in Zibo area, Shandong Province, China. *Sci China* 43(2):141–150

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