Numerical Simulation of the Effect about Groundwater Level Fluctuation on the Concentration of BTEX Dissolved into Source Zone

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Abstract: The water level fluctuation of groundwater will affect the BTEX dissolution in the fuel leakage source zone. In order to study the effect, a leakage test of gasoline was performed in the sand-tank model in the laboratory, and the concentrations of BTEX along with water level were monitored over a long period. Combined with VISUAL MODFLOW software, RT3D module was used to simulate the concentrations of BTEX, and mass flux method was used to evaluate the effects of water level fluctuation on the BTEX dissolution. The results indicate that water level fluctuation can significantly increase the concentration of BTEX dissolved in the leakage source zone. The dissolved amount of BTEX can reach up to 2.4 times under the water level fluctuation condition. The method of numerical simulation combined with mass flux calculation can be used to evaluate the effect of water level fluctuation on BTEX dissolution.

1. Introduction
Monoaromatic hydrocarbons mainly including benzene, toluene, ethyl-benzene, and xylenes (referred to as BTEX) have several characteristics about solubility and mobility, which make it easy to penetrate through the soil vadose zone and stay in the aquifer. Additionally, it has some disadvantages about toxic, deformed, carcinogenic and hard to degrade. The water quality deterioration caused by oil leakage is a severe problem for humanity at present.

Monoaromatic hydrocarbons have a state of natural attenuation in the aquifer. The fluctuation of groundwater level will obviously improve the state, changing the migration of nitrate, dissolved oxygen and oxidation-reduction potential and so on [1]. The seasonal change can lead to the repeated eluviation at the smear zone. It also causes LNAPL (light non-aqueous phase liquid) to make vertical motion, and then influences the BTEX concentration [2]. At the same time, the fluctuation of water level around the smear zone may improve the biodegradation, but the increase amount of BTEX dissolved in groundwater is much more than consumed by degradation. Therefore, the amount of dissolved BTEX will increase significantly [3]. The trend of LNAPL pollution caused by water level
fluctuation has been studied by some scholars, and they have made the simulation about natural attenuation by giving the adsorption conditions or electron acceptor for a certain organic pollutants or total petroleum hydrocarbon [4, 5]. There are few reports about the amount of BTEX dissolving in the source area using numerical simulation methods.

In order to determine the dissolved amount of BTEX caused by water level fluctuation, MODFLOW with its sub-module RT3D (multi-component interaction model of the migration) were used to simulate the natural attenuation process and the concentration changes of BTEX under the water level fluctuation condition. Combined with the effective dissolved amount of 63 mg/L of BTEX in gasoline with the steady water level, the BTEX dissolution was simulated under the condition of water level fluctuation and used to calculate BTEX mass flux. This work about BTEX dissolution under the condition of water level fluctuation can provide a reference for the actual contaminated site.

2. Materials and Methods

2.1. Experimental Situation

The design of aquifer model used in this experiment is based on the generalized shallow sandy aquifers in the field. The dimension of the aquifer model is 5.8 m long, 2.9 wide and 1.30 high. Two narrow slots of 0.2 m wide is located on both east and west sides, respectively, and a 0.2 m impermeable wall divides the aquifer model into the north and south parts. The aquifer is 0.9 m thick, made of sand with 0.05-0.25 cm particle size. Groundwater pumped from nearby shallow aquifer was injected as supply water. The model has 40 sampling holes including A-E and 8 water level observation holes including W1-W8. The specific model structure is shown in Figure 1.

![Figure 1. The plane figure of the aquifer model.](image)

Before the experiment, the model was pumped and injected systematically to estimate hydrogeologic 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 was designed at the 45 cm height of the source wells of the model.

After the experiment began, water level was relatively stable before the first 77 days. Water level occurred fluctuations in some extent, as shown in Table 1. During the period of experiment, BTEX concentrations were monitored A-E holes per month, detected by using an Agilent 6890 N gas chromatograph, and BTEX attenuation was paid attention. Significantly, The BTEX concentrations...
increased, correspondingly to each rise of the water level.

![Table 1. The fluctuation of water level](image)

| Period(day) | Water level changes | Water level range (cm) | Average water level (cm) |
|------------|--------------------|-----------------------|--------------------------|
| -76th      | Stable             | 48.1-51.4             | 49.8                     |
| 77th-78th  | Rise               | 50.4-64.3             | 57.4                     |
| 78th-128th | Fall               | 64.3-50.8             | 56.1                     |
| 129th-147th| Rise               | 50.8-63.4             | 57.0                     |
| 148th-167th| Stable             | 63.4-64.1             | 61.3                     |
| 168th-173th| Fall               | 64.1-53.1             | 54.1                     |
| 174th-237th| Stable             | 53.1-49.3             | 50.9                     |
| 238th-285th| Rise               | 49.3-61.5             | 57.4                     |

2.2. Mass Flux

Mass flux refers to the total mass of a certain solute in a unit of time through a section perpendicular to the flow direction. In this paper, the in-site cross-section method and time-moment method were used to estimate the mass flux of BTEX concentration. The formulas are shown in the reference [6].

