

Article

Quantitative Assessment of Organic Mass Fluxes and Natural Attenuation Processes in a Petroleum-Contaminated Subsurface Environment

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Abstract: We perceived a trend in the study and practice of petroleum-contaminate sites. Monitored natural attenuation (MNA) can reduce the contaminant concentrations in the soil and groundwater, and it is a method that can remediate the petroleum-contaminated site effectively. MNA is becoming a research focus. This study evaluated MNA using a series of lab-based bench-scale experiments and a large amount of monitoring data from field samplings. Based on the in-site total petroleum hydrocarbon (TPH) results, we used statistical methods, the Mann-Kendall test, and mass fluxes in order to evaluate the MNA of petroleum-contaminated sites in groundwater. The results showed that the TPH concentrations were decreasing, and the plume became smaller. The attenuation rate was from 0.00876 mg/d to 0.10095 mg/d; remediating the petroleum contamination site would cost 1.3 years to 10.6 years. The plume reached a quasi-steady state, and mass flux declined. The most essential process of MNA was biodegradation, and the second was sorption. During the monitoring period, 393 g of TPH was attenuated, including 355 g of TPH degraded by microbes. Biodegradation upstream of the plume was more serious. Iron(III) and manganese were the main electron acceptors utilized by microbes during the monitored period. MNA was in progress, and it can be an effective method to remediate the petroleum-contaminated site. Lab-based bench-scale experiments were performed with much monitoring data from the field samplings in order to understand the fate and transport mechanism of the petroleum contamination from the land surface to shallow groundwater according to site conditions.

Keywords: monitored natural attenuation; mass fluxes; petroleum-contaminated site; groundwater; Mann-Kendall test



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1. Introduction

The dependence on petroleum as an indispensable resource for our today's life is increasing. During petroleum exploitation, transporting, and processing, spillage and contamination of the groundwater and soil environment are hard to avoid. Petroleum hydrocarbons are very common contaminants in groundwater [1]. It is extremely important to clean up the contaminated soil and subsurface environment in a cost-effective manner [2,3]. MNA has become a preferred choice for the remediation of petroleum-contaminated groundwater for decades [4]. An increasing interest in implementing low-cost, environmentally friendly, and nonintrusive solutions such as MNA has been observed in recent years in many sites worldwide [5–8]. MNA involves low exposure risk for cleanup and requires less equipment and labor involvement than most other methods [7]. Monitoring for many

years can be costly but may cost less than other methods [9]. In China, the extensive study of MNA at the laboratory scale is moving into the study of petroleum-contaminated sites due to the great real-world demand [10–12].

MNA can be used as the sole remedial solution [13], or when other methods will not work or are expected to take almost as long. Sometimes, MNA is used as a final cleanup step after other methods for polishing purposes [14,15]. Some of these naturally occurring physical, chemical, and biological processes can transform contaminants to less harmful forms or immobilize them in the subsurface, therefore reducing contaminant concentrations in groundwater [16–18]. Attenuation mechanisms encompass physical dilution, physicochemical sorption, ion exchange, chemical dissolution/precipitation or complexation, and microbial metabolic processes [19,20]. Many studies found that aerobic and anaerobic biodegradation are the major processes for the reduction of contaminant mass in the subsurface [21,22]. Biodegradation is generally considered the most important process for contaminated site remediation because it is destructive, unlike sorption, dilution, and volatilization [23]. Biodegradation would reduce the mass and toxicity of contaminants in the groundwater and soils. The biodegradation of aerobic microbes is more efficient than that of anaerobic microbes [24,25]. Once oxygen is completely used or becomes limiting, microbes utilize nitrate, followed by manganese, iron, and sulfate [26]. However, if the rate of biodegradation is not significant enough to contain the plume, MNA will not be sufficient to protect aquifers and downgradient receptors [27]. So, ensuring the attenuation effect is the first and foremost task by estimating the trend of a plume, monitoring the concentration, and calculating the remediation period [28–31]. Theories, such as the Mann–Kendall test, are often used to define the stability of a contaminant plume based on concentration trends at individual wells [32–34]. It is widely used in hydrology.

There are multiple methods for estimating biodegradation. First-order kinetics may be able to approximately reproduce the mass and dimensions of contaminant plumes that follow from a far more complex degradation model but are often regarded as imprecise or even conceptually incorrect [16,30,35]. One shortcoming, for example, is that their resolution is not fine enough to reflect plume fringes of the intrinsic biodegradation and their limiting factors of electron acceptors from the surrounding subsurface environment [36]. A substantial problem is the negligence of various hydrogeological variables and attenuation processes that may occur in subsurface environments (e.g., advection, dispersion, mixing). The resulting first-order rate constants thus describe bulk attenuation rather than local in situ biodegradation kinetics [37].

Another reactive model used for the in situ quantification of biodegradation is Michaelis–Menten (MM) kinetics, also known as Monod, no-growth kinetics, which presents the situations that the initial cell number is much greater than that could be produced using the substrate present at time zero [16,38]. The MM model originates from biochemistry and is generally applied for enzyme kinetics in the quasi-stationary state. It relates the maximum turnover rate of one specific enzyme to the present substrate concentration (single compound) in the medium. The MM model requires that the amount of enzyme remains constant during the experiment and is not particularly useful for in-site simulation.

Mass flux reflecting the contaminant mass loss through the control planes (CPs) perpendicular to the groundwater flow direction is often calculated to quantify the natural attenuation of petroleum hydrocarbons [39–41]. The 2D method and 3D mass balance approach for determining plume mass loss [42] have been used to estimate the natural attenuation. The 3D mass balance approach is more accurate but needs more monitoring information. Due to aquifer heterogeneity, the resulting plume delineation is strongly influenced by the positioning and number of monitoring wells [43–45]. In the application of the method, a few issues need to be addressed. Firstly, it is important to choose appropriate CPs and determine their lengths by the TPH concentration in groundwater, which can be an easy way but is actually sometimes not accurate. When enough monitoring wells are not available at the site, a pumping well is needed [41]. Secondly, the vertical distribution of TPH is to be delineated, and the mass quantity of plume compounds transformed between

synoptic sampling events is estimated on the basis of dissolved phase concentrations, sorption characteristics, and groundwater flux [46,47]. Although the assumption of sorption ideality is often applied, laboratory and field experiments can often provide evidence of the solute behavior that deviates from ideality. Thirdly, it is hard to calculate the TPH fluxes at each CP at various times under the presence of microbial degradation [48]. Therefore, many assumptions are to be made generally during the assessment.

