Study on the Effect of Sulfate on the Degradation of BTEX in Leakage Area of Gasoline by Using Numerical Simulation

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Abstract. In order to explore the migration of sulfate electron acceptors injected into aqueous media, and study the specific attenuation of BTEX with sulfate injecting. In this study, the laboratory sand tank was used for the injecting and natural attenuation monitoring experiments. The combination of MODFLOW and RT3D was used to simulate the attenuation process of sulfate and natural degradation of BTEX. The results showed that the concentration of sulfate in the source area was significantly lower than that of the surrounding area at the 600th day after injected on the 416th day and BTEX concentration also gradually tends to zero. The injection experiments were conducted for a total of 46 days with the injected sulfate quality of 1488.24 g, and the calculated sulfate output of 1320.52 g. It can be seen that the input was significantly higher than the output and the sulfate loss could be judged as acting on Redox reactions. Sulfate promoted the degradation of BTEX. The numerical simulation was carried out for the water flow model and water quality model calibration, the normalized RMS of water flow model and water quality model are 9.8% and 8% respectively, which are less than 10% of the conventional limit. The model can accurately simulate the migration of sulfate and BTEX attenuation and predict the further pollution of BTEX. And can be applied to the actual site contaminated by BTEX that has important practical significance.

1. Introduction

BTEX (benzene, toluene, ethyl-benzene, and xylenes) has several disadvantages such as toxic, deformed, carcinogenic and hard to degrade. Simultaneously, the characteristics about solubility, volatility and mobility, which make it easy to penetrate through the soil vadose zone and stay in the aquifer. Therefore the water quality deterioration caused by oil leakage is a severe problem for humanity at present. However, some of the gasoline pipelines and underground sealed gasoline tanks have been used a long time, distributed widely and they are not reasonable to design. And human factors such as malicious piracy or accidental third-party damage factors leaked the gasoline storage tank [1, 2].

In the natural environment, the potential electron acceptors for oxidizing organic matter under anaerobic conditions include nitrate, ferric, sulfate and tetravalent manganese and so on [3]. Among them, sulfate as an effective potential electron acceptor, the concentration in groundwater is generally low. However, due to the supply of sulfate in the rainwater, the dissolution of fertilizers in the soil, and
the infiltration of septic tanks and landfill sulfate, the concentration of groundwater in some areas will be significantly increased. While polluting the groundwater aquifer, it also provides the corresponding electron acceptor [4, 5]. Studies on the degradation of BTEX by sulfate as a terminal electron acceptor have already begun in foreign countries in the early 1990s, and later there is evidence that the comprehensive repair methods of sulfate and ferric iron is more effective [6]. Relevant scholars given the adsorption conditions or electron acceptor and performed the natural attenuation simulation for some organic pollutants or total petroleum hydrocarbons. However, there are few reports about the stimulative effect of some electron acceptors on the natural attenuation of BTEX by using numerical simulation method. Therefore, MODFLOW and its sub-module RT3D multi-component migration model was used to simulate the pollution state of gasoline, the migration process of sulfate and the specific degradation process of BTEX.

2. Materials and methods

2.1. Experimental situation

The aquifer model used in the experiment is based on the generalized design of shallow sandy aquifers in the field. And the specific experimental setup and the previous experimental scheme have been described [7].

Before the experiment, the model was pumped and injected systematically to estimate hydrogeological parameters by using fresh shallow groundwater. The water level was controlled at the height of 50 cm above the bottom of the model. After that, 3 L traditional gasoline was injected into the north part and equivalent of 10% ethanol gasoline was injected into the south part at the same time. The average flow rate of injection was about 500 mL/h, and the injection points were designed at the 45 cm height of the source wells of the model.

The north sampling points are from A2-E4, and the south points are from A6-E8 including most of the holes and shelves. A1-E1 and A5-E5 did not add to the experiment, because the two rows of holes in the direction of the reverse flow and the concentration is too low, so it’s no significance to research.
For the holes that did not detect the pollutant in long-term observation, the concentration is considered to be 0 mg/L. The sampling tool for the experiment was a peristaltic pump. After the sample was taken out into a 25 ml brown bottle, a standard pipette was used immediately to take 5ml of the test sample into a 10 ml Agilent headspace bottle cap. And 1g NaCl is placed in the headspace bottle to poison the microorganisms in the samples and prevent them from degrading the contaminants in the bottles to increase the analysis error. The samples were placed in a refrigerator at a temperature of 4°C and analyzed within 3 days. BTEX is detected using a gas chromatograph equipped with a flame ionization detector and a packed column. The minimum water quality limit is 0.002 mg/L.