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.

3. Results and Discussion

3.1. The BTEX Concentration Changed with Water Level Fluctuation in the Source Area

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 pollutant flow rate was 500 ml/h. Since the model has electron acceptor, the initial concentration of each component is 4.5 mg/L dissolved oxygen, 16 mg/L sulfate, 3.8 mg/L nitrate. 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. The time step was calculated as 10 d [7]. 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 2.

Because the injection hole is located at a depth of 45 cm and the simulated water flow is similar to the one-dimensional flow. The central line at the water level of 45 cm is most impacted by the water level fluctuation. Therefore, the change of BTEX concentration is the most significant near the source region or within the source region affected by water level fluctuation, and it is more likely to be due to other factors at the downstream pore position. The model simulation results of pollution source area are shown in Figure 2.
Table 2. Parameters that have been corrected

| Model parameters                        | Value, unit | Source |
|-----------------------------------------|-------------|--------|
| 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  |        |
| Specific yield                          | 0.2         |        |
| Specific storage                        | 1.0×10⁻³ (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               | 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]   |

77th day 106th day 128th day 146th day

163th day 173th day 237th day 285th day

Figure 2. The BTEX concentration changed along with the water level fluctuation at north source zone.

The water level fluctuated 3 times in all. During the period with a stable water level before the 76th day, the concentration of BTEX in the source area first increased and then decreased. The concentration becomes higher when pollutants flow through the hole at this stage, and then decreased gradually with the natural attenuation effect. After a sudden increase in water level on day 77, the BTEX concentration increased significantly, and after the rise of the water level slowed down, the concentration decreased gradually. After a slow rise in water level at 129 days, the contaminant concentration increased. The water level gradually decreased from 148 days to 167 days after being stable for 20 days, and by day 182, it dropped to the initial level. At this point BTEX concentration also decreased gradually. At the end of the experiment, when the concentration of pollutants was very low and after the water level had risen, the BTEX concentration increased.

3.2. The Mass Flux of Source Area Fluctuates with Water Level Fluctuation in Downstream Section

With the flux analysis can be seen that the difference of mass flux is obvious before and after the three water level fluctuations. Before the first water level fluctuation, the mean mass flux on both sides was
35.5 mg/d on day 71. After the fluctuation and on day 103, the mean mass flux on both sides was 78.1 mg/d. Before the second fluctuation, the mean mass flux on both sides was 75.1 mg/d on day 128. After the fluctuation and on day 163, the mean mass flux on both sides was 110.7 mg/d. Before the third water level fluctuation, the mean mass flux on both sides was 12.7 mg/d on day 237. After the water level fluctuation and on day 285, the mean mass flux on both sides was 50.4 mg/d. The observations, calculated results of mass flux are shown in Table 3. The mass flux results of observations are derived directly from the concentration observations into the relevant calculation formula, and the mass flux results of calculated is calculated by the value which is simulated by the MODFLOW software. Comparing the results showed that the simulation accuracy has improved.

**Table 3. The mass flux changed along with the times.**

| Time(d) | 71   | 103  | 106  | 118  | 128  | 142  | 163  | 173  | 237  | 285  |
|---------|------|------|------|------|------|------|------|------|------|------|
| Mass flux | The 2\textsuperscript{nd} section | calculated | 26.3 | 54.9 | 73.4 | 71.0 | 61.1 | 55.0 | 98.9 | 79.7 | 5.5 | 53.8 |
|         | observations | 30.3 | -    | 84.1 | 62.8 | -    | 51.1 | -    | 70.8 | 3.8  | -   |
|         | The 6\textsuperscript{th} section | calculated | 39.7 | 101.3 | 146.3 | 112.4 | 92.0 | 93.4 | 122.4 | 111.9 | 19.9 | 47.0 |
|         | observations | 40.7 | -    | 148.5 | 113.5 | -    | 96.5 | -    | 123.3 | 15.9  | -   |

In summary, water level fluctuation will promote the dissolution of BTEX. After gasoline polluted the 45 cm layer of the aquifer, it will move with the flow of water. Most of the pollutants floating in the surface of groundwater are absorbed in the soil and rocks. Coupled with its own volatility, diffusion and dispersion, the concentration of BTEX in the smear zone increased greatly. Therefore, a sudden increase in water level will dissolve the pollutants in the water body, resulting in a substantial increase in the concentration of pollutants in the water body. When the water level drops, BTEX concentration will be reduced due to the water away from the source area. In real subsurface aquifers, away from the source area, the concentration of pollutants increases as the water level rises, due to the effect of dilution, which is also illustrated in the literature [14].