In this article, a study for the quantitative assessment of an organic contaminant plume at the typical petroleum contaminated site in NE China under a framework of the government core funding program (863) for clean and novel science and technology in the resources and environment section is reported. Extensive field surveys focusing on geology, hydrogeology, geochemistry, and fractions of the petroleum contaminants were carried out systematically in order to understand the contaminant hydrogeological processes and potential in situ remediation with enhanced monitored natural attenuation (e-MNA), air/bio sparging (AS/BS), and/or permeable reactive barriers (PRB). With the support of much monitoring data from the field samplings, a series of lab-based bench-scale experiments were conducted to understand the fate and transport mechanism of the petroleum contamination from land surface to shallow groundwater according to this site condition. The mathematical, statistical model, Mann–Kendall test, and mass flux were reported in this study. The major objectives of this study were to (1) evaluate the attenuation process of petroleum hydrocarbons in the subsurface, (2) assess the contributions of intrinsic biodegradation patterns and other processes by the mass flux approach, and (3) quantify the organic contaminant plume by using the Mann–Kendall model. The effectiveness of employing MNA as an in situ remedial strategy can then be achieved for this site.

2. Materials and Methods

2.1. Study Area

The study site is located in the east of Songnen fluvial plain, China. It is in the temperate continental monsoon climate, with a dry and windy spring, hot and rainy summer, cool fall, and cold winter. The average temperature over multiple years is 4.7 °C, but it has had the extreme climate of 37.5 °C in summer and −37.8 °C in winter in recent years. The average annual precipitation is 436 mm, and of that, over 70% occurs in summer (i.e., June–August).

The elevation of the ground level of the site is between 130.7 and 139.4 m above sea level. The aquifer layer is Holocene alluvium spread out over the valley of the first terrace. The surface layer of the aquifer is drab silt (Figure 1). The lower layer is fine sand, sand, and gravel, being 20–22 m thick. The groundwater table is from 3 to 4.5 m depth below ground level. The groundwater flow direction generally is from the southeast to northwest. The hydraulic gradient is from 0.002 to 0.008. According to slug tests, the hydraulic conductivity is between 0.5 and 12.9 m/d at this site.

There are four oil production wells around the site, and one of the faulty production wells in the upper gradient of the site has been leaking for some years, having also been fixed for some time. This faulty oil well has also produced a petroleum spill pit on the surface that was believed to be a main contamination source for this site (Figure 2). The most recent cut off was in April 2009, which should have cured the leak completely.

2.2. Sample Collection and Analysis

There are twelve boreholes and one potable well at the site for groundwater monitoring, all being located at the down gradient area of the petroleum spill (Figure 2). Perpendicular to the groundwater flow, three CPs were assigned for the plume assessment in this study, each of them containing two or three monitoring wells (Figure 2). All of the CPs were ensured by Formula (6) below, which ignored the influence of depth. The hydro-geochemical parameters were monitored from September 2009 to March 2010. These included six campaigns of TPH concentration sampled monthly, except for February 2010 from 13 monitoring wells. Other major ions including calcium, magnesium, sodium,

potassium, chloride, and bicarbonate/carbonate were sampled in September 2009, January 2010, and March 2010 so that a good trend of hydro-geochemistry could be obtained. Electron acceptors and environment parameters including nitrate, nitrite, ammonium, total iron, iron(III), manganese, sulphate, sulfide, pH, oxidation reduction potential (ORP), conductivity, temperature, and salinity were also analyzed in September 2009, October 2009, November 2009, January 2010, and March 2010. The environment parameters were tested in situ during field sampling using Hanna, and then the sample for TPH, major ions, and electron acceptors were taken for further laboratory analysis. The TPH concentration before the pumping test was higher than after, and it showed that petroleum hydrocarbon concentration decreased with depth. To ensure the effect of MNA, the surface concentration of TPH was used in the estimation.

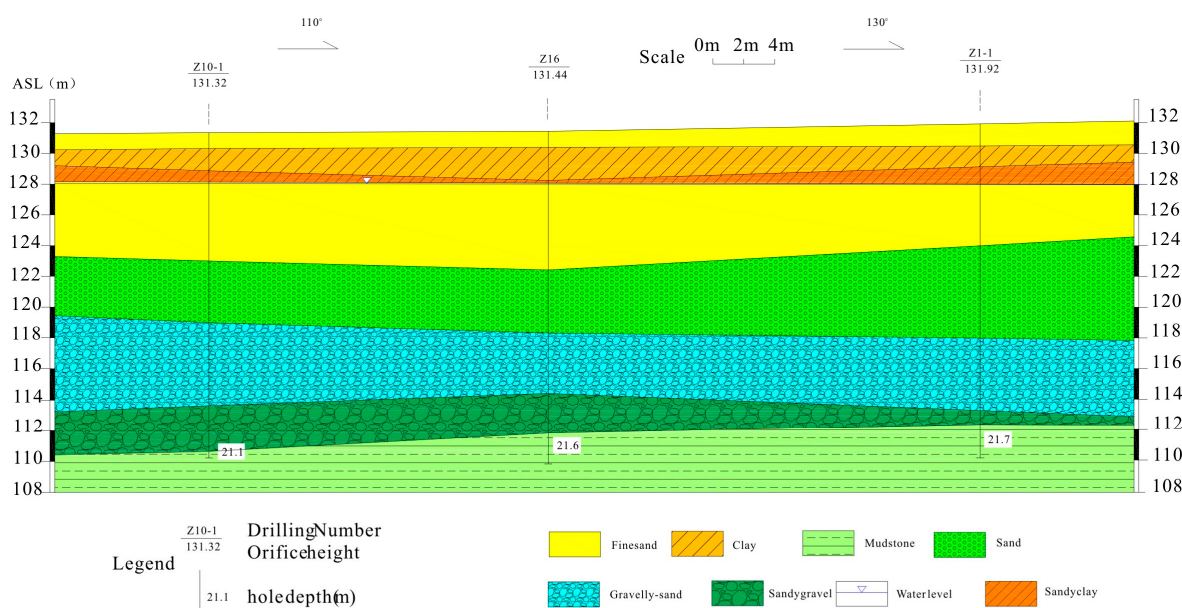


Figure 1. Geological cross-section A-A' of the field site.

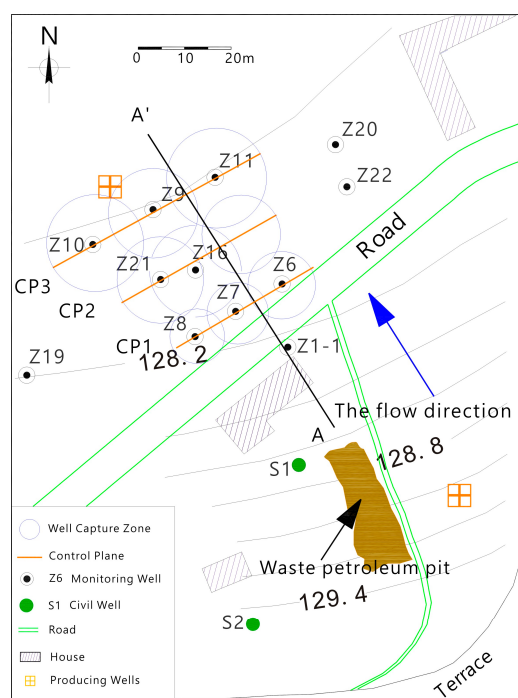


Figure 2. Site overview with the location of the employed wells and control planes.