The previous pilot project was to study the effect of groundwater level fluctuations on the degradation of BTEX and has been described in other papers. In order to study the promotion effect of sulfate on degradation of BTEX in gasoline-contaminated aquifers, sodium sulfate solution was injected into the water from inlet on both sides of the aquifer by using a peristaltic pump on the 416-461 days. The flow rate was 30 ml / min, the sulfate concentration was 330 mg/L and the actual concentration was 335.9 mg/L. And continue to observe the degradation of BTEX to 671 days. In the medium to late stages of the experiment, control of water level stability, so as not to interfere with the experimental results.

2.2. The comparison of sulfate of input and output
In order to prove that the degradation of BTEX is the result of sulfate redox reaction, the input amount during the sulfate injection experiment was calculated. The sand tank was divided into several small grids by the calculate way of grid method. With the help of the sulfate concentration indexing contour Figure Computation to calculate the sand sulfate output. The injection experiments were conducted for a total of 46 days with a sulfate weight of 1488.24 g cast and a calculated sulfate output of 1320.52 g. It can be seen that the input was significantly higher than the output and the sulfate loss could be judged as acting on Redox reactions.

2.3. Numerical Simulation
The initial water level of the flow model was 0.5 m and the initial BTEX concentration was no detectable. Boundaries of the east and west sides belong to the first type of boundary condition, and other boundaries belong to zero flow condition. The top has evaporation boundaries. And set up the well boundary at east-west flume head observation well location and pollutant injection hole. The water flow model was corrected by parameter inversion, adjustment of hydraulic conductivity, water supply and water storage coefficient.
Table 1. Parameters that have been corrected

| Model parameters                        | Value, unit | Source |
|-----------------------------------------|-------------|--------|
| Hydraulic conductivity:                 |             |        |
| Horizontal hydraulic conductivity       | 41 m/d      | measured |
| Vertical hydraulic conductivity         | 4.1 m/d     | [8]    |
| Porosity                                | 0.3         | measured |
| Groundwater velocity                    | 0.207 m/d   | measured |
| Bulk density                            | 1700 kg/m³  | [9]    |
| Specific yield                          | 0.2         |        |
| Specific storage                        | 1.0×10⁻⁵ (1/m)| [8] |
| Amount of evaporation                   | 0.1 mm/d    |        |
| Dispersion (N side model):              |             |        |
| Longitudinal                           | 0.025 m     | [10]   |
| Transverse horizontal                  | 0.075 m     | parameter calibration |
| Transverse vertical                    | 0.003 m     | parameter calibration |
| Dispersion (S side model):              |             |        |
| Longitudinal                           | 0.025 m     | [10]   |
| Transverse horizontal                  | 0.012 m     | parameter calibration |
| Transverse vertical                    | 0.006 m     | parameter calibration |
| BTEX transport velocity                 | 0.019 m/d   | calculated |
| First-order reaction rate (BTEX)        | 0.0002 (1/day) | [11] |
| Partition coefficient (K_d)            | 7.73×10⁻⁴ m³/kg | [12] |
| BTEX effective solubility (gasoline)    | 44-112 mg/L | [13]   |
| Time step                               | 10 d        | calculated |

In the water quality model, a water injection well was set up at the pollution source, simulating the release of pollutants by setting a continuous boundary of point source injection. The initial concentration of dissolved oxygen, sulfate and nitrate is 4.5 mg/L, 16 mg/L and 3.8 mg/L respectively by instrumental analysis. Shallow groundwater contains a large number of electron acceptors, so the influent sink boundary conditions was set up for the concentration of continuous injection on the boundary. In the shallow groundwater, the dissolved oxygen was 7.5 mg/L, nitrate was 3.5 mg/L and sulfate was 16 mg/L, and they were the average values of multiple measurements. By adjusting the effective solubility of BTEX within a reasonable range and fitting with the observation concentration data which changes caused by water level fluctuations to adjust parameters repeatedly. The model parameters are shown in Table 1.