3.3. **The BTEX Concentration Simulation Dissolved in Source Zone**

Water level fluctuations will have an effect of elution for LNAPL, and it will accelerate the dissolution of monocyclic aromatic hydrocarbons significantly. So the amount of dissolved pollutants increased sharply [6]. According to the literature, the effective solubility of BTEX is generally 63 mg/L.

**Table 4. The concentration gradient of contamination in source zone.**

| Period(d) | 0-77 | 77-78 | 78-128 | 128-148 | 148-167 | 167-173 | 173-237 | 237-285 |
|-----------|------|------|--------|---------|---------|---------|---------|---------|
| North side (mg/L) | 74.8 | 129.9 | 118.1 | 133.9 | 124.0 | 122.1 | 21.7 | 63 |
| South side (mg/L)  | 63.0 | 126.0 | 144.2 | 145.7 | 149.6 | 129.9 | 25.6 | 68.9 |

After concentration correction, it was concluded that the continuous injection flow of the corresponding injection hole was 0.0036 m\(^3\)/d. The value we set can accurate simulate of BTEX dissolution relatively without water level fluctuation. Furthermore, through the calibration fitting with experimental results, the effective dissolved concentration of BTEX under every fluctuating condition was obtained with the stable injection flow. Finally, the model simulated the release concentration of BTEX pollutants caused by water fluctuation in the laboratory aquifer model by calibration parameters. And the concentration is the value of the point source boundary. The specific data are shown in Table 4, and it can provide data for the real reference to contaminated sites.
4. Conclusions
Fluctuation of water level will seriously affect the quality of groundwater in the source area. A rise in the water level will cause a lot more BTEX to dissolve into the groundwater sharply, resulting in a high BTEX concentration in the source area. A drop in the water level will alleviate the pollution in the source area. The method of numerical simulation combined with mass flux calculation can be used to evaluate the effect of water level fluctuation on BTEX dissolution. The BTEX dissolution under the condition of water level fluctuation can provide a reference for the actual contaminated site.

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6. References
[1] Yuan Zhi-ye and Bai Shun-guo. Study on the transport of pollutants in soil under the condition of groundwater level rising and falling. Hebei: Hebei Agricultural University, 2013.
[2] Alan E, Kelew P M, Lynch, et al. Concentration trends and water-level fluctuations at underground storage tank sites. Environ Earth Sci, 2011, 62: 985–998.
[3] Richard D, Martin H, Schroth. Effect of water-table fluctuation on dissolution and biodegradation of a multi-component, light nonaqueous-phase liquid. Journal of Contaminant Hydrology, 2007, 94:235-248.
[4] Prommer H, Barry D A, Davis G.B. Modelling of physical and reactive processes during biodegradation of a hydrocarbon plume under transient groundwater flow conditions. Journal of Contaminant Hydrology, 2002, 59:113–131.
[5] Jason N, Samuel W. A Case Study in the Use of 3-Dimensional Ground Water Modeling and Solute Transport Engines as a Tool in Site Assessment. Environment and Pollution, 2014, 3(2):55–64.
[6] Aris R. On the dispersion of linear kinematic waves. Mathematical and Physical Sciences, 1958. 245(1241):268-277.
[7] Chen X S, Brooks M C, Wood A L. The uncertainty of mass discharge measurements using pumping methods under simplified conditions. Journal of Contaminant Hydrology, 2014, 156:16-26.
[8] Wang Zhi-wei and Shan Xin-yu. Simulation of Aerobic Biodegradation of BTEX Plume in Groundwater. Taiwan: National Chiao Tung University, 2012.
[9] Hudak P F. Chloride and Nitrate Distributions in the Hickory Aquifer, Central Texas, USA. Environment International. 2000, 25(4):393–401.
[10] John W H and Molson. Numerical Simulation of Hydrocarbon Fuel Dissolution and Biodegradation in Groundwater, Waterloo, Ontario, Canada, 2000.
[11] Suarez M P., and Rifai H S. Modeling Natural Attenuation of Total BTEX and Benzene Plumes with Different Kinetics. Ground Water Monitoring and Remediation, 2004, 24(3):53-68.
[12] Abdorreza V, Mohammad Z, Ezzat R, et al. Field-Scale Modeling of Benzene, Toluene, Ethyl-benzene, and Xylenes (BTEX) Released from Multiple Source Zones. Bioremediation Journal, 2012, 16(3):156–176.
[13] Johnson P C, Marian W K and James D C. Quantitative Analysis for the Cleanup of Hydrocarbon Contaminated Soils by In-Situ Soil Venting. Ground water, 1990, 28(3):413-429.
[14] Jamieson P D, Porter J R, Wilson D R. A test of computer simulation model ARC-WHEAT1 on wheat crops grown in New Zealand. Field Crops Research, 1991, 27(4):337-350.