The sample for TPH analysis was taken with amber glass bottles. For data quality control, samples for Fe/Mn were added with hydrochloric acid, and samples for sulfide were added with 1 mol/L sodium hydroxide and 1 mol/L zinc acetate as chemical stabilizers. The sampling bottles were attempted with no head space and sealed with aluminum foil paper, shipped avoiding sunlight, and kept at 4 °C for further lab analysis.

Total petroleum hydrocarbons were detected by infrared spectrophotometry (JDS-108U+). K^+ and Na^+ were determined by flame atomic absorption spectrophotometry; Ca^{2+} , Mg^{2+} , NO_3^- , Cl^- , and Fe(III) were determined by the titration method; and SO_4^{2-} was determined by the turbidity method. Analytical methods adopted the Quality Standards for Groundwater (GB/T 14848-2017) [49] of China. The other main instruments used to determine the groundwater properties included a multiparameter water quality analyzer (Hach-HQ40).

3. Results

3.1. Contamination and Attenuation Processes

3.1.1. Spatial Distribution of TPH

The plume of TPH was at a downgradient of the waste petroleum pit (WPP) that was based on the analysis of the flow direction and the distribution of the TPH concentration, in addition to the fact that the TPH concentration of Z10 and Z19 was excessively high. The TPH concentration of Z1-1 was 15.08 mg/L, which was highest in September 2009 because it is the nearest monitoring well to the WPP. The TPH concentration in the plume ranged from 6.21 mg/L to 15.08 mg/L. At the edge of the plume, the TPH concentration was 2.99 mg/L. The TPH concentration decreased, with distance ranging from 7.06 mg/L to 2.99 mg/L. The TPH concentration of Z10 was influenced by both downstream producing wells and upstream contamination, and it was the highest in October 2009. From November 2009 to March 2010, the TPH concentration of Z10 was higher than Z6, Z7, and Z8. The spatial distributing of TPH concentration was largely the same from September 2009 to March 2010. Contamination areas were at the downstream area of the WPP and Z10 (Figure 3).

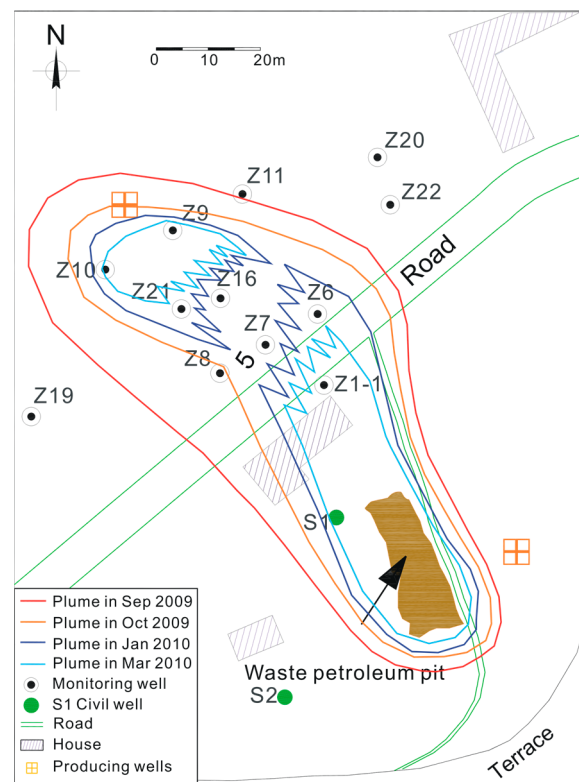


Figure 3. Distribution of TPH concentrations.

3.1.2. TPH along the Flowline

Figure 4 shows the TPH concentration along the flowline from the contaminating source. Abscissa represents the distance from the source to monitoring, and the origin point represents the edge of WPP (Figure 1, A-A'). The concentrations of TPH were reduced along the groundwater flow from source zones to downstream areas. Investigating the results revealed that the decreases of TPH concentrations were significant. The contamination, which was far away from the contamination sources, usually had a longer role of natural attenuation, including soil adsorption, dilution, mixture, and biodegradation. The trend was more obvious in September and October 2009.

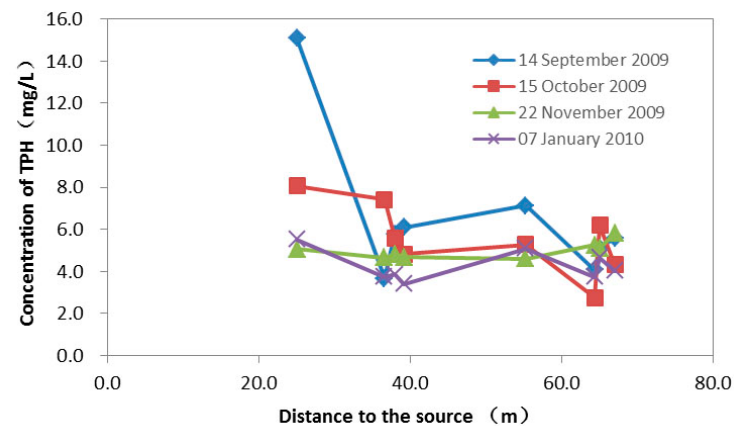


Figure 4. The TPH concentrations along the flowline from the contaminating source.

3.1.3. Temporal Variation of TPH

The distribution of TPH changed during the monitoring period. These changes mainly reflected that the TPH concentration was decreasing, and the plume was wilting. The highest concentration was 15.08 mg/L in September 2009, dropping to 4.77 mg/L in March 2010. Approximately 78% of TPH was attenuated. On the edge of the plume, the attenuation trend was smooth, and 45% of TPH was attenuated on average. The TPH concentrations increased from September 2009 to October 2009 in Z6, Z7, Z9, Z10, Z16, and Z21. This variation was due to the migration of contamination. The same trend occurred in Z11 from October 2009 to November 2009. In another period, the TPH concentration decreased. Overall, in almost all of the monitoring wells, the TPH concentration decreased (Figure 5), and 36.6% of TPH was attenuated on average in all of the monitoring wells. The final concentration of TPH was decreased to 6 mg/L.