3. Results and discussion

3.1. The rationality evaluation of parameter and simulation
Figure 2. The scatter and fitting diagram of ground water level observation - calculating data’s
Figure 3. The scatter diagram and calibration residual histogram of BTEX concentration observation - calculating

Model parameters are shown together in Table 1 with the source of the data within the empirical range. In addition, figure 2 shows the time series of the model water level, which can reflect the calibration of the model intuitively. The latter shows that most of the data points approximate $X = Y$, a straight line at 45 degrees. The normalized RMS is about 9.8%, lower than the conventional limit of 10% [14]. All of these evidences show that the observed values are well fitted to the calculated values, which indicates that the simulation accuracy of groundwater flow field is high.
The operation of the solute transport model program is based on a reasonable calibration of the water flow model. The calibration and test are similar to the flow model. The observed and calculated values of BTEX concentration need to be compared with each other, and the two are compared and analyzed in a certain time series. The parameters of the model can be simulated repeatedly to reasonably simulate the solute's physical, chemical and biological Degradation process. The normalized RMS in the Figure 3 is 8%, which is less than the conventional limit of 10%. The standard residual histogram shows that the calibration residual distribution about the observation point is very similar to the normal distribution curve. And most residuals are distributed around groups of zero, which indicated the fitting is accurate. In general, the solute transport model can better simulate the migration of BTEX in the aquifer.

3.2. The simulation of sulfate transport

![Figure 4: Sulfate transport profiles at 430th, 440th, and 600th days](image)

After the high concentrations of sulfate ions injected with groundwater into the sand tank model, there will be gradually form a high concentration boundary in the water injection tank on the east side. And the concentration of the sulfate in east water tank was 334.6 mg/L at the end of the sulfate
infusion. Sulfate will move inside the sand tank gradually. According to the result of discontinuous experiment, using the numerical simulation method to match the simulation result with it, we can get the migration of sulfate at any time and judge the degradation of BTEX. As shown in Fig. 4, after the sulfate was injected on the 416th day, it can be seen at the 600th day that the sulfate ion concentration in the source area was significantly lower than that in the periphery, indicating that it has a certain promotion effect on the degradation of BTEX.

The true groundwater environment is also like this. Contaminated groundwater sometimes requires the injection of one or more electron acceptors to accelerate microbial degradation. The combination of MODFLOW and RT3D simulates and predicts the migration and attenuation of injected drugs. However, due to the complex geological conditions, the simulation of groundwater environment will be more complicated.

3.3. The analysis of sulfate degradation for BTEX

![Figure 5. The concentration and time series fitting map about source zone](image-url)
By analyzing the concentration and time series about source zone, we can see that the concentration of BTEX in the south is obviously higher than that in the north. In the Day 461, the BTEX monitoring results of C2-45 in the north were 4.412 mg/L, the values of C6-45 in the south were 31.805 mg/L, because the ethanol injected on the south has a certain inhibitory effect on the degradation of BTEX [15]. After the high concentration of sulfate into the aquifer, BTEX concentration showed a significant reduction in state immediately. And according to the meshing method, the input was significantly higher than the output. On the one hand, it is proved that sulfate is an efficient electron acceptor, which can accelerate the natural attenuation of BTEX and promote its redox reaction. On the other hand, it can be seen that the combination of MODFLOW and RT3D can accurately simulate the attenuation process of BTEX in the case of injecting electron acceptors, which can be applied to the real site contaminated by BTEX, which has important practical significance.

4. Conclusion
Sulfate has a significant effect on the natural attenuation process of BTEX. On the other hand, the combined use of MODFLOW and RT3D can reasonably simulate the distribution of groundwater flow field, electron acceptor and BTEX in aqueous media. It is also possible to perform a valuable simulation of the amount of pollutant dissolved. In this study, numerical simulation was used to simulate the migration of sulfate into groundwater aquifer and the attenuation of BTEX. The simulation parameters and simulation results were further analyzed and corrected. The model could provide pollution prediction for BTEX pollution caused by oil leakage in a real groundwater environment.

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