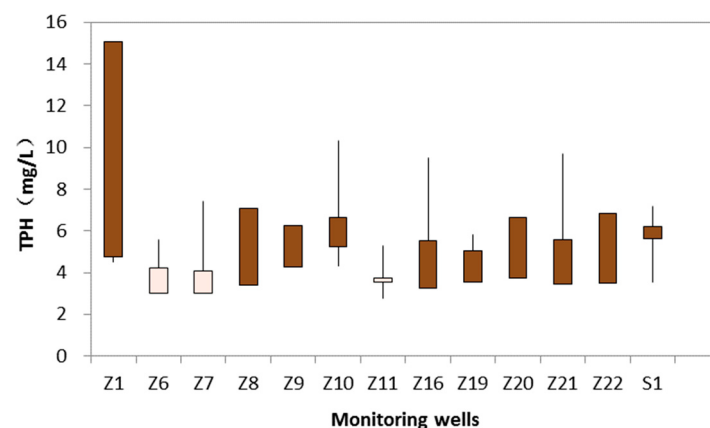


Figure 5. Temporal variation of the TPH concentrations.

3.1.4. Hydrogeochemistry and Biogeochemistry

Based on the investigation of groundwater level, the groundwater flow direction was from the southeast to the northwest (Figure 1). The main anion in the site was the bicarbonate ion, and the content was usually not less than 60%, except Z22. The distributing of bicarbonate ions associated with the TPH concentration, which was high at the downstream of WPP, reaching 2 mg/L, such as with Z6, Z7, Z8, and Z22. In peripheral monitoring wells (Z10, Z11, Z19, Z20, and S1), bicarbonate ion concentrations were lower than 1 mg/L (Figure 6). The evapotranspiration process reacted in the area where the bicarbonate ion concentration was high, and the cations were either sodium ions or sodium ions and calcium ions. Chloride ions were another major anion in the study area, and they were widely distributed downstream of the WPP. After the cleanup the source, the enrichment area of chloride ions became more significant. The main cations in the groundwater were sodium ions and calcium ions. The sodium ions were distributed in the west of the study area, and calcium ions were distributed in the east of the study area (Figure 6). The enrichment of calcium ions and bicarbonate was the result of the leaching process, and the enrichment of sodium ions and chloride ions was the result of the evapotranspiration process. The distribution of the hydrochemical type was formed by recharging not only from the upper gradient area but also from the second Songhua River [50].

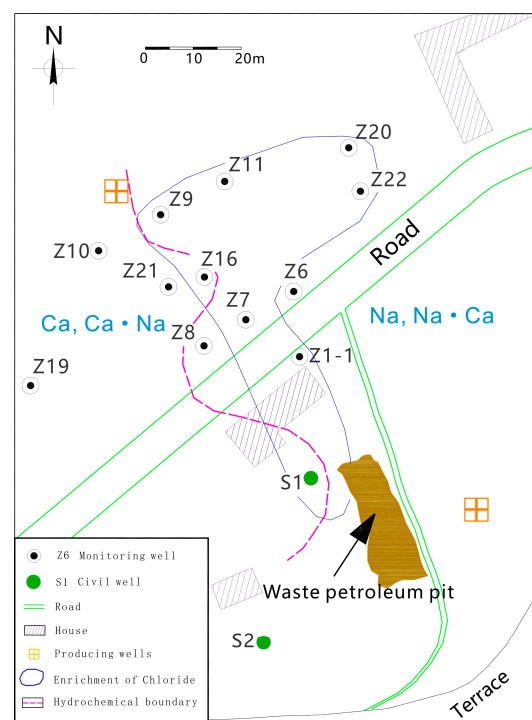


Figure 6. Chemical types and distributions of chlorine.

During the monitoring period, the concentration of dissolved oxygen (DO) was very low. DO concentrations in the high-TPH wells were lower than in the low-TPH wells, and DO concentrations typically were less than 1 mg/L. In the heavily contaminated area, especially near the WPP, the DO concentrations were less than 0.1 mg/L (Z1-1, Z6, Z7, and Z8). These data fully prove that aerobic biodegradation was occurring at this site.

The decreasing trends of nitrate concentrations also can be observed. Nitrate concentrations in the contaminated areas ranged from 1.2 to 14.0 mg/L (Table 1). Higher TPH and lower nitrate were detected near the source, and DO was depleted. The nitrate concentrations decreased from September 2009 to January 2010, and they were stable from January to March 2010 (1 mg/L). The ammonium concentrations increased from September

to November 2009. The average ammonium concentrations ranged from 0.142 mg/L to 1.03 mg/L. This showed that denitrification was occurring on the site.

Table 1. Summary of water quality data intervals for monitoring wells in September 2009 to March 2010.

	September 2009	October 2009	November 2009	January 2010	March 2010
TPH (mg/L)	3.7–15.1	2.8–12.0	4.3–6.6	3.4–6.8	3.2–5.6
pH	6.8–7.6	6.8–8.3	7.9–8.6	7.3–9.7	7.2–7.9
ORP	−163.0–36.4	−137.6–45.7	−130.2–−45.4	−160.9–−77.4	−126.5–−21.5
NO ₃ [−] (mg/L)	1.2–14.0	1.2–3.0	-	0.6–2.0	0.6–4.0
NH ₄ ⁺ (mg/L)	0.1–0.3	0.2–1.3	0.56–1.86	-	-
Mn ²⁺ (mg/L)	0.68–2.98	0.05–2.27	0.90–4.89	0.85–5.23	0.36–3.52
Total Fe (mg/L)	1.7–27.8	0.3–20.9	0.1–10.9	2.0–13.3	0.8–47.1
Fe ³⁺ (mg/L)	0.1–1.1	0.1–0.3	0.1–0.6	0.1–0.5	0.2–0.8
SO ₄ ^{2−} (mg/L)	0.2–142.7	0.2–104.7	0.3–70.8	4.8–48.0	7.9–42.5

Parallel results were measurable for the distribution of manganese in groundwater in September 2009. Manganese is the production of manganese dioxide, which is a component of soil. Mn(II) occurs because of the metabolism by microbes [51]. Downstream of WPP, the average manganese concentrations increased (1.51 to 1.93 mg/L). The average iron(III) concentrations were as high as 0.337 to 7.79 mg/L in wells, while background levels were approximately 1.112 mg/L. Iron(III) concentrations can be used as an indicator of anaerobic degradation of the petroleum hydrocarbons at the site.

Sulfate can be reduced to sulfide by microbes. The background level of sulfate was 143 mg/L. In wells downstream of WPP (Z1-1, Z6, Z7, Z8, Z11, and Z16), the sulfate concentrations were less than 50 mg/L, lower than the farther wells.

Oxidation reduction potential (ORP) indicates that the groundwater environment was weak oxidation to weak restoration (36.4–163.0) in September 2009. ORP was lower downstream of WPP, and the lowest was Z1-1. This illuminates that petroleum contaminated Z1-1 first, and Z1-1 experienced natural attenuation for a long time. ORP decreased from September 2009 to January 2010 (36.81 dropped average) and increased from January to March 2010 (35.01 raised averagely) in some wells (Z1-1, Z6, Z7, Z8, etc.) downstream of WPP. This showed that electron acceptors were depleted, and biodegradation was unable to continue. Groundwater was in a neutral environment in September 2009 (the average pH was 7.23). Compared with the ORP, higher ORP and lower pH were detected near the source zones from September 2009 to January 2010. The pH decreased from January to March 2010 (1.24 dropped average).

3.2. Quantitative Assessment of Biodegradation Processes

3.2.1. Statistical Methods

The evaluation of MNA based on statistical methods was calculated by the TPH concentrations to confirm the flowline, the attenuation rate, and the half-life of petroleum pollutants. It is defined as

$$C(t) = Ae^{\frac{1}{\lambda}t}, \quad (1)$$

$C(t)$ is the concentration function, λ is half-life, t is time, and A is the initial concentration.

3.2.2. Mann–Kendall Test

The zero hypothesis H_0 to time series arrays $(x_1, \dots, x_n)$ is n independent and the random variable distribution of the same sample, and alternative hypothesis H_1 is a bilateral examination. For the related $k, j \leq n$ and $k \neq j$, and x_k and x_j distribution is not the same; inspection of the statistical variable S is based on the following formula:

$$S = \sum_{i=1}^{n-1} \sum_{k=i+1}^n \text{sgn}(x_k - x_i), \quad (2)$$

x_k, x_i are particular values in a sequence of data; n is the length of data; and

$$\text{sgn}(\theta) = \begin{cases} 1, \theta > 0 \\ 0, \theta = 0 \\ -1, \theta < 0 \end{cases}, \quad (3)$$

$\text{sgn}(\theta)$ is the cumulative amount of time series. The Mann–Kendall test requires at least four independent samples of the time [52]. The normal statistical distribution of S is

$$Z_C = \begin{cases} \frac{S-1}{\sqrt{\text{var}(s)}}, S > 0 \\ 0, S = 0 \\ \frac{S+1}{\sqrt{\text{var}(s)}}, S < 0 \end{cases}, \quad (4)$$

Variance:

$$\text{var}[s] = \frac{[n(n-1)(2n+5) - \sum_t t(t-1)(2t+5)]}{18}, \quad (5)$$

For the trend in the bilateral inspection, at a given confidence level α , if $|Z| \geq Z_{1-\alpha/2}$, then the original assumption is unacceptable. That means time-series data versus an obvious is upward or downward trend at a confidence level. Statistical variables can determine the trend of the plume, and based on the corresponding numerical credibility trends, have complete the plume assessment. For statistical variables Z , if greater than 0, it is and upward trend; if less than 0, it is a downward trend. The absolute values of Z were greater than or equal to 1.28, 1.64, and 2.32 at the time, showing that Z passed the reliability of the 90%, 95%, and 99% significance tests, respectively.

In this test, the plume stability is represented as decreasing, probably decreasing, stable, no trend, probably increasing, and increasing at given confidence levels.

3.2.3. Mass Flux

This method is based on four assumptions: (1) the monitoring wells of each CP could contain the plume, the diffusion effect in the longitudinal and vertical profile is negligible, and the TPH distribution in the direction is linear; (2) verified by multiple pumping tests, the TPH concentrations in groundwater and depth meet the power function; (3) adsorption and desorption are instantaneous, and the aquifer is homogeneous and isotropic, with the proportion of adsorption to desorption being 1:3; and (4) volatilization of TPH in groundwater is negligible [39].

In this article, three transects were drawn at distances of 38 m, 58 m, and 66 m from the main source location (Figure 1). The mass fluxes were calculated for the six different sampling periods. The development of the well capture area with time can be described as

$$r(t) = \sqrt{\frac{Qt}{\pi H n_e}}, \quad (6)$$

$r(t)$ is the radius (L) of the well capture zone at time t . Q is the pumping rate (L³ T⁻¹). T is the time (T). H is the aquifer thickness (L), and n_e is the effective porosity (–).

The Darcy law can be described as

$$Q = KAI, \quad (7)$$

K is the hydraulic conductivity (L T⁻¹), A is the area of the cross-section (L²), and I is the hydraulic gradient (–).

The TPH concentration in groundwater and depth meet the power function:

$$C(h) = C_0 \times h^{-0.385}, \quad (8)$$

$C(h)$ is the concentration of TPH (mg/L) at depth (m), C_0 is the concentration at the surface of the aquifer (mg/L), and h is depth (m).

The mass flux of TPH M_{di} ($M T^{-1}$) related to an individual sampling port located within each CP is then defined as

$$M_{di} = C_i q_i A_i, \quad (9)$$

C_i is the concentration measured at the sampling location ($M L^{-3}$), q_i is the specific discharge perpendicular to CP ($L T^{-1}$), and A_i is the capture area (m^2). The total mass discharge M_d ($M T^{-1}$) crossing a groundwater fence with n sampling ports can subsequently be calculated as

$$M_d = \sum_i^n M_{di} = \sum_i^n C_i(h) dh \times K_i I_i \times [2r_i(t)]^2 H, \quad (10)$$

K_i is the coefficient of permeability (m/d), I_i is hydraulic slope (–), and H is the thickness of the confined aquifer (m).

The mass flux between two CPs can be described by the following equality:

$$M_{d_{CP1-CP2}} = \frac{M_{d_{CP1}} - M_{d_{CP2}}}{2} \times \frac{L}{V}, \quad (11)$$

$M_{d_{CP1-CP2}}$, $M_{d_{CP1}}$, and $M_{d_{CP2}}$ represent the measured compound-specific mass fluxes between CP1 and CP2 (g/d); at CP1 and CP2 (g), L is the distance between CP1 and CP2 (m), and V is the average groundwater velocity (m/d). The adsorbance can be described by the following equality:

$$M_a = k_f \times M_d, \quad (12)$$

M_a is adsorbance, and k_f is the absorption coefficient. The amount of microbial degradation is the decrement of M_a and M_d . Compound-specific total mass fluxes ($M T^{-1}$) are quantified at different distances from a contaminant source zone using either point scale or integral investigation approaches. If the average travel time Δt (T) between the two existing control planes is known, it is possible to quantify the compound-specific effective first-order natural attenuation rate constant (T^{-1}) [40]:

$$\lambda = -\ln\left(\frac{M_{d_{CP2}} + M_{a_{CP2}}}{M_{d_{CP1}} + M_{a_{CP1}}}\right) \frac{1}{\Delta t}, \quad (13)$$

λ (T^{-1}) is the effective natural attenuation rate constants.

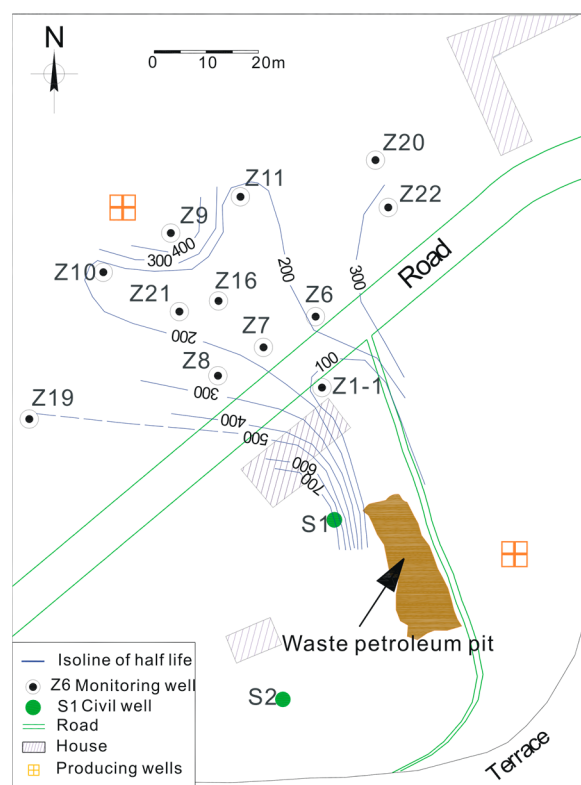
4. Discussion

4.1. Statistical Methods

The results of statistical methods are shown in Table 2. Z1-1 is the nearest monitoring well to the WPP. Its natural attenuation rate is 0.101 mg/d, and 68% of TPH attenuated in 105 days, with its half-life being 87 days. The natural attenuation rate of Z7 is 0.043 mg/d, and 47% of TPH attenuated in 83 days; the natural attenuation rate of Z16 is 0.026 mg/d, and 61% TPH attenuated in 162 days; the natural attenuation rate of Z16 is 0.012 mg/d, and 31% of TPH attenuated in 162 days. The components of petroleum are complex. The longer the distance to the 344 source, the harder the attenuation (Figure 7). Attenuation rate curves followed the exponential distribution, $y = 0.33911e^{-0.0522x}$, $R_2 = 0.9868$. Without human intervention, the remediation time of S1 will cost 10.6 years, which is the longest time in the site. After 3 years, 53.8% of monitoring wells will achieve the remediate goals; after 5 years, 76.9% will achieve the remediate goals; and after 7 years, 92% of monitoring wells will achieve the remediate goals.

Table 2. Estimation from point concentrations.

Location	Initial Concentration (mg/L)	Distance to the Source (m)	Attenuation Time (d)	Attenuation Rate (mg/d)	Half-Life (d)	Remediation Time (a)
Z1-1	15.1	25.1	105	0.101	87	1.3
Z6	5.8	38.0	115	0.017	270	3.5
Z7	7.4	36.6	83	0.043	130	1.8
Z8	6.1	39.2	115	0.023	212	2.8
Z9	6.2	65.1	162	0.012	472	6.2
Z10	10.3	68.4	73	0.082	84	1.3
Z11	5.3	64.4	46	0.035	145	2.0
Z16	8.3	49.0	194	0.026	182	2.6
Z19	5.6	67.1	194	0.011	500	6.5
Z20	6.6	64.4	162	0.018	288	3.9
Z21	9.7	52.0	162	0.039	168	2.4
Z22	7.1	55.3	194	0.019	327	4.3
S1	7.3	8.8	194	0.009	775	10.6

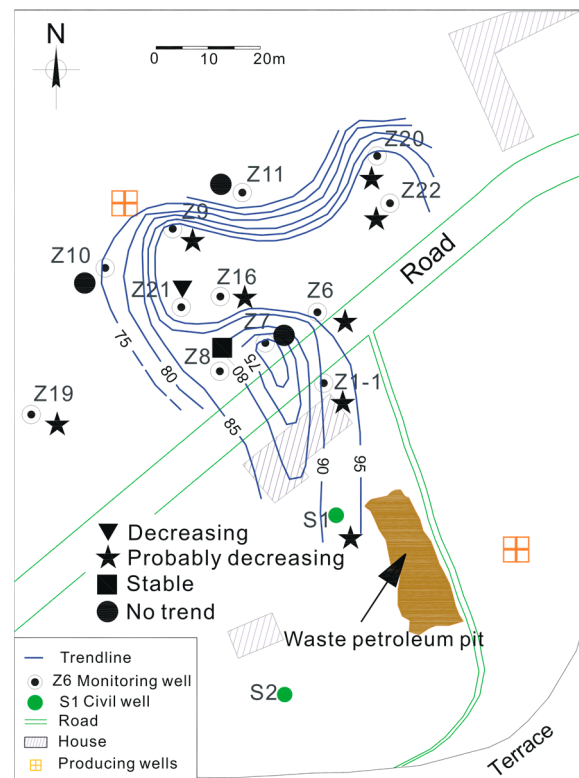
**Figure 7.** Distributions of half-life results of TPH concentrations in the monitoring wells.

4.2. Trend Analysis Based on the Mann–Kendall Test

Table 3 shows that none of the wells were found to be increasing or probably increasing, as well as showing eight decreasing or probably decreasing wells (69%). Only Z8 was stable; Z7, Z10, and Z11 had no trend, and attenuation in these monitoring wells was not apparent. Z10 and Z11 might have been contaminated, being near the producing well. The initial concentrations of Z6, Z7, and Z8 were relatively lower than in other wells. There was no decreasing trend downstream of WPP (Figure 8). These results support the conclusions that the TPH plume was stable or declining. We can also detect that the attenuation trend in the plume was more obvious than at the edge of the plume; for adsorption and dispersion, it was more efficient in the initial condition.

Table 3. Results of the Mann–Kendall trend analyses.

	Concentration Trend	Confidence Level (%)
Z1-1	Probably decreasing	93
Z6	Probably decreasing	97
Z7	No trend	69
Z8	Stable	83
Z9	Probably decreasing	97
Z10	No trend	79
Z11	No trend	56
Z16	Probably decreasing	97
Z19	Probably decreasing	93
Z20	Probably decreasing	96
Z21	Decreasing	99
Z22	Probably decreasing	97
S1	Probably decreasing	93

**Figure 8.** Distributions of the trend analysis results of TPH concentrations in the monitoring wells.

4.3. The Analysis Based on Mass Flux

The TPH concentrations were given by the data of six monitoring periods. Aquifer thickness was equal to the well depth minus the aeration zone depth. The hydraulic gradient was calculated by the water level. Mass flux results are shown in Figure 9. The mass flux of TPH generally reduced over time, only increasing slightly in January 2010. The fluctuation occurred mainly when the TPH concentration was relatively small. Test accuracy was impacted by the fluctuation. According to the changes of mass flux, it could be seen that $CP1 > CP2 > CP3$. The mass flux of CP1 was 1415 mg/d in September 2009, which reduced to 524 mg/d in January 2010, and then it rebounded slightly to 580 mg/d. CP2 and CP3 had the same trend (Figure 9). This indicated that the TPH concentrations through each section decreased. Natural attenuation was carried on in the contaminated plume, and TPH in the site reached the half-steady state from time to time.

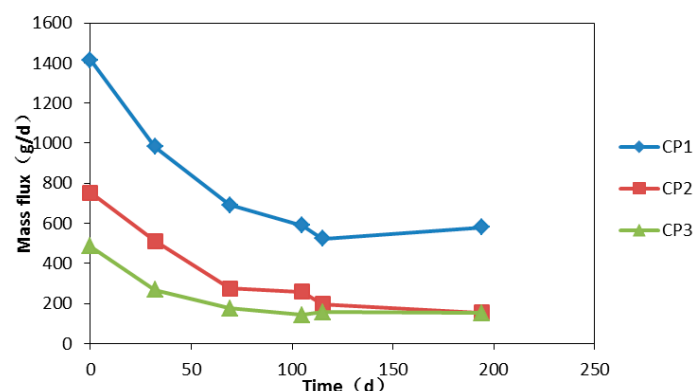


Figure 9. Changes in mass fluxes of each control plane.

The main attenuation processes were adsorption, volatilization, biodegradation, and dispersion. Based on the research of Suarez (2002) [39], the volatilization of TPH in groundwater is negligible. Once the medium and environment are fixed, adsorption and dispersion are stable, so the decrement of mass flux can be considered as the approximate contribution of biodegradation. We calculated the biodegradation using Formulas (9)–(11), and the results are listed in Table 4. Based on the mass flux data in time and space, biodegradation of TPH and natural attenuation were able to be analyzed. However, if the mass flux is reduced, the soil particle will resolve part of the petroleum hydrocarbons, and then the biodegradation of capacity will be the sum of reduction and desorption. We were able to calculate desorption by using Formula (12). From September 2009 to March 2010, biodegradation due to mass flux reduction between CP1 and CP2 was 215 g; total flux reduction was 242 g through calculus, and biodegradation occupied 89% of the total attenuation. This explained why microbial degradation was a major attenuation mechanism in the site. Similarly, from September 2009 to March 2010, biodegradation calculated by mass flux between CP2 and CP3 was 140 g; total mass reduction was 152 g, and biodegradation occupied 92% of the total attenuation. During this process, the adsorption capacity between CP1 to CP2 was from 81 g down to 27 g, and adsorption shrank. In the monitoring process, adsorption and biodegradation declined continuously, but the biodegradation ratio increased. The biodegradation ratio at the upstream was 64–89%, and the biodegradation rate downstream was 70–92%. The average biodegradation rate in the upstream was 0.4911 mg/d/m³, and it was 0.338 mg/d/m³ downstream. The attenuation rate upstream was higher than downstream.

In short, the following were found: (1) Calculations showed that attenuation stably occurred in the plume, the mass flux of each CP was reducing, and there were more contaminants upstream than downstream. (2) Adsorption and biodegradation were the main attenuation processes; biodegradation was more efficient. (3) Biodegradation increased, and adsorption decreased with time. The biodegradation capacity was 383 g.

The three findings above were able to be used to estimate the natural attenuation of petroleum-contaminated sites. Comprehensive results could reflect the intensity and trend of natural attenuation. The distribution and concentrations were able to verify the trend analysis results compared to the monitoring results. Natural attenuation occurred in the groundwater of the petroleum-contaminated site, and the TPH concentrations decreased continuously. Attenuation strength in the plume was higher than the edge, and attenuation patterns were different.

4.4. The Division of Functional Areas and the Utilization of Electron Acceptor

OPR is the parameter that indicates redox conditions of groundwater in the site. According to Norris and Drápela's research [32,53], when microorganisms consume electron acceptors, ORP indicates the utilization of an electron acceptor. If pH is known, ORP can be determined, as shown in Figure 10. When pH = 7 and temperature is 25 °C, if Eh is more than 740, it is an aerobic condition, and oxidation can occur in the area. If Eh is less than

740, it is an anaerobic condition, and there is no oxygen available; thus, denitrification can happen in the area [54]. However, biodegradation in the site is a complex process. pH and temperature are changeable, so Fetter, C.W [55] studied the relationship between Eh and various ions under different pH values, as shown in Figure 11. Thus, microbial functional areas of the site can be speculated.

Table 4. The result of mass flux and the contribution of each attenuation.

Time (d)		0	32	69	105	115	194
CP1–CP2	Mass flux (mg)	243,868	168,081	108,778	95,533	80,997	82,453
	Adsorbed mass (mg)	81,289	56,027	36,259	31,844	26,999	27,484
	Total mass (mg)	325,157	224,108	145,037	127,377	107,996	109,937
	Mass flux decreased (mg)	0	75,787	135,090	148,335	162,871	161,415
	Adsorbed mass decreased (mg)	0	25,262	45,030	49,445	54,290	53,805
	Biodegradation (mg)	0	101,049	180,120	197,780	217,161	215,220
	Total attenuation (mg)	81,289	157,076	216,379	229,624	244,160	242,704
	Biodegradation ratio (%)	0	64	83	86	89	89
CP2–CP3	Attenuation rate (%)	25	48	67	71	75	75
	Mass flux (mg)	139,415	87,636	50,803	45,171	39,551	34,223
	Adsorbed mass (mg)	46,472	29,212	16,934	15,057	13,184	11,408
	Total mass (mg)	185,887	116,848	67,737	60,228	52,734	45,631
	Mass flux decreased (mg)	0	51,780	88,613	94,244	99,865	105,192
	Adsorbed mass decreased (mg)	0	17,260	29,538	31,415	33,288	35,064
	Biodegradation (mg)	0	69,040	118,150	125,659	133,153	140,257
	Total attenuation (mg)	46,472	98,251	135,084	140,716	146,336	151,664
	Biodegradation ratio (%)	0	70	87	89	91	92
	Attenuation rate (%)	25	53	73	76	79	82

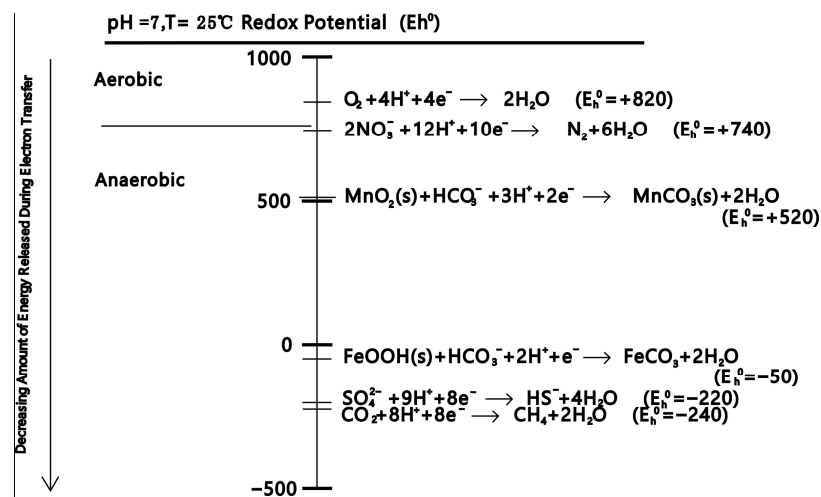


Figure 10. Redox potentials for various electron acceptors (based on Norris and Drápela) [32,53].

Furthermore, electron acceptor concentration is also an effective way to determine the microbial functional areas. Electron acceptors of the site have background values, and anomalies are usually caused by microorganisms. Therefore, concentrations of electron acceptors can reflect the microbial functional areas, at least those existing or taking place.

Based on Norris and Drápela's research, we can determine that the site was utterly anaerobic. Denitrification and manganese reduction occurred in all monitoring wells of the site. Until September 2009, iron reduction occurred in all of the wells except Z19 and S1, and sulfate reduction and methanogenesis did not occur during the monitored period. However, there was a zone whose sulfate concentration was lower than the background value; ORP was unable to prove it, so we considered that sulfate reduction had occurred before the monitored period.

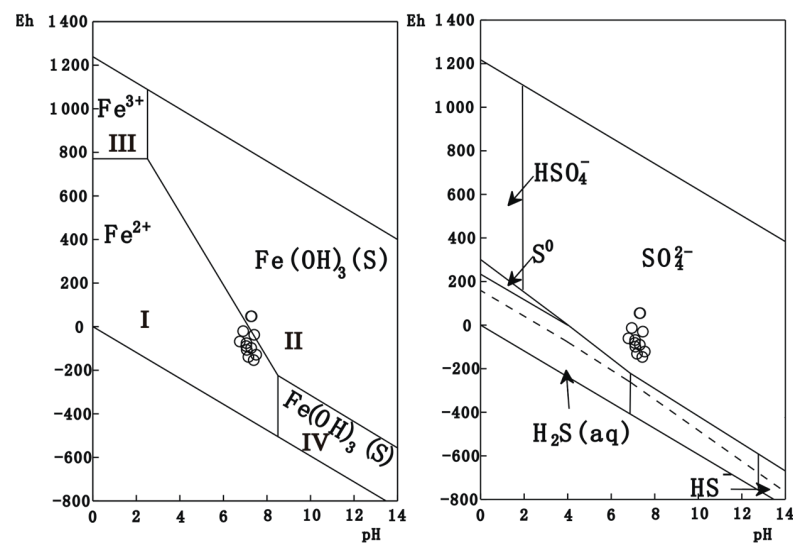


Figure 11. The relationship between Eh, pH, Fe, and S (based on Fetter) [55].

Suppose all electron acceptors in each monitoring well had an unchanged background value. Within the monitoring period, all the monitoring wells' concentrations were at a lower level, except S1. Manganese had a similar trend with iron, so the main boundary was unable to be distinguished, and manganese was assigned to the same boundary. An apparent low value area was able to be obtained through sulfate concentrations change analysis. This area is downstream of WPP and could maintain stability during the monitoring period. It could also prove that sulfate reduction had taken place before the monitored period. Through the analysis of electron acceptor concentrations, the boundaries of iron, manganese, and sulfate in the site were able to be identified, as shown in Figure 12.

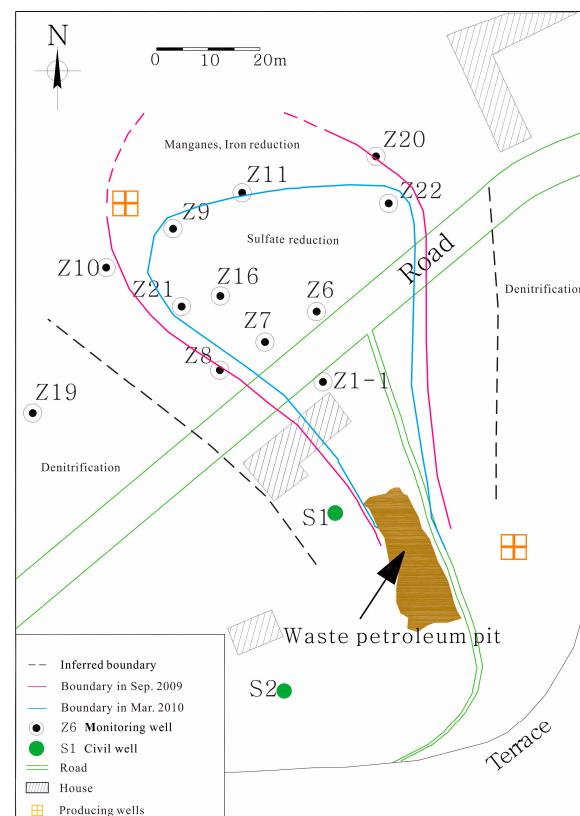


Figure 12. Electron acceptor zones in the groundwater.

By comparing the results, the boundary of the functional area remained unchanged. Only the reduction area of manganese and iron expanded slightly.

5. Conclusions

Based on the results monitored from petroleum-contaminated sites, we estimated MNA by statistical methods, the Mann–Kendall test, and mass flux, and thus we came to the following conclusions:

The contamination in the site was severe and needed remediation.

The TPH concentrations were decreasing in the monitoring period but still seriously exceeded the standard (Quality Standards for Groundwater (GB/T 14848-2017) [49] of China).

The attenuation rate in the site was from 0.00876 mg/L to 0.10095 mg/L, and the relationship between attenuation rate and distance met the exponential distribution. Remediation time was from 1.3 years to 10.6 years. Analysis of the TPH trend indicated that 62% of wells had decreasing or probably decreasing trends: these support the conclusion that the TPH plume is shrinking. Mass fluxes of the three CPs and changes in the plume also indicated that the TPH plume had reached a quasi-steady state and that mass flux was declining. The attenuation trend in the plume was more evident than the edge. The most essential process of MNA is biodegradation, and the second important is sorption. During the monitoring period, 393 g TPH attenuated, including 355 g TPH degraded by microbe. Biodegradation in the upstream is stronger. Iron(III) and manganese were the main electron acceptors utilized by microbes during the monitored period.

Based on the result of monitoring and estimation, we were able to come to the same result: MNA is in progress, and MNA can be an effective method to remediate the petroleum-contaminated site.